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Technical Report

APPLICATIONS OF THE DIRECTIONAL PHONON FREQUENCY FUNCTIONS IN NEUTRON SCATTERING INVESTIGATIONS OF HIGH POLYMERS

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ABSTRACT

The incoherent and coherent differential neutron scattering cross-sections for crystalline polymers are written in terms of the amplitude-weighted directional frequency functions. These functions describe the dependence of the cross-sections on the vibrational frequencies and displacements of the scattering nuclei. For the sth scatterer, the one-phonon directional G-function is:

$$G_s^{\alpha\beta}(\epsilon) = \frac{1}{N} \sum_{j\underline{q}} \gamma^{\overset{*}{\alpha s}}(\underline{q})\ \gamma^{\beta s}(\underline{q})\ \delta(\epsilon - \hbar\,\omega_j(\underline{q}))$$

where there are N values of q, the phonon wave vector, for a crystal containing N unit cells. In this analysis, only phonon wave vectors directed parallel to the molecular chain axes are considered. $\gamma_j^{\beta s}(\underline{q})$ is the polarization vector of the sth nucleus in the βth direction, for the phonon in the jth branch of the dispersion curves with wave vector $\underline{q}$. The summation is performed over those values of $\underline{q}$ and j for which the neutron energy transfer is $\epsilon = \hbar\,\omega_j(\underline{q})$, where $\omega_j(\underline{q})$ is the frequency of the phonon.

The two-phonon G-functions are also defined and the orientation averages are performed, for both unoriented and stretch-oriented long chain polycrystalline polymers.

The orientation average of the Debye-Waller factor is performed separately from that of the remainder of the cross-section. The validity of this rather common approximation is evaluated.

The vibrational frequencies and polarization vectors, which are required for the construction of the directional frequency functions, are obtained from the solutions of the dynamical matrix equations, which are written in terms of cartesian space group symmetry coordinates. To accomplish this, coordinate transformations are performed on published intramolecular and intermolecular internal coordinate force constant matrices.

In addition to a detailed discussion of the symmetry analysis and force constant transformation for each of the three polymers polyethylene, polyvinylchloride and polytetrafluoroethylene, the following results are displayed:

I. Single-Chain Polyethylene
  a. Normal and Deuterated Polyethylene Dispersion Curves
  b. Normal Polyethylene Transverse and Longitudinal One-Phonon Frequency Functions

II. Crystalline Polyethylene Lattice
  a. Low frequency Normal and Deuterated Polyethylene Dispersion Curves
  b. Polarization vector squares for Normal Polyethylene torsion and stretch-bend dispersion curve branches as a function of chemical repeat unit phase angle, in graphical form
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  d. One-phonon Transverse and Longitudinal Frequency Functions for both Normal and Deuterated polyethylene over the entire frequency range
  e. Low frequency two-phonon transverse and longitudinal Frequency Functions
  f. Directional Debye-Waller Coefficients as a function of temperature

III. Single-Chain Syndiotactic Polyvinylchloride
  a. Dispersion Curves
  b. Polarization vector squares as a function of the chemical repeat unit phase angle in increments of $\pi/5$, in tabular form
  c. One-phonon transverse and longitudinal Frequency Functions for hydrogen motions
  d. One-phonon unoriented Frequency Functions for carbon and chlorine motions
  e. Directional Debye-Waller Coefficients at liquid nitrogen temperature

IV. Dispersion Curves for Single-Chain Polytetrafluoroethylene (Planar Approximation)

In addition, the normal polyethylene composite one- and two-phonon frequency functions, which are weighted by the Debye-Waller factors, are compared to published frequency spectra obtained from experimental cross-sections for a stretch-oriented sample. The comparison of the calculated polyvinylchloride frequency functions with experimental values must however await the results of experiments which are now in progress.

CHAPTER 1

INTRODUCTION

Microscopic neutron scattering cross-sections, for neutron energies much higher than the chemical binding energy of atoms in a molecule, can be calculated assuming that the atoms are essentially free. On the other hand, when the neutron energy is of the order of the energy of vibration of the scattering nuclei, it is necessary to carefully consider the molecular dynamics in calculating the cross-sections. This must be done, for example, in calculating the low energy neutron scattering cross-sections to be used in studies of neutron thermalization in nuclear reactor materials.

From a more broad viewpoint, knowledge of the microscopic properties of materials, whether destined for use in a reactor or not, is becoming increasingly important. Such knowledge can be obtained from inelastic scattering measurements using low energy neutrons with wave lengths comparable to interatomic spacings and energies comparable to vibrational energies. The neutrons then serve as probes for investigating the microscopic dynamical properties of the material. In these experiments measurements of the gain or loss in neutron energies and neutron momenta, which are compactly described in terms of the differential neutron scattering cross-section, lead to increased knowledge of the atomic vibrational frequencies and displacements.

Theoretical calculations of terms related to the scattering cross-section, such as those undertaken in this study, should greatly aid in obtaining a better understanding of the experimental neutron scattering results.

This analytical investigation was primarily motivated by a desire to better understand the neutron scattering measurements which have been performed on normal and deuterated polyethylene.[1-12] In addition, it was motivated by other scattering experiments on crystalline polyvinylchloride and polytetrafluoroethylene (Teflon) which are either in progress or planned for the near future.

Therefore, the main objective of this investigation was the calculation of those terms in the neutron scattering cross-sections of crystalline polyethylene, polyvinylchloride and polytetrafluoroethylene which contain information regarding their atomic motions. To be more explicit this main objective, which was threefold, was to calculate:

1. The one-and two-phonon directional frequency functions and the Debye-Waller factors for both normal and deuterated polyethylene.
2. The one-phonon directional frequency functions and Debye-Waller factors for polyvinylchloride.
3. The frequency vs. phonon wave vector dispersion curves for polytetrafluoroethylene.

The additional goal was the comparison of these quantities with the available experimental results, with the expectation that this would lead to an increased understanding of the molecular dynamics of these polymers and perhaps eventually to a better description of the neutron scattering interaction itself.

CHAPTER 2

NEUTRON SCATTERING THEORY

Before concentrating attention on any one of these molecular crystals, it is first necessary to examine the neutron scattering cross-section and those terms mentioned above which are primarily sensitive to the atomic motions. Since incoherent scattering from the hydrogen atoms in these polymers is predominant, unless deuterium is substituted for the light hydrogen atoms the incoherent cross-section will be discussed first.

A. INCOHERENT SCATTERING CROSS-SECTION

Summerfield has shown[13] that the incoherent neutron scattering cross-section for an atom in a long chain polymer such as polyethylene is, under certain approximations, proportional to an amplitude weighted directional frequency function, $G^{\alpha\beta}(\epsilon)$. This G-function for the sth atom, can be written as

$$G_s^{\alpha\beta}(\epsilon) = \frac{1}{N} \sum_{jq} \gamma_j^{\alpha s^*}(q)\gamma_j^{\beta s}(q)\delta(\epsilon - \hbar\omega_j(q)) \qquad (2.1)$$

where there are N values of q, the phonon wave vector, which is assumed in these calculations to be directed parallel to the polymer chain axes. N is the number of unit cells along this chain direction. $\gamma_j^{\beta s}(q)$ is the atom's polarization vector in the βth direction for the jth branch of the dispersion curves, for wave vector q. The summation in equation (2.1) is over those values of q and j for which the energy transfer, $\epsilon = \hbar\omega_j(q)$, where $\omega_j(q)$ is the frequency of the phonon in the jth branch with wave vector q.

The polarization vectors, which are mass-weighted displacement vectors, are orthonormal,[14] so

$$\sum_{j} \gamma_j^{\alpha s *}(q)\gamma_j^{\beta s}(q) = \delta_{\alpha\beta} \tag{2.2}$$

and

$$\sum_{\alpha, s} \gamma_j^{\alpha s *}(q)\gamma_{j'}^{\alpha s}(q) = \delta_{jj'} \tag{2.3}$$

where the summation on s is over all atoms in a unit cell.

The mass weighting takes the form

$$\gamma_j^{\alpha s}(q) = m_s^{1/2}\xi_j^{\alpha s}(q) \tag{2.4}$$

where $\xi_j^{\alpha s}(q)$ is the displacement along the αth cartesian coordinate axis for the sth atom.

Actual calculations are performed using the phase shift between adjacent chemical repeat units, δ_c, rather than q or the phase shift between unit cells which is

$$\Theta = qc$$

where c is the unit cell dimension along the chain axis direction. Special care must then be taken to see that the eigenvector solutions to the equations of motion are properly normalized* as required by Eq. (2.3).

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*See, for example, the section on Dispersion Curves and Polarization Vectors in Chapter 5.

Since the incoherent scattering is primarily from the protons, the s index is omitted in the following equations, which then refer only to scattering from hydrogen.

The G-function is of major importance insofar as it contains both the frequency and displacement information for the crystal. The relationship between this function and the differential incoherent scattering cross-section for a hydrogen atom is given by[5,12,13]:

$$\frac{d^2\sigma}{d\Omega d\epsilon} = N \frac{k_f}{k_i} \frac{\sigma_o}{4\pi} < e^{-Z(o)} \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} e^{-i\epsilon t/\hbar} e^{Z(t)} > \qquad (2.5)$$

since Z(t) is defined as

$$Z(t) = \sum_{\alpha\alpha'} \frac{\hbar^2}{2m} \kappa_\alpha \kappa_{\alpha'} \int_{-\infty}^{\infty} d\epsilon' \frac{G^{\alpha\alpha'}(\epsilon')}{\epsilon'} \left[\frac{e^{i\epsilon' t'/\hbar}}{1-e^{-\beta\epsilon'}} + \frac{e^{-i\epsilon' t/\hbar}}{e^{\beta\epsilon'}-1} \right] . \qquad (2.6)$$

The symbol < > indicates the usual thermal average and, in addition, an appropriate average over molecular orientations.

The initial and final neutron momenta are, respectively, $\hbar k_i$ and $\hbar k_f$. σ_o is the bound hydrogen atom scattering cross-section. κ_α and $\kappa_{\alpha'}$ are the αth and α'th components of the neutron momentum transfer vector $\underline{\kappa} = \underline{k}_i - \underline{k}_f$ and m is the mass of the hydrogen atom. The neutron energy loss is denoted by ϵ. In the case when β, which is equal to $1/kT$, is large neutron upscatter in energy is relatively unimportant. That is, a reduced number of phonons is available for low temperature annihilation events. Then the last term in Z(t) is insignificant and phonon creation events are dominant.

It is convenient for comparisons between theoretical and experimental results in hydrogenous materials to introduce a function:

$$G_{\underline{\kappa}} = \frac{8m\pi}{\sigma_o \hbar^2 \kappa^2} \frac{k_i}{k_f} \frac{\epsilon(1-e^{-\beta\epsilon})}{N} \frac{d^2\sigma_{inelastic}}{d\Omega d\epsilon} \tag{2.7}$$

which can be extracted from the experimental results for $\frac{d^2\sigma}{d\Omega d\epsilon}$, in a neutron downscattering experiment.

Stretching a polymer film tends to orient the molecular chain axes along the stretch direction. In an experiment on such a stretched target, the neutron momentum transfer vector $\underline{\kappa}$ can be aligned either parallel or perpendicular to the stretch direction. For the parallel alignment, the so-called longitudinal G-function is obtained, where[5]

$$G_{\underline{\kappa}_{||}}(\epsilon) \equiv G_L(\epsilon). \tag{2.8}$$

For the perpendicular alignment, the transverse experimental G-function is obtained, where

$$G_{\underline{\kappa}_{\perp}}(\epsilon) \equiv G_T(\epsilon). \tag{2.9}$$

In an experiment on a polycrystalline target, in which all relative alignments between $\underline{\kappa}$ and the chain axes are possible, the unoriented experimental G-function is measured, where

$$G_{\underline{\kappa}}(\epsilon) \equiv G(\epsilon). \tag{2.10}$$

These experimental results are in fact Debye-Waller factor weighted spectra. This can be seen by writing $G_{\underline{\kappa}}(\epsilon)$ in terms of $Z(t)$ as

$$G_{\underline{\kappa}}(\epsilon) = \frac{2m}{\hbar^2\kappa^2} \epsilon(1-\beta\epsilon) < e^{-Z(o)} \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} e^{-i\epsilon t/\hbar}[e^{Z(t)}-1]> \tag{2.11}$$

and noting that in the longitudinal case, the Debye-Waller factor is

$$e^{-2W_L} = < e^{-Z(o)} >_L \qquad (2.12)$$

while in the transverse case it is approximated by*

$$e^{-2W_T} \approx < e^{-Z(o)} >_T \qquad (2.13)$$

where

$$2W_L = \int_0^\infty \frac{\hbar^2\kappa^2}{2m} \frac{ctgh(\beta\epsilon/2)}{\epsilon} G_L^I(\epsilon)\, d\epsilon \qquad (2.14)$$

and

$$2W_T = \int_0^\infty \frac{\hbar^2\kappa^2}{2m} \frac{ctgh(\beta\epsilon/2)}{\epsilon} G_T^I(\epsilon)\, d\epsilon. \qquad (2.15)$$

$G_L^I(\epsilon)$ and $G_T^I(\epsilon)$ are determined from the respective longitudinal and transverse orientation averages of the amplitude weighted directional frequency functions described in Eq. (2.1). These averages and the approximations involved are discussed in a following section.

B. ONE- AND TWO-PHONON DIRECTIONAL FREQUENCY FUNCTIONS

The experimentally determined $G_{\underline{\kappa}}(\epsilon)$ function, in general, contains contributions from multiphonon events in which two or more phonons are created and/or annihilated. This is in addition to the more important contributions from events in which a single phonon is either created or annihilated. In order to evaluate the extent to which two phonon contributions may be included

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*See the section on Orientation Averages, this chapter.

in experimental results, the cross-section is written in terms of Sjölander's phonon expansion.[16] Equation (2.5) then becomes[5]

$$\frac{d^2\sigma}{d\Omega d\epsilon} = N \frac{k_f}{k_i} \frac{\sigma_o}{4\pi} < e^{-Z(o)} \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} e^{-i\epsilon t/\hbar}[1 + Z(t) + \frac{Z^2(t)}{2} + \ldots] > . \qquad (2.16)$$

Z(t) is given in Eq. (2.6) as a function of $G^{\alpha\alpha'}(\epsilon')$. This may also be rewritten as

$$Z(t) = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} d\epsilon' \frac{\tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon') \cdot \underline{\kappa}}{\epsilon'} \left[\frac{e^{i\epsilon' t/\hbar}}{1-e^{-\beta\epsilon'}} + \frac{e^{-i\epsilon' t/\hbar}}{e^{\beta\epsilon'} - 1}\right] \qquad (2.17)$$

where $G^{\alpha\beta}(\epsilon')$ is the matrix element for the αth row and βth column of the matrix $\underline{\underline{G}}(\epsilon')$. This latter form is more convenient for performing the orientation averages where only the terms in $[\tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon') \cdot \underline{\kappa}]$ are directionally dependent.

From Eq. (2.16) the cross-section for an atom, including the two phonon term, is

$$\frac{d^2\sigma}{d\Omega d\epsilon} \approx \frac{d^2\sigma(o)}{d\Omega d\epsilon} + \frac{d^2\sigma(1)}{d\Omega d\epsilon} + \frac{d^2\sigma(2)}{d\Omega d\epsilon} . \qquad (2.18)$$

Since the phonon number in a low temperature target is small phonon annihilation produces a negligible contribution to the cross-section. Using Eq. (2.17), and performing the time integrations, the contributions for neutron downscattering events only are therefore

$$\frac{d^2\sigma(o)}{d\Omega d\epsilon} = \frac{N\sigma_o}{4\pi} \frac{k_f}{k_i} \delta(\epsilon) < e^{-Z(o)} > \qquad (2.19)$$

and

$$\frac{d^2\sigma_{(1)}}{d\Omega\, d\epsilon} = \frac{N\sigma_o}{4\pi}\frac{k_f}{k_i}\frac{\hbar^2}{2m} < \frac{e^{-Z(o)}\, \tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa}}{\epsilon(1-e^{-\beta\epsilon})} > \qquad (2.20)$$

$$\frac{d^2\sigma_{(2)}}{d\Omega d\epsilon} = \frac{\sigma_o}{4\pi}\frac{k_f}{k_i}\left(\frac{\hbar^2}{2m}\right)^2 \frac{N}{2} < e^{-Z(o)} \int_0^\infty \frac{d\epsilon' \,[\tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon') \cdot \underline{\kappa})(\tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon-\epsilon') \cdot \underline{\kappa})]}{\epsilon'(\epsilon-\epsilon')(1-e^{-\beta\epsilon'})(1-e^{-\beta(\epsilon-\epsilon')})} > . \qquad (2.21)$$

The orientation averages may now be obtained. Myers has already given the result for the one phonon term, for both a polycrystalline sample and a stretch-oriented sample.[12] To obtain the Debye-Waller factors, $e^{-Z(o)}$ is separately averaged and is replaced by $e^{-<Z(o)>}$. For a polycrystalline target, the results are

$$< \tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} >_p = \frac{\kappa^2}{3}\sum_{\alpha=1}^{3} G^{\alpha\alpha}(\epsilon) = \kappa^2 G^{I}(\epsilon) \qquad (2.22)$$

and

$$< Z(o) >_p = 2W = \int_0^\infty d\epsilon \,\frac{\hbar^2 \kappa^2}{2m}\,\frac{\mathrm{ctgh}(\beta\epsilon/2)}{\epsilon}\, G^I(\epsilon). \qquad (2.23)$$

For a longitudinally oriented stretched target there are no approximations in obtaining the results

$$< \tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} >_L = \kappa^2 G^{33}(\epsilon) = \kappa^2 G^I_L(\epsilon) \qquad (2.24)$$

and

$$< Z(o) >_L = 2W_L = \int_0^\infty \frac{\hbar^2 \kappa^2}{2m}\,\frac{\mathrm{ctgh}(\beta\epsilon/2)}{\epsilon}\, G^{33}(\epsilon) d\epsilon \qquad (2.25)$$

where $\alpha = 3$ denotes the stretch direction.

For $\underline{\kappa}$ aligned perpendicular to the stretch direction, the transverse orientation average $< e^{-Z(o)} \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} >$ is approximated by separately averaging $e^{-Z(o)}$ to obtain

$$< \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} >_{Tr.} = \frac{\kappa^2}{2} [G^{11}(\epsilon) + G^{22}(\epsilon)] = \kappa^2 G_T^I(\epsilon) \qquad (2.26)$$

and:

$$< Z(o) >_{Tr.} = 2W_T = \int_0^\infty d\epsilon \frac{\hbar^2 \kappa^2}{2m} \frac{ctgh(\beta\epsilon/2)}{\epsilon} \left[\frac{G^{11}(\epsilon) + G^{22}(\epsilon)}{2} \right] . \qquad (2.27)$$

In the section on Orientation Averages, which follows, this approximation is shown to be valid when $G^{11}(\epsilon) \approx G^{22}(\epsilon)$.

The one phonon directional G-functions are therefore defined as

$$G_L^I(\epsilon) = G^{33}(\epsilon) \qquad (2.28)$$

$$G_T^I(\epsilon) = 1/2[G^{11}(\epsilon) + G^{22}(\epsilon)] \qquad (2.29)$$

and the polycrystalline one phonon G-function is defined as

$$G^I(\epsilon) = 1/3\ G_L^I(\epsilon) + 2/3\ G_T^I(\epsilon) = 1/3\ [G^{11}(\epsilon) + G^{22}(\epsilon) + G^{33}(\epsilon)] . \qquad (2.30)$$

The Debye-Waller factors have been separately averaged, which is equivalent to replacing the one phonon contribution to the cross-section

$$< e^{-Z(o)} \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} > \qquad (2.31)$$

with

$$e^{-\langle Z(o) \rangle} \langle \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} \rangle \, . \tag{2.32}$$

The accuracy of this approximation will now be evaluated and the two-phonon orientation average will also be obtained.

C. ORIENTATION AVERAGES

Preliminary calculations of the directional Debye-Waller coefficients, using the approximation that

$$\langle e^{-Z(o)} \, \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} \rangle \approx e^{-2W} \langle \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} \rangle$$

indicate that for 90° scattering experiments on polyethylene to a fixed final energy $E_f = 30$ millivolts, 2W is approximately given by

$$2W \approx 0.01 \frac{\hbar^2 \kappa^2}{2m} = 0.01 \, [2E_f + \epsilon] \tag{2.33}$$

so that the range of values of 2W is

$$.6 \leq 2W \leq 1.3$$

for

$$0 \leq \epsilon \leq 70 \text{ mev.} \tag{2.34}$$

The values of 2W for polyvinylchloride, which are given in Chapter 6, are also found to be in approximate agreement with this polyethylene value.

Therefore, expanding around $2W = 1$, let

$$e^{-2W} \approx e^{x-1}$$

$$e^{x} = e^{(1-2W)} \approx 1 + x + x^2/2 + \ldots$$

for small x. Then

$$e^{x} \approx 1 + (1-2W) + \frac{(1-2W)^2}{2} = \frac{5}{2} - 2(2W) + \frac{(2W)^2}{2}$$

or

$$e^{-2W} \approx \frac{1}{e}\left[\frac{5}{2} - 2\,(2W) + \frac{(2W)^2}{2}\right] . \qquad (2.36)$$

This is an excellent approximation with less than 1% error for 2W in the range of 0.6 to 1.3. Therefore the average can be written as

$$< e^{-Z(o)}\tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} > \; \approx \; \frac{1}{e} < \left[\frac{5}{2} - 2Z(o) + \frac{Z^2\,(o)}{2}\right]\left[\tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa}\right] > \qquad (2.37)$$

where

$$\tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} = \kappa^2\{G^{11} \cos^2 \phi \sin^2\theta + G^{22} \sin^2 \phi \sin^2\theta + G^{33} \cos^2\theta$$
$$+ 2G^{12} \cos \phi \sin \phi \sin^2\theta + 2\, G^{13} \cos \phi \cos \theta \sin \theta + 2\, G^{23} \sin \phi \sin \theta \cos \theta\} \qquad (2.38)$$

with θ and ϕ as shown in Fig. 2.1.

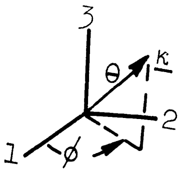

Fig. 2.1. Momentum transfer vector orientation angles.

In Eq. (2.37), Z(o) is given by:

$$Z(o) = \frac{\hbar^2}{2m} \int_0^\infty d\epsilon' \, \frac{\mathrm{ctgh}(\beta\epsilon'/2)}{\epsilon'} \, \tilde{\underline{\kappa}} \cdot \underline{\underline{G}}(\epsilon') \cdot \underline{\kappa} \, . \qquad (2.39)$$

In the longitudinal case, no orientation average is required. However, using these relations, (2.38) and (2.39), the transverse orientation average, for $\Theta = \pi/2$, may be written

$$< e^{-Z(o)} \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} >_{Tr.} \approx \frac{5}{2e} \kappa^2 G_T^I(\epsilon) - \frac{2}{e} \frac{\hbar^2 \kappa^4}{2m} < \int_0^\infty d\epsilon' \frac{\operatorname{ctgh}(\beta\epsilon'/2)}{\epsilon'} \times [G^{11}(\epsilon')\cos^2\phi + G^{22}(\epsilon') \sin^2\phi]$$

$$\times [G^{11}(\epsilon)\cos^2\phi + G^{22}(\epsilon) \sin^2\phi] > + \frac{1}{2e}\left(\frac{\hbar^2 \kappa^3}{2m}\right)^2 < \int_0^\infty d\epsilon' \frac{\operatorname{ctgh}(\beta\epsilon'/2)}{\epsilon'} \times [G^{11}(\epsilon')\cos^2\phi + G^{22}(\epsilon')\sin^2\phi]$$

$$\times \int_0^\infty d\epsilon'' \frac{\operatorname{ctgh}(\beta\epsilon''/2)}{\epsilon''} [G^{11}(\epsilon'')\cos^2\phi + G^{22}(\epsilon'')\sin^2\phi][G^{11}(\epsilon)\cos^2\phi + G^{22}(\epsilon)\sin^2\phi] > \tag{2.40}$$

where $G^{12}(\epsilon)$ is calculated to be zero for all values of ϵ. Since the aligned crystallites have random orientations about the stretch direction axis, the integration over the angle ϕ is performed and the result is:

$$< e^{-Z(o)} \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa} >_{Tr.} \approx \frac{5}{2e} \kappa^2 G_T^I(\epsilon) - \frac{2}{e} \frac{\hbar^2 \kappa^4}{2m} \int_0^\infty d\epsilon' \frac{\operatorname{ctgh}(\beta\epsilon'/2)}{\epsilon'}$$

$$\times \{G^{11}(\epsilon')[\tfrac{3}{8}G^{11}(\epsilon) + \tfrac{1}{8}G^{22}(\epsilon)] + G^{22}(\epsilon')[\tfrac{1}{8}G^{11}(\epsilon) + \tfrac{3}{8}G^{22}(\epsilon)]\}$$

$$+ \frac{1}{2e}\left(\frac{\hbar^2 \kappa^3}{2m}\right)^2 \int_0^\infty d\epsilon' \int_0^\infty d\epsilon'' \frac{\operatorname{ctgh}(\beta\epsilon'/2)}{\epsilon'} \frac{\operatorname{ctgh}(\beta\epsilon''/2)}{\epsilon''} \{G^{11}(\epsilon')G^{11}(\epsilon'')[\tfrac{5}{16}G^{11}(\epsilon) + \tfrac{1}{16} G^{22}(\epsilon)]$$

$$+ G^{11}(\epsilon')G^{22}(\epsilon'')[\tfrac{1}{16}G^{11}(\epsilon) + \tfrac{1}{16}G^{22}(\epsilon)] + G^{22}(\epsilon')G^{11}(\epsilon'')[\tfrac{1}{16}G^{11}(\epsilon) + \tfrac{1}{16}G^{22}(\epsilon)]$$

$$+ G^{22}(\epsilon')G^{22}(\epsilon'')[\tfrac{1}{16}G^{11}(\epsilon) + \tfrac{5}{16}G^{22}(\epsilon)]\} .$$

Performing the energy integrations leads to

$$< e^{-Z(o)} \underline{\tilde{\kappa}} \circ \underline{\underline{G}}(\epsilon) \circ \underline{\kappa} >_{Tr.} \approx \frac{5}{2e} \kappa^2 G^I_T(\epsilon) - \frac{2\kappa^2}{e}\{(2W_{11})[\frac{3}{8}G^{11}(\epsilon) + \frac{1}{8}G^{22}(\epsilon)]$$

$$+ (2W_{22})[\frac{1}{8}G^{11}(\epsilon) + \frac{3}{8}G^{22}(\epsilon)]\} + \frac{\kappa^2}{2e}\{(2W_{11})^2[\frac{5}{16}G^{11}(\epsilon) + \frac{1}{16}G^{22}(\epsilon)]$$

$$+ \frac{1}{8}(2W_{11})(2W_{22})[G^{11}(\epsilon) + G^{22}(\epsilon)] + (2W_{22})^2[\frac{1}{16}G^{11}(\epsilon) + \frac{5}{16}G^{22}(\epsilon)]\}. \qquad (2.41)$$

Assuming that $2W_{11} \approx 2W_{22}$, which is a good approximation for polyethylene, the average becomes

$$< e^{-Z(o)} \underline{\tilde{\kappa}} \circ \underline{\underline{G}}(\epsilon) \circ \underline{\kappa} >_{Tr.} \approx \frac{5}{2e}\kappa^2 G_T(\epsilon) - \frac{2\kappa^2}{e}\{(2W_{11})[\frac{G^{11}(\epsilon) + G^{22}(\epsilon)}{2}]\}$$

$$+ \frac{\kappa^2}{2e}\{(2W_{11})^2[\frac{G^{11}(\epsilon) + G^{22}(\epsilon)}{2}]\}$$

or:

$$< e^{-Z(o)} \underline{\tilde{\kappa}} \circ \underline{\underline{G}}(\epsilon) \circ \underline{\kappa} >_{Tr.} \approx \left[\frac{5}{2e} - \frac{2}{e}(2W_{11}) + \frac{(2W_{11})^2}{2e}\right] \kappa^2 G^I_T(\epsilon). \qquad (2.42)$$

But this is

$$< e^{-Z(o)} \underline{\tilde{\kappa}} \circ \underline{\underline{G}}(\epsilon) \circ \underline{\kappa} >_{Tr.} \approx e^{-<Z(o)>} < \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \circ \underline{\kappa} >. \qquad (2.43)$$

providing that the value of $(2W_{11})$ can be replaced by $(2W_T)$, which follows if $G^{22}(\epsilon) \approx G^{11}(\epsilon)$ in:

$$G^I_T(\epsilon) = \frac{G^{11}(\epsilon) + G^{22}(\epsilon)}{2} \qquad (2.44)$$

and

$$2W_T = \frac{\hbar^2 \kappa^2}{2m} \int_0^\infty d\epsilon' \frac{\mathrm{ctgh}(\beta\epsilon'/2)}{\epsilon'} G^I_T(\epsilon') . \qquad (2.45)$$

The requirements and approximations involved then in replacing

$$< e^{-Z(o)} \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \kappa >$$

by

$$e^{-< Z(o) >} < \underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \kappa >$$

for the range of ϵ and κ^2 of interest here, are that

$$G^{12}(\epsilon) = 0, \quad \text{for all } \epsilon$$

$$2W_{11} \approx 2W_{22}$$

$$G^{11}(\epsilon) \approx G^{22}(\epsilon), \quad \text{for all } \epsilon. \tag{2.46}$$

The first requirement is completely satisfied for polyethylene and for the second, the discrepancy between $2W_{11}$ and $2W_{22}$ is less than 2% of the larger value. The third requirement is not satisfied for all ϵ since the difference between $G^{11}(\epsilon)$ and $G^{22}(\epsilon)$ is as much as 8% of the larger value at some ϵ.

The two phonon orientation average will now be obtained, assuming again that the Debye-Waller factor may be separately averaged. Then

$$< [\underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon) \cdot \underline{\kappa}]^2 > = < [\kappa^2(G^{11} \cos^2\phi \sin^2\Theta + G^{22} \sin^2\phi \sin^2\Theta + $$

$$+ G^{33} \cos^2\Theta + 2 G^{12} \cos\phi \sin\phi \sin^2\Theta + 2 G^{13} \cos\phi \cos\Theta \sin\Theta$$

$$+ 2 G^{23} \sin\phi \cos\Theta \sin\Theta]^2 > \tag{2.47}$$

In the longitudinal case, the result is

$$< [\underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon') \cdot \underline{\kappa}]^2 >_L \;=\; [\, \kappa^2 G^I_L(\epsilon')\, \kappa^2 G^I_L(\epsilon'')\,]. \qquad (2.48)$$

For the transverse orientation, when $\Theta = \pi/2$, the average is

$$\frac{1}{2\pi} \int_0^{2\pi} d\phi \; [\, \kappa^2 (G^{11}(\epsilon') \cos^2\phi + G^{22}(\epsilon') \sin^2\phi + 2\, G^{12}(\epsilon') \cos\phi \sin\phi)]^2 \qquad (2.49)$$

but $G^{12}(\epsilon)$ is zero for all ϵ. The result is

$$< [\underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon') \cdot \underline{\kappa}]^2 >_{Tr.} \;=\; \{\, \kappa^4 [\tfrac{3}{8} G^{11}(\epsilon') G^{11}(\epsilon'') + \tfrac{1}{8} G^{11}(\epsilon') G^{22}(\epsilon'') + \tfrac{1}{8}\, G^{22}(\epsilon') G^{11}(\epsilon'') + \tfrac{3}{8} G^{22}(\epsilon') G^{22}(\epsilon'')\,]\}. \qquad (2.50)$$

Since

$$G^I_T(\epsilon') \;=\; \frac{G^{11}(\epsilon') + G^{22}(\epsilon')}{2} \qquad (2.51)$$

then

$$\kappa^4 G^I_T(\epsilon') G^I_T(\epsilon'') \;=\; \frac{\kappa^4}{4} \{ G^{11}(\epsilon') G^{11}(\epsilon'') + G^{22}(\epsilon') G^{22}(\epsilon'') + G^{11}(\epsilon') G^{22}(\epsilon'') + G^{22}(\epsilon') G^{11}(\epsilon'')\}. \qquad (2.52)$$

Notice that this is not identical to the two phonon orientation result in equation (2.50), so that the statement

$$< [\underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon') \cdot \underline{\kappa}][\underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon'') \cdot \underline{\kappa}] >_{Tr.} \;\approx\; \kappa^4 G^I_T(\epsilon') G^I_T(\epsilon'') \qquad (2.53)$$

is valid only if $G^{11}(\epsilon) \approx G^{22}(\epsilon)$, for all ϵ. This is the same requirement as that for the validity of the separate averaging of the Debye-Waller factor.

For an unoriented polycrystalline sample, the two-phonon orientation average must be performed over both ϕ and Θ angles. Again, if $G^{12}(\epsilon) = 0$, the polycrystalline average of

$$< [\underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon') \cdot \underline{\kappa}] [\underline{\tilde{\kappa}} \cdot \underline{\underline{G}}(\epsilon'') \cdot \underline{\kappa}] > \qquad (2.54)$$

is

$$< \kappa^4 [G^{11}(\epsilon')G^{11}(\epsilon'')\cos^4\phi \sin^4\phi + G^{11}(\epsilon')G^{22}(\epsilon'') \cos^2\phi \sin^2\phi \sin^4\Theta$$

$$+ G^{11}(\epsilon')G^{33}(\epsilon'') \cos^2\phi \sin^2\Theta \cos^2\Theta + 2\, G^{11}(\epsilon')G^{13}(\epsilon'') \cos^3\phi \cos\Theta \sin^3\Theta$$

$$+ 2\, G^{11}(\epsilon')G^{23}(\epsilon'') \cos^2\phi \sin\phi \cos\Theta \sin^3\Theta + G^{22}(\epsilon')G^{11}(\epsilon'') \cos^2\phi \sin^2\phi \sin^4\Theta$$

$$+ G^{22}(\epsilon')G^{22}(\epsilon'') \sin^4\phi \sin^4\Theta + G^{22}(\epsilon')G^{33}(\epsilon'') \sin^2\phi \sin^2\Theta \cos^2\Theta$$

$$+ 2\, G^{22}(\epsilon')G^{13}(\epsilon'') \sin^2\phi \cos\phi \cos\Theta \sin^3\Theta + 2\, G^{22}(\epsilon')G^{23}(\epsilon'') \sin^3\phi \cos\Theta \sin^3\Theta$$

$$+ G^{33}(\epsilon')G^{11}(\epsilon'') \cos^2\phi \sin^2\Theta \cos^2\Theta + G^{33}(\epsilon')G^{22}(\epsilon'') \sin^2\phi \sin^2\Theta \cos^2\Theta$$

$$+ G^{33}(\epsilon')G^{33}(\epsilon'') \cos^4\Theta + 2\, G^{33}(\epsilon')G^{13}(\epsilon'') \cos\phi \cos^3\Theta \sin\Theta$$

$$+ 2\, G^{33}(\epsilon')G^{23}(\epsilon'') \sin\phi \cos^3\Theta \sin\Theta + 2\, G^{13}(\epsilon')G^{11}(\epsilon'') \cos^3\phi \sin^3\Theta \cos\Theta$$

$$+ 2\, G^{13}(\epsilon')G^{22}(\epsilon'') \sin^2\phi \sin^3\Theta \cos\Theta + 2\, G^{13}(\epsilon')G^{33}(\epsilon'') \cos^3\Theta \cos\phi \sin\Theta$$

$$+ 4\, G^{13}(\epsilon')G^{23}(\epsilon'') \cos\phi \sin\phi \cos^2\Theta \sin^2\Theta$$

$$+ 2\, G^{23}(\epsilon')G^{11}(\epsilon'')\cos^2\phi \sin\phi \sin^3\Theta \cos\Theta + 2\, G^{23}(\epsilon')G^{22}(\epsilon'')\sin^3\phi\cos\Theta\sin^3\Theta$$

$$+ 2\, G^{23}(\epsilon')G^{33}(\epsilon'')\sin\phi\cos^3\Theta\sin\Theta + 4\, G^{23}(\epsilon')G^{13}(\epsilon'')\cos\phi\sin\phi\cos^2\Theta\sin^2\Theta] > . \tag{2.55}$$

The final result, after integrating over Θ and ϕ, is

$$< [\underline{\tilde{\kappa}} \circ \underline{\underline{G}}(\epsilon') \circ \underline{\kappa}][\underline{\tilde{\kappa}} \circ \underline{\underline{G}}(\epsilon'') \circ \underline{\kappa}] > \; = \; \kappa^4\{\tfrac{3}{8}[\tfrac{3}{8}G^{11}(\epsilon')G^{11}(\epsilon'') + \tfrac{1}{8}G^{11}(\epsilon')G^{22}(\epsilon'')$$

$$+ \tfrac{1}{8}G^{22}(\epsilon')G^{11}(\epsilon'') + \tfrac{3}{8}G^{22}(\epsilon')G^{22}(\epsilon'')] + \tfrac{3}{8}[G^{33}(\epsilon')G^{33}(\epsilon'')]$$

$$+ \tfrac{1}{16}[G^{11}(\epsilon')G^{33}(\epsilon'') + G^{22}(\epsilon')G^{33}(\epsilon'') + G^{33}(\epsilon')G^{11}(\epsilon'') + G^{33}(\epsilon')G^{22}(\epsilon'')]\}. \tag{2.56}$$

Then the two-phonon unoriented G-function is given by

$$G^{II}(\epsilon) = \tfrac{3}{8}G^{II}_{T}(\epsilon) + \tfrac{3}{8}G^{II}_{L}(\epsilon) + \tfrac{1}{4}G^{II}_{TL}(\epsilon) \tag{2.57}$$

where if $\epsilon'' = (\epsilon - \epsilon')$, Eqs. (2.20), (2.21), and (2.56) may be used to define the two phonon directional G-functions as

$$G^{II}_{T}(\epsilon) = \frac{\epsilon(1-e^{-\beta\epsilon})}{2}\left(\frac{\hbar^2\kappa^2}{2m}\right)\int_0^\infty d\epsilon'\, [\tfrac{3}{8}G^{11}(\epsilon')G^{11}(\epsilon'') + \tfrac{1}{8}G^{11}(\epsilon')G^{22}(\epsilon'')$$

$$+ \tfrac{1}{8}G^{22}(\epsilon')G^{11}(\epsilon'') + \tfrac{3}{8}G^{22}(\epsilon')G^{22}(\epsilon'')]$$

$$\times \frac{1}{\epsilon'(\epsilon-\epsilon')(1-e^{-\beta\epsilon'})(1-e^{-\beta(\epsilon-\epsilon')})} \tag{2.58}$$

$$G^{II}_{L}(\epsilon) = \frac{\epsilon(1-e^{-\beta\epsilon})}{2}\left(\frac{\hbar^2\kappa^2}{2m}\right)\int_0^\infty d\epsilon'\, [G^{33}(\epsilon')G^{33}(\epsilon'')]$$

$$\times \frac{1}{\epsilon'(\epsilon-\epsilon')(1-e^{-\beta\epsilon'})(1-e^{-\beta(\epsilon-\epsilon')})}$$

$$G^{II}_{TL}(\epsilon) = \frac{\epsilon(1-e^{-\beta\epsilon})}{8}\left(\frac{\hbar^2\kappa^2}{2m}\right)\int_0^\infty d\epsilon' \left[\frac{G^{11}(\epsilon')G^{33}(\epsilon'')+G^{22}(\epsilon')G^{33}(\epsilon'')+G^{33}(\epsilon')G^{11}(\epsilon'')+G^{33}(\epsilon')G^{22}(\epsilon'')}{\epsilon'(\epsilon-\epsilon')(1-e^{-\beta\epsilon'})(1-e^{-\beta(\epsilon-\epsilon')})}\right]$$

If $G^{11}(\epsilon) \approx G^{22}(\epsilon)$ for all ϵ, then these equations may be rewritten as

$$G^{II}_{T}(\epsilon) = \frac{\epsilon(1-e^{-\beta\epsilon})}{2}\left(\frac{\hbar^2\kappa^2}{2m}\right)\int_0^\infty d\epsilon' \frac{G^{I}_{T}(\epsilon')\,G^{I}_{T}(\epsilon-\epsilon')}{\epsilon'(\epsilon-\epsilon')(1-e^{-\beta\epsilon'})(1-e^{-\beta(\epsilon-\epsilon')})}$$

$$G^{II}_{L}(\epsilon) = \frac{\epsilon(1-e^{-\beta\epsilon})}{2}\,\frac{\hbar^2\kappa^2}{2m}\int_0^\infty d\epsilon' \frac{G^{I}_{L}(\epsilon')\,G^{I}_{L}(\epsilon-\epsilon')}{\epsilon'(\epsilon-\epsilon')(1-e^{-\beta\epsilon'})(1-e^{-\beta(\epsilon-\epsilon')})}$$

$$G^{II}_{TL}(\epsilon) = \frac{\epsilon(1-e^{-\beta\epsilon})}{4}\,\frac{\hbar^2\kappa^2}{2m}\int_0^\infty \frac{G^{I}_{T}(\epsilon')G^{I}_{L}(\epsilon-\epsilon') + G^{I}_{L}(\epsilon')G^{I}_{T}(\epsilon-\epsilon')}{\epsilon'(\epsilon-\epsilon')(1-e^{-\beta\epsilon'})(1-e^{-\beta(\epsilon-\epsilon')})} \quad . \qquad (2.59)$$

These equations are used in evaluating the two-phonon G-functions in this report. The unoriented two-phonon G-function is approximated by

$$G^{II}(\epsilon) \approx \frac{1}{3}\,G^{II}_{L}(\epsilon) + \frac{2}{3}\,G^{II}_{T}(\epsilon) \qquad (2.60)$$

rather than by Eq. (2.57), since this is more convenient due to its similarity with the one-phonon unoriented G-function. This step is partially justified by experimental results[12] in which the sum $1/3\ G(\epsilon)_{\kappa_\parallel} + 2/3\ G(\epsilon)_{\kappa_\perp}$ from parallel and transverse oriented experiments matches the unoriented results for the energy region in which two-phonon effects are believed to predominate.

D. INCOHERENT APPROXIMATION FOR COHERENT SCATTERING CROSS-SECTION

The coherent neutron scattering cross-section may be written as[15,16]:

$$\frac{d^2\sigma_{coh}}{d\Omega d\epsilon} = \frac{k_f}{k_i}\sum_{ss'} a_s a_{s'}\, e^{i\underline{\kappa}\cdot(\underline{r}^{os'}-\underline{r}^{os})}\, e^{-1/2\,[Z^\circ_{ss}(o) + Z^\circ_{s's'}(o)]}$$

$$\times \sum_{\ell} e^{i\underline{\kappa}\cdot\underline{R}^{\ell}}\,\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{-i\epsilon t/\hbar}\, e^{Z^{os}_{\ell s'}}\, dt \qquad (2.61)$$

where the equilibrium position of the s'th nucleus in the ℓth unit cell is $\underline{R}^\ell + \underline{r}^{os'}$, as shown in Fig. 2.2 . $\underline{R}^\ell$ is the position of the ℓth cell relative to the crystal coordinate system origin at the zeroeth unit cell and $\underline{r}^{os'}$ is the position of the s'th atom relative to the origin of the ℓth unit cell. The coherent scattering length for the sth nucleus is a_s.

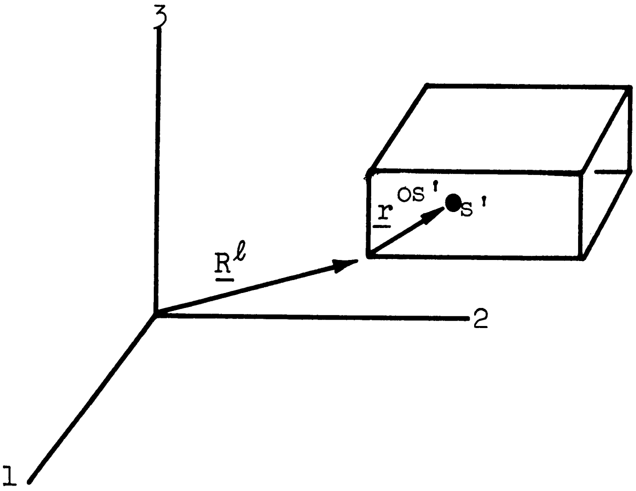

Fig. 2.2. Equilibrium position of a nucleus in the ℓth unit cell.

In the above equation, $Z^{os}_{\ell s'}(t)$ is given by

$$Z^{os}_{\ell s'}(t) = -\sum_{\alpha\alpha'} \frac{\hbar^2}{2(m_s m_{s'})^{1/2}} \kappa_\alpha \kappa_{\alpha'} \int_{-\infty}^{\infty} d\epsilon' \, \frac{G^{os\alpha}_{\ell s'\alpha'}(\epsilon')}{\epsilon'} \left[\frac{e^{i\epsilon' t/\hbar}}{1-e^{-\beta\epsilon'}} + \frac{e^{-i\epsilon' t/\hbar}}{e^{\beta\epsilon'}-1} \right] . \tag{2.62}$$

This reduces to Z(t) in Eq. (2.6) for the incoherent case, when $\ell = 0$ and $s = s'$, since the G-function in Eq. (2.62) is defined as

$$G^{os\alpha}_{\ell s'\alpha'}(\epsilon') = \frac{1}{N} \sum_{\underline{q}j} \gamma_j^{os\alpha *}(\underline{q}) \, \gamma_j^{\ell s'\alpha'}(\underline{q}) \, e^{i\underline{q} \cdot \underline{R}^\ell} \delta(\epsilon - \hbar\omega_j(\underline{q})) \tag{2.63}$$

for $\epsilon > 0$, where

$$G^{os\alpha}_{\ell s'\alpha'}(-\epsilon') = G^{os\alpha *}_{\ell s'\alpha'}(+\epsilon') .$$

For κ large enough so that the changes in κ which accompany changes in ϵ are relatively small, κ can be treated as a continuous variable and the sum

$$\sum_{\ell} e^{i\underline{\kappa}\cdot\underline{R}^{\ell}} = \sum_{\ell_1=0,\ell_2=0,\ell_3=0}^{N_a-1,N_b-1,N_c-1} e^{i[\kappa_1\ell_1 a + \kappa_2\ell_2 b + \kappa_3\ell_3 c]} \qquad (2.64)$$

can be replaced by its average over values of κ. Since

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} d\kappa_1\, e^{i\kappa_1(\ell_1 a)} = \delta(\ell_1 a)$$

the average value of each term in the sum

$$\sum_{\ell_1=0}^{N_a-1} e^{i\kappa_1\ell_1 a}$$

is zero except for the term in which $\ell_1 = 0$. Therefore

$$\sum_{\ell_1} e^{i\kappa_1\ell_1 a} = \delta_{o\ell_1} \qquad (2.65)$$

or

$$\sum_{\ell} e^{i\underline{\kappa}\cdot\underline{R}^{\ell}} = \delta_{o\ell}$$

A similar result is obtained for

$$\sum_{ss'} e^{i\underline{\kappa}\cdot(\underline{r}^{os'} - \underline{r}^{os})} = \delta_{ss'} \,. \qquad (2.66)$$

Therefore the cross-section Eq. (2.61) may be rewritten as

$$\frac{d^2\sigma coh}{d\Omega d\epsilon} \simeq \frac{k_f}{k_i}\sum_{s} a_s^2\, e^{-Z_{ss}^{o}(o)}\, \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{-i\epsilon t/\hbar}\, e^{Z_{os}^{os}(t)}\,dt \qquad (2.67)$$

which is of the same form as Eq. (2.5) for the incoherent cross-section. When κ is large and $\ell = 0$ as required by Eq. (2.65), Eq. (2.63) is

$$G_{os\alpha'}^{os\alpha}(\epsilon') = \frac{1}{N} \sum_{\underline{q}j} \overset{*}{\gamma}{}_j^{os\alpha}(\underline{q})\, \gamma_j^{os\alpha'}(\underline{q})\, \delta(\epsilon - \hbar\omega_j(\underline{q})) \qquad (2.68)$$

which is the same as Eq. (2.1). Therefore when κ is "large," the coherent cross-section can be written in terms of the phonon expansion as in Eq. (2.16) for the incoherent cross-section. The directional G-functions in the incoherent approximation for the coherent cross-section can also be defined as they are in Eqs. (2.24) and (2.26).

CHAPTER 3

LATTICE DYNAMICS

The vibrational frequencies and cartesian displacement vectors necessary for the construction of the directional frequency functions may be obtained from the solutions to the equations of motion for the system. The usual method would be to first solve Wilson's GF matrix equations[17,18] for the displacements in internal coordinates followed by a transformation to cartesian coordinates. However, due to the large number of cartesian eigenvector solutions required in this analysis, a cartesian coordinate dynamical matrix equation is first obtained so that only one transformation between coordinate systems is necessary.

A. DYNAMICAL MATRIX EQUATION

In matrix notation, the potential energy of vibration, V, is given by:

$$2V = \underline{R}^{\dagger}\underline{\underline{F}}\underline{R} \qquad (3.1)$$

where $\underline{\underline{F}}$ is a matrix of internal coordinate force constants with matrix elements, in the harmonic approximation for the potential, given by:

$$f_{ij} = \frac{\partial^2 V}{\partial R_i \partial R_j} \quad . \qquad (3.2)$$

$\underline{R}$ is a displacement vector in internal coordinates with components R_i which denote changes in interatomic distances or in the angles between bonds. If a single crystal containing N unit cells with m atoms per cell is considered, the $\underline{\underline{F}}$ matrix and $\underline{R}$ vector are of order 3mN x 3mN and 3mN, respectively.*

The internal coordinate displacement vector and a cartesian displacement vector, $\underline{X}$, are related through the equation:

$$\underline{R} = \underline{\underline{B}}\,\underline{X} \tag{3.3}$$

where the elements of $\underline{\underline{B}}$ are determined by the geometry of the crystal.

In internal coordinates, the kinetic energy is given by:

$$2T = \dot{\underline{R}}^{\dagger}\,\underline{\underline{G}}^{-1}\,\dot{\underline{R}} \tag{3.4}$$

where

$$\underline{\underline{G}} = \underline{\underline{B}}\,\underline{\underline{M}}^{-1}\,\underline{\underline{B}}^{\dagger} \tag{3.5}$$

and $\underline{\underline{M}}^{-1}$ is a diagonal matrix with elements equal to the reciprocal masses of all atoms in the system. Making use of Eqs. (3.1) and (3.3), the potential energy in cartesian coordinates is given by[19]:

$$2V = \underline{X}^{\dagger}\,\underline{\underline{B}}^{\dagger}\,\underline{\underline{F}}\,\underline{\underline{B}}\,\underline{X} \tag{3.6}$$

which may be rewritten as:

$$2V = \underline{X}^{\dagger}\,\underline{\underline{F}}_{c}\,\underline{X} \tag{3.7}$$

where the cartesian coordinate force constant matrix is:

$$\underline{\underline{F}}_{c} = \underline{\underline{B}}^{\dagger}\,\underline{\underline{F}}\,\underline{\underline{B}} \tag{3.8}$$

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*Neglecting redundant coordinates.

In cartesian coordinates, the kinetic energy is given by:

$$2T = \dot{\underline{X}}^{\dagger} \, \underline{\underline{M}} \, \dot{\underline{X}} \tag{3.9}$$

where in analogy with the definition of $\underline{\underline{G}}$ in Eq. (3.5) the $\underline{\underline{G}}_c$ matrix in cartesian coordinates is defined as:

$$\underline{\underline{G}}_c \equiv \underline{\underline{M}}^{-1} \quad . \tag{3.10}$$

Notice that this is a diagonal matrix.

There is a system of normal coordinates in which $\underline{\underline{F}}_c$ is also a diagonal matrix. Therefore:

$$\underline{X} = \underline{\underline{L}}_c \, \underline{Q} \tag{3.11}$$

where $\underline{Q}$ is the normal coordinate vector and $\underline{\underline{L}}_c$ is the transformation matrix. Then:

$$2V = \underline{Q}^{\dagger} \, \underline{\underline{L}}_c^{\dagger} \, \underline{\underline{F}}_c \, \underline{\underline{L}}_c \underline{Q} \tag{3.12}$$

or:

$$2V = \underline{Q}^{\dagger} \, \underline{\underline{\Lambda}} \, \underline{Q} \tag{3.13}$$

where:

$$\underline{\underline{\Lambda}} = \underline{\underline{L}}_c^{\dagger} \, \underline{\underline{F}}_c \, \underline{\underline{L}}_c \ . \tag{3.14}$$

The kinetic energy may also be written using Eqs. (3.9), (3.10), and

(3.11) as:

$$2T = \underline{\dot{Q}}^{\dagger}\, \underline{\underline{L}}_c^{\dagger}\, \underline{\underline{G}}_c^{-1}\, \underline{\underline{L}}_c\, \underline{\dot{Q}} \qquad (3.15)$$

where:

$$\underline{\underline{L}}_c^{\dagger}\, \underline{\underline{G}}_c^{-1}\, \underline{\underline{L}}_c = \underline{\underline{E}} \quad . \qquad (3.16)$$

Since E is the unit matrix:

$$\underline{\underline{L}}_c^{\dagger} = \underline{\underline{L}}_c^{-1}\, \underline{\underline{G}}_c \qquad (3.17)$$

and so finally Eq. (3.14) becomes:

$$\underline{\underline{L}}_c^{-1}\, \underline{\underline{G}}_c\, \underline{\underline{F}}_c\, \underline{\underline{L}}_c = \underline{\underline{\Lambda}} \qquad (3.18)$$

or:

$$\underline{\underline{G}}_c\, \underline{\underline{F}}_c\, \underline{\underline{L}}_c = \underline{\underline{L}}_c\, \underline{\underline{\Lambda}} \qquad (3.19)$$

which is analogous to the Wilson GF equation in internal coordinates. The matrix $\underline{\underline{\Lambda}}$ is a diagonal matrix whose elements are the squares of the frequencies of vibration and $\underline{\underline{L}}_c$ is a matrix of column vectors whose components are the atomic displacements in cartesian coordinates. To facilitate solutions for $\underline{\underline{\Lambda}}$ and $\underline{\underline{L}}_c$, a symmetrical form for $\underline{\underline{G}}_c\underline{\underline{F}}_c$ is obtained.[20] Then:

$$\underline{\underline{C}}\,\underline{\underline{\Gamma}}_c = \underline{\underline{\Gamma}}_c\underline{\underline{\Lambda}} \qquad (3.20)$$

where:

$$\underline{\underline{C}} = \underline{\underline{G}}_c^{1/2}\,\underline{\underline{F}}_c\,\underline{\underline{G}}_c^{1/2} \tag{3.21}$$

$$\underline{\underline{\Gamma}}_c \equiv \underline{\underline{G}}_c^{-1/2}\,\underline{\underline{L}}_c \tag{3.22}$$

and

$$\underline{\underline{G}}_c^{1/2}\,\underline{\underline{G}}_c^{1/2} = \underline{\underline{G}}_c\,. \tag{3.23}$$

The $\underline{\underline{\Gamma}}_c$ matrix contains column vectors with components equal to the cartesian atomic displacements, each weighted by the square root of the atomic mass. These are the polarization vectors for which $\underline{\underline{\Gamma}}_c^{\dagger}\,\underline{\underline{\Gamma}}_c = \underline{\underline{E}}$, in agreement with Eq. (3.16).

It is the dynamical matrix Eq. (3.20) which must be solved for the eigenfrequencies and eigenvectors.

B. CARTESIAN SYMMETRY COORDINATE TRANSFORMATION

The use of the space group symmetry of a crystal makes it possible to perform a transformation to cartesian symmetry coordinates which block diagonalizes the dynamical matrix, $\underline{\underline{C}}$. All symmetry elements in that subgroup of the space group which leave the phonon wave vector, $\underline{q} \equiv \underline{q}_c$, invariant may be utilized[21]. (In this report, the wave vector is assumed in each case to be directed along the molecular chain axes which are parallel to the unit cell c axis.) The symmetry coordinate displacement vector is $\underline{S}$, where:

$$\underline{S} = \underline{\underline{U}}\,\underline{X} \tag{3.24}$$

and $\underline{\underline{U}}$ is the matrix of coefficients for the transformation. Then the dynamical matrix equation becomes:

$$\underline{\underline{U}}\,\underline{\underline{C}}\,\underline{\underline{U}}^{\dagger}\,\underline{\underline{U}}\,\underline{\underline{\Gamma}}_{c} = \underline{\underline{U}}\,\underline{\underline{\Gamma}}_{c}\,\underline{\underline{\Lambda}}$$

or:

$$\underline{\underline{C}}^{s}\,\underline{\underline{\Gamma}}_{c}^{s} = \underline{\underline{\Gamma}}_{c}^{s}\,\underline{\underline{\Lambda}} \qquad (3.25)$$

in cartesian symmetry coordinates, where:

$$\underline{\underline{C}}^{s} = \underline{\underline{U}}\,\underline{\underline{C}}\,\underline{\underline{U}}^{\dagger} \ . \qquad (3.26)$$

For convenience in the computer calculations, $\underline{\underline{U}}$ is written as a product of a phase dependent matrix and a diagonal matrix, $\underline{\underline{U}}(\pm)$, whose elements are appropriate powers of (-1) required for the symmetry coordinates. The phase referred to is that between adjacent chemical repeat units. It is:

$$\delta_c = \frac{qc}{2}$$

when c is the unit cell dimension along the chain axis direction and there are two chemical repeat units per unit cell, which are related by a glide or screw fractional translation. Therefore:

$$\underline{\underline{U}} \equiv \underline{\underline{U}}(\delta_c)\,\underline{\underline{U}}(\pm) \qquad (3.27)$$

and

$$\underline{\underline{\Gamma}}_{c}^{s} = \underline{\underline{U}}(\delta_c)\,\underline{\underline{U}}(\pm)\,\underline{\underline{\Gamma}}_{c} \ . \qquad (3.28)$$

The block diagonalized dynamical matrix may then be written as:

$$\underline{\underline{C}}^{s} = \underline{\underline{U}}(\delta_c)\,\underline{\underline{C}}(\underline{+})\,\underline{\underline{U}}(\delta_c)^{\dagger} \qquad (3.29)$$

where:

$$\underline{\underline{C}}(\underline{+}) = \underline{\underline{U}}(\underline{+})\,\underline{\underline{C}}\,\underline{\underline{U}}(\underline{+})^{\dagger} \;. \qquad (3.30)$$

The last transformation is performed by using:

$$\underline{\underline{B}}^{s} \equiv \underline{\underline{B}}\,\underline{\underline{U}}(\underline{+})^{\dagger} \qquad (3.31)$$

so that:

$$\underline{\underline{C}}(\underline{+}) = \underline{\underline{U}}(\underline{+})\,\underline{\underline{G}}_{c}^{1/2}\underline{\underline{F}}_{c}\underline{\underline{G}}_{c}^{1/2}\underline{\underline{U}}(\underline{+})^{\dagger} \qquad (3.32)$$

or:

$$\underline{\underline{C}}(\underline{+}) = \underline{\underline{G}}_{c}^{1/2}[\underline{\underline{B}}^{s\dagger}\underline{\underline{F}}\,\underline{\underline{B}}^{s}]\,\underline{\underline{G}}_{c}^{1/2} . \qquad (3.33)$$

The above treatment is adequate when performing a single-chain analysis using only intramolecular force constants and one-dimensional space group (line group) symmetry. In the general case, when intermolecular forces are also included:

$$\underline{\underline{F}}_{c} = \underline{\underline{B}}^{\dagger}\underline{\underline{F}}\,\underline{\underline{B}} + \underline{\underline{B}}'^{\dagger}\,\underline{\underline{F}}'\underline{\underline{B}}' \qquad (3.34)$$

where the intermolecular transformation matrix $\underline{\underline{B}}'$ is defined by:

$$\underline{R}' = \underline{\underline{B}}'\underline{X} \qquad (3.35)$$

and $\underline{\underline{F}}'$ is the internal coordinate intermolecular force constant matrix. The result is that when intramolecular and intermolecular forces are both used and three dimensional space group symmetry is employed, the dynamical matrix equation to be solved is Eq. (3.25):

$$\underline{\underline{C}}^{s}\,\underline{\underline{\Gamma}}^{s}_{c} = \underline{\underline{\Gamma}}^{s}_{c}\,\underline{\underline{\Lambda}}$$

where:

$$\underline{\underline{C}}^{s} = \underline{\underline{U}}(\delta_c)\,\underline{\underline{C}}(\pm)\,\underline{\underline{U}}(\delta_c)^{\dagger}$$

as before, but now:

$$\underline{\underline{C}}(\pm) = \underline{\underline{U}}(\pm)\,\underline{\underline{G}}_{c}^{1/2}\,\underline{\underline{F}}_{c}\,\underline{\underline{G}}_{c}^{1/2}\,\underline{\underline{U}}(\pm)^{\dagger} \qquad (3.36)$$

with $\underline{\underline{F}}_{c}$ given by Eq. (3.34) so that:

$$\underline{\underline{C}}(\pm) = \underline{\underline{G}}_{c}^{1/2}\,[\underline{\underline{B}}^{s\dagger}\,\underline{\underline{F}}\,\underline{\underline{B}}^{s} + \underline{\underline{B}}'^{s\dagger}\,\underline{\underline{F}}'\,\underline{\underline{B}}'^{s}]\,\underline{\underline{G}}_{c}^{1/2}$$

which is written as:

$$\underline{\underline{C}}(\pm) = \underline{\underline{G}}_{c}^{1/2}[\underline{\underline{A}} + \underline{\underline{A}}']\,\underline{\underline{G}}_{c}^{1/2} \qquad (3.37)$$

where:

$$\underline{\underline{A}} = \underline{\underline{B}}^{s\dagger}\,\underline{\underline{F}}\,\underline{\underline{B}}^{s} \qquad (3.38)$$

and:

$$\underline{\underline{A}}' = \underline{\underline{B}}'^{s\dagger}\,\underline{\underline{F}}'\,\underline{\underline{B}}'^{s}\ . \qquad (3.39)$$

These are, respectively, the cartesian intramolecular and intermolecular force constant matrices.

Since $\underline{\underline{U}}(\delta_c)$ and $\underline{\underline{G}}_c^{1/2}$ are both diagonal, $\underline{\underline{C}}^s$ may be rewritten as:

$$\underline{\underline{C}}^s = \underline{\underline{G}}_c^{1/2}\{\underline{\underline{U}}(\delta_c)\ [\underline{\underline{A}} + \underline{\underline{A}}'\,]\ \underline{\underline{U}}(\delta_c)^{\dagger}\}\ \underline{\underline{G}}_c^{1/2} \qquad (3.40)$$

or finally as:

$$\underline{\underline{C}}^s = \underline{\underline{G}}_c^{1/2}[\underline{\underline{A}}(\delta_c) + \underline{\underline{A}}'(\delta_c)]\ \underline{\underline{G}}_c^{1/2} \qquad (3.41)$$

where:

$$\underline{\underline{A}}(\delta_c) = \underline{\underline{U}}(\delta_c)\ \underline{\underline{A}}\ \underline{\underline{U}}(\delta_c)^{\dagger} \qquad (3.42)$$

and:

$$\underline{\underline{A}}'(\delta_c) = \underline{\underline{U}}(\delta_c)\ \underline{\underline{A}}'\ \underline{\underline{U}}(\delta_c)^{\dagger} \quad . \qquad (3.43)$$

C. CARTESIAN FORCE CONSTANT MATRICES

The intramolecular and intermolecular force constant matrices, $\underline{\underline{F}}$ and $\underline{\underline{F}}'$, may be transformed to cartesian coordinates as indicated in Eqs. (3.38) and (3.39). Consider, for example, the intramolecular cartesian force constant matrix:

$$\underline{\underline{A}} = \underline{\underline{B}}^{s\dagger}\ \underline{\underline{F}}\ \underline{\underline{B}}^s = \underline{\underline{\tilde{B}}}^s\ \underline{\underline{F}}\ \underline{\underline{B}}^s \qquad (3.44)$$

where the matrix elements of $\underline{\underline{B}}^s$ are real numbers.

The $\underline{\underline{F}}$, $\underline{\underline{B}}^s$, and $\tilde{\underline{\underline{B}}}^s$ matrices are partitioned into submatrices, as shown in Eqs. (3.45), (3.46), and (3.47). Each $\underline{\underline{F}}$ and $\underline{\underline{B}}^s$ submatrix contains (3 h + no. redundant coordinates) rows, where h is the number of atoms per chemical repeat unit along a chain axis. The index n labels a chemical repeat unit. Then:

$$\underline{\underline{F}} = \begin{array}{c|cccccccc|}
 & n-3 & n-2 & n-1 & R_n & n+1 & n+2 & n+3 & n+4 \\
n-3 & & & & \ddots & & & & \\
n-2 & & \cdots & \cdots & \underline{\underline{F}}_{n-2,n} & \ddots & & \bigcirc & \\
n-1 & \cdots & \cdots & \cdots & \underline{\underline{F}}_{n-1,n} & \underline{\underline{F}}_{n-1,n+1} & \ddots & & \\
R_n & \ddots & \underline{\underline{F}}_{n,n-2} & \underline{\underline{F}}_{n,n-1} & \underline{\underline{F}}_{n,n} & \underline{\underline{F}}_{n,n+1} & \underline{\underline{F}}_{n,n+2} & \ddots & \\
n+1 & & \ddots & \underline{\underline{F}}_{n+1,n-1} & \underline{\underline{F}}_{n+1,n} & \underline{\underline{F}}_{n+1,n+1} & \underline{\underline{F}}_{n+1,n+2} & \underline{\underline{F}}_{n+1,n+3} & \ddots \\
n+2 & & & \ddots & \underline{\underline{F}}_{n+2,n} & \underline{\underline{F}}_{n+2,n+1} & \underline{\underline{F}}_{n+2,n+2} & \underline{\underline{F}}_{n+2,n+3} & \underline{\underline{F}}_{n+2,n+4} \\
n+3 & & \bigcirc & & \ddots & \cdots & \cdots & \cdots & \cdots \\
n+4 & & & & & \ddots & \cdots & \cdots & \cdots
\end{array} \qquad (3.45)$$

$$
\underline{\underline{B}}^s = \begin{array}{c|cccccccc|}
 & n-3 & n-2 & n-1 & X_n & n+1 & n+2 & n+3 & n+4 \\
\hline
n-4 & \cdots & \cdots & \cdots & \diagdown & & & & \\
n-3 & \cdots & \cdots & \cdots & \diagdown & & \bigcirc & & \\
n-2 & \cdots & \cdots & \cdots & \underline{\underline{B}}^s_{n-2,n} & \diagdown & & & \\
n-1 & \diagdown & \underline{\underline{B}}^s_{n-1,n-2} & \underline{\underline{B}}s_{n-1,n-1} & \underline{\underline{B}}^s_{n-1,n} & \underline{\underline{B}}^s_{n-1,n+1} & \diagdown & & \\
R_n & & \diagdown & \underline{\underline{B}}^s_{n,n-1} & \underline{\underline{B}}^s_{n,n} & \underline{\underline{B}}^s_{n,n+1} & \underline{\underline{B}}^s_{n,n+2} & \diagdown & \diagdown \\
n+1 & & & \diagdown & \underline{\underline{B}}^s_{n+1,n} & \cdots & \cdots & & \diagdown \\
n+2 & \bigcirc & & & \diagdown & \underline{\underline{B}}^s_{n+2,n+1} & \cdots & & \\
n+3 & & & & \diagdown & & \cdots & &
\end{array}
\tag{3.46}
$$

$$
\underline{\underline{\tilde{B}}}^s = \begin{array}{c|ccccccccc|}
 & n-4 & n-3 & n-2 & n-1 & \tilde{R}_n & n+1 & n+2 & n+3 & n+4 \\
\hline
n-3 & & & & \diagdown & & & & & \\
n-2 & & & \cdots & \cdots & \diagdown & & \bigcirc & & \\
n-1 & & & \cdots & \cdots & \underline{\underline{\tilde{B}}}^s_{n+1,n} & \diagdown & & & \\
\tilde{X}_n & \diagdown & & \underline{\underline{\tilde{B}}}^s_{n,n+2} & \underline{\underline{\tilde{B}}}^s_{n,n+1} & \underline{\underline{\tilde{B}}}^s_{n,n} & \underline{\underline{\tilde{B}}}^s_{n,n-1} & \diagdown & & \\
n+1 & & & \diagdown & \cdots & \underline{\underline{\tilde{B}}}^s_{n-1,n} & \cdots & \cdots & \diagdown & \\
n+2 & & \bigcirc & & \diagdown & \underline{\underline{\tilde{B}}}^s_{n-2,n} & \cdots & \cdots & & \diagdown \\
n+3 & & & & & & \cdots & \cdots & & \\
 & & & & & \diagdown & & \cdots & &
\end{array}
\tag{3.47}
$$

In Eq. (3.47) the notation $\tilde{\underline{\underline{B}}}^s_{n,n+1}$ denotes the transpose of the submatrix found in the nth row and (n+1)st column of the B^s matrix.

From Eq. (3.44), a submatrix in the partitioned $\underline{\underline{A}}$ matrix is given by:

$$\underline{\underline{A}}_{n,m} = \sum_{\alpha\beta} (\tilde{\underline{\underline{B}}}^s)_{n,\alpha} \underline{\underline{F}}_{\alpha,\beta} \underline{\underline{B}}^s_{\beta,m} \quad . \tag{3.48}$$

This is the submatrix for the negative of cartesian forces on atoms in the nth chemical repeat unit resulting from unit positive displacements of atoms in the mth unit. In this equation, $(\tilde{\underline{\underline{B}}}^s)_{n,\alpha}$ is the submatrix found in the nth row and αth column of $\tilde{\underline{\underline{B}}}^s$. From Eq. (3.47), this n, αth submatrix of the transposed $\underline{\underline{B}}^s$ matrix is the transpose of the α, nth submatrix of the $\underline{\underline{B}}^s$ matrix.

Since:

$$\underline{\underline{F}}_{r,c} = \underline{\underline{F}}_{o,c-r} = \underline{\underline{F}}_{n,c-r+n} \tag{3.49}$$

and:

$$\underline{\underline{F}}_{n,n+1} = \tilde{\underline{\underline{F}}}_{n,n-1}$$

Eq. (3.48) becomes:

$$\underline{\underline{A}}_{n,m} = \sum_{\alpha\beta} (\tilde{\underline{\underline{B}}}^s)_{n,\alpha} \underline{\underline{F}}_{o,\beta-\alpha} \underline{\underline{B}}^s_{\beta,m} \quad . \tag{3.50}$$

Further, since:

$$\underline{\underline{B}}^s_{r,c} = \underline{\underline{B}}^s_{o,c-r}$$

then if:

$$\gamma = \beta - \alpha$$

the result, for forces on the zeroeth unit, is:

$$\underline{\underline{A}}_{o,m} = \sum_{\alpha,\gamma} (\underline{\underline{\tilde{B}}}^{s})_{o,\alpha} \underline{\underline{F}}_{o,\gamma} \underline{\underline{B}}^{s}_{o,m-\gamma-\alpha}. \qquad (3.51)$$

The limits on the indices α and γ are determined by the range of the internal coordinates and nonzero forces assumed in a given model. Usually these limits are determined by the internal rotation (torsion) force constant, since changes in this coordinate affect atoms at the greatest distance from the zeroeth unit.

D. PHASE DEPENDENT MATRIX EQUATIONS

The $\underline{\underline{A}}$ and $\underline{\underline{A}}'$ submatrices are obtained from the set of internal force constants through transformations which are described by Eq. (3.51). The phase dependent matrices $\underline{\underline{A}}(\delta)$ and $\underline{\underline{A}}'(\delta)$ are then given by Eqs. (3.42) and 3.43). Using Eq. (3.41), the block diagonalized dynamical matrix $\underline{\underline{C}}^{s}$ is then obtained. There will be N_c phase dependent blocks, where N_c is the number of unit cells along the direction parallel to the chain axes. That is, there are N_c values of q for $-\frac{\pi}{c} \leq q \leq + \frac{\pi}{c}$ or $-\pi \leq \theta < \pi$, where the phase between unit cells $\theta = qc$.

Since the space groups used in this report contain twofold screw-rotation or mirror-glide elements, there is a further block diagonalization of each (3m x 3m) phase dependent block into smaller matrices, where m is the number of atoms in a unit cell. These smaller blocks are identified in terms of the phase between adjacent chemical repeat units, $\delta_c = \theta/2$.

These observations are amplified in the individual sections in which phase dependent dynamical matrices are discussed for the various molecular crystals. See for example the section in Chapter 4, for polyethylene.

CHAPTER 4

SINGLE-CHAIN POLYETHYLENE

An extended transplanar model of the polyethylene chain is used, as described below.

A. CHAIN STRUCTURE AND COORDINATES

A single chain of polyethylene consists of a planar zig-zag configuration of CH_2 chemical repeat units as shown in Fig. 4.1.[22]

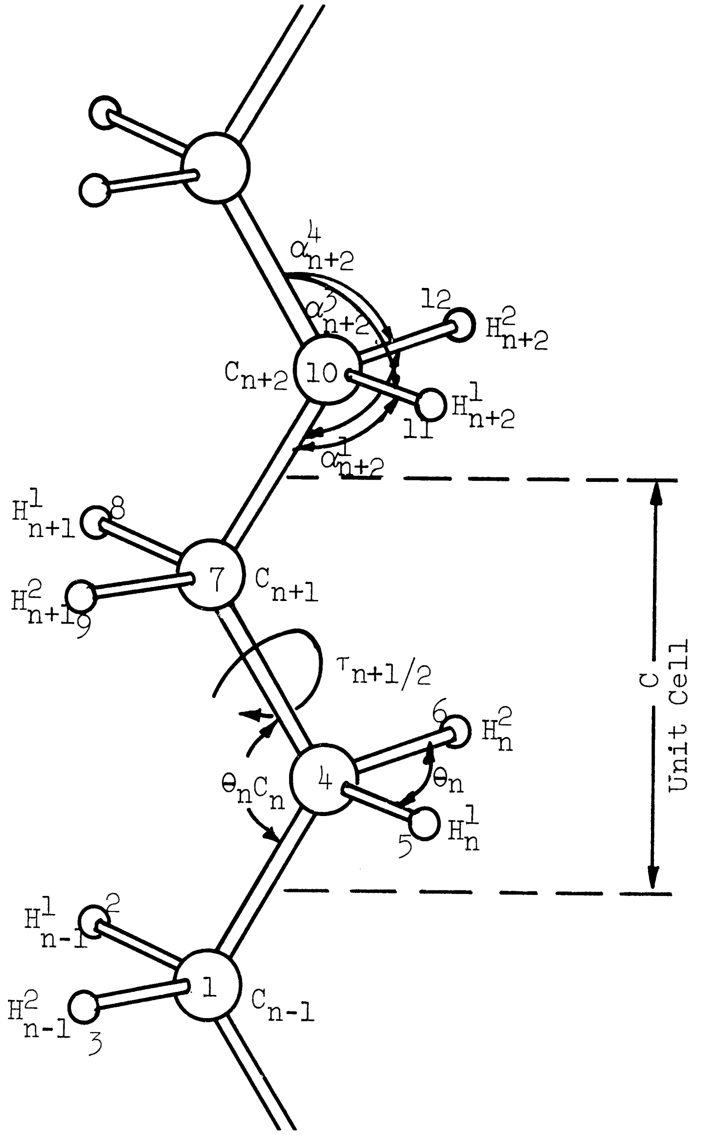


Fig. 4.1. Polyethylene chain structure.

The interatomic bond lengths and angles are given in Table I.[23]

TABLE I

POLYETHYLENE REPEAT UNIT DIMENSIONS

$r_{C-H} = 1.07 Å$

$r_{C-C} = 1.533 Å$

$\cancel{\theta}_{C-C-C} = 111°54'$

$\theta_{H-C-H} = 107°$

$\alpha_{H-C-C} = 109°28'$

$C = 2.54 Å$

The internal coordinates for each chemical repeat unit[24] are described in Table II.

TABLE II

POLYETHYLENE CHEMICAL REPEAT UNIT INTERNAL COORDINATES

Coordinate	Atoms	Type
$r_{n+1/2}$	C_n-C_{n+1}	stretch
r_n^{H1}	$C_n-H_n^1$	stretch
r_n^{H2}	$C_n-H_n^2$	stretch
$\cancel{\theta}_n$	$C_{n+1}-C_n-C_{n-1}$	bend
θ_n	$H_n^1-C_n-H_n^2$	bend
α_n^1	$C_{n-1}-C_n-H_n^1$	bend
α_n^2	$C_{n-1}-C_n-H_n^2$	bend
α_n^3	$C_{n+1}-C_n-H_n^1$	bend
α_n^4	$C_{n+1}-C_n-H_n^2$	bend
$\tau_{n+1/2}$	C_n-C_{n+1}	torsion

A (10 x 9) submatrix of the partitioned $\underline{\underline{B}}^s$ matrix, which relates the change in the internal coordinates of the nth chemical repeat unit to unit displacements in cartesian coordinates for the (n+1)'st unit, is shown in Eq. (4.1).

$$\underline{\underline{B}}^s_{n,n+1} = \begin{array}{c|ccccccccc|}
 & \Delta X^c_{n+1} & \Delta Y^c_{n+1} & \Delta Z^c_{n+1} & \Delta X^{H1}_{n+1} & \Delta Y^{H1}_{n+1} & \Delta Z^{H1}_{n+1} & \Delta X^{H2}_{n+1} & \Delta Y^{H2}_{n+1} & \Delta Z^{H2}_{n+1} \\
\Delta r_{n+1/2} & & & & & & & & & \\
\Delta r^{H1}_n & & & & & & & & & \\
\Delta r^{H2}_n & & & & & & & & & \\
\Delta \cancel{\theta}_n & & & & & & & & & \\
\Delta \theta_n & & & & & & & & & \\
\Delta \alpha^1_n & & & & & 10 \times 9 & & & & \\
\Delta \alpha^2_n & & & & & & & & & \\
\Delta \alpha^3_n & & & & & & & & & \\
\Delta \alpha^4_n & & & & & & & & & \\
\Delta \tau_{n+1/2} & & & & & & & & &
\end{array} \qquad (4.1)$$

Only the row and column labels are shown. The actual intramolecular $\underline{\underline{B}}$ matrix elements, which are obtained in a computer program using a method similar to that employed by Overend and Scherer,[25] are shown in the Appendix. For single-chain polyethylene, the chain-oriented cartesian coordinate systems shown in Fig. 4.2 are used.

The equations on pages 55-61 of Wilson's book[18] are used to calculate the $\underline{\underline{B}}$ matrix elements, except that a negative sign between $(e_{12} \times e_{23})$ and

(e_{43} x e_{32}) is changed to a positive sign[26] in equation (22). In addition, the torsion coordinate:

$$\Delta\tau = \sum_{i=1} \Delta\tau_i/9 \qquad (4.2)$$

for nontetrahedral geometry is used.[26,27]

The submatrices, $\underline{\underline{B}}^{s}_{r,c}$, which obey the relation $\underline{\underline{B}}^{s}_{r,c} = \underline{\underline{B}}^{s}_{o,c-r}$ as mentioned previously, are obtained using Eq. (3.31), which is:

$$\underline{\underline{B}}^{s} = \underline{\underline{B}}\,\underline{\underline{U}}(\pm)^{\dagger}.$$

This transformation is effected by simply applying the (±) signs to the matrix elements of $\underline{\underline{B}}$ as required by the symmetry coordinates, which are described in a following section. These required sign changes may also be viewed in terms of alternating cartesian coordinate systems which have like orientation in each CH^2 unit relative to the H^1 and H^2 atoms. These right-handed coordinate systems are shown in Fig. 4.2.

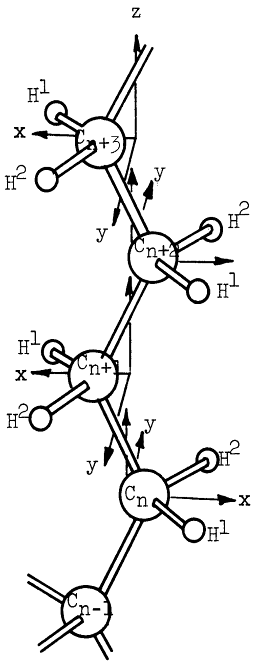


Fig. 4.2. Repeat unit cartesian coordinate systems for polyethylene chain.

B. INTRAMOLECULAR FORCE CONSTANTS

In terms of the internal coordinates, one of the 10 x 10 submatrices of the partitioned 20N x 20N force constant matrix, $\underline{\underline{F}}$, is:

$$\underline{\underline{F}}_{n,n+1} = \begin{array}{c|cccccccccc|}
 & \Delta r_{n+3/2} & \Delta r^{H1}_{n+1} & \Delta r^{H2}_{n+1} & \Delta \cancel{\theta}_{n+1} & \Delta \theta_{n+1} & \Delta \alpha^{1}_{n+1} & \Delta \alpha^{2}_{n+1} & \Delta \alpha^{3}_{n+1} & \Delta \alpha^{4}_{n+1} & \Delta \tau_{n+3/2} \\
\Delta r_{n+1/2} & & & & & & & & & & \\
\Delta r^{H1}_{n} & & & & & & & & & & \\
\Delta r^{H2}_{n} & & & & & & & & & & \\
\Delta \cancel{\theta}_{n} & & & & & & & & & & \\
\Delta \theta_{n} & & & & & & & & & & \\
\Delta \alpha^{1}_{n} & & & & & & & & & & \\
\Delta \alpha^{2}_{n} & & & & & & & & & & \\
\Delta \alpha^{3}_{n} & & & & & & & & & & \\
\Delta \alpha^{4}_{n} & & & & & & & & & & \\
\Delta \tau_{n+1/2} & & & & & & & & & &
\end{array} \qquad (4.3)$$

which again indicates only the row and column labels. The actual matrix elements are taken from the work of Schachtschneider and Snyder,[28] with the exception of the torsion force constant for which a value of 0.107 mdyne-Å/rad^2 was substituted.[24] These intramolecular force constant matrix elements are given in the Appendix.

Each of the 9 x 9 submatrices of the partitioned cartesian coordinate force constant matrix, $\underline{\underline{A}}$, will have labels as shown in Eq. (4.4).

$$\underline{\underline{A}}_{n,n+1} = \begin{array}{c|ccccccccc|} & \Delta X^{c}_{n+1} & \Delta Y^{c}_{n+1} & \Delta Z^{c}_{n+1} & \Delta X^{H1}_{n+1} & \Delta Y^{H1}_{n+1} & \Delta Z^{H1}_{n+1} & \Delta X^{H2}_{n+1} & \Delta Y^{H2}_{n+1} & \Delta Z^{H2}_{n+1} \\ \Delta X^{c}_{n} & & & & & & & & & \\ \Delta Y^{c}_{n} & & & & & & & & & \\ \Delta Z^{c}_{n} & & & & & & & & & \\ \Delta X^{H1}_{n} & & & & & & & & & \\ \Delta Y^{H1}_{n} & & & & & 9 \times 9 & & & & \\ \Delta Z^{H1}_{n} & & & & & & & & & \\ \Delta X^{H2}_{n} & & & & & & & & & \\ \Delta Y^{H2}_{n} & & & & & & & & & \\ \Delta Z^{H2}_{n} & & & & & & & & & \end{array} \qquad (4.4)$$

The submatrix $\underline{\underline{A}}_{o,m}$ is given by Eq. (3.51), where the choice of force constants dictates that:

$$-2 \leq m \leq +2$$

since torsion coordinate changes in the nth repeat unit affect atoms in units as far away as (n+2) and torsion coordinate changes in unit (n-2) affect atoms in unit n.

Other limits on indices are:

$$-2 \leq \alpha \leq +1$$

$$-1 \leq (m - \gamma - \alpha) \leq +2$$

which are dictated by the range of the internal coordinates, and:

$$-2 \leq \gamma \leq +2$$

which follows from the choice of internal force constants.

Since:

$$\underline{\underline{A}}_{o,m} = \tilde{\underline{\underline{A}}}_{o,\overline{m}}$$

and

$$\underline{\underline{A}}_{n,m} = \underline{\underline{A}}_{o,m-n}$$

all nonzero submatrices of $\underline{\underline{A}}$ near the diagonal are known if $\underline{\underline{A}}_{o,o}$, $\underline{\underline{A}}_{o,\overline{1}}$ and $\underline{\underline{A}}_{o,\overline{2}}$ are obtained.

C. LINE GROUP SYMMETRY ANALYSIS

An isolated polyethylene molecule in the extended configuration has the one-dimensional V_h space group symmetry.[29] There are eight symmetry elements in the V_h line group, as indicated in Fig. 4.3, which are defined in Table III.

TABLE III

V_h LINE GROUP SYMMETRY ELEMENTS

Element	Description
T_n	Pure translation along chain axis of magnitude nc.
$\overline{C}_2$	Rotation about chain axis through angle π, followed by fractional translation of magnitude c/2 along chain.
$\overline{\sigma}_v$	Mirror reflection in plane normal to C-C-C skeletal plane, followed by fractional translation of magnitude c/2 along chain.
σ_v	Mirror reflection in skeletal plane.
σ_h	Mirror reflection in plane of CH_2 group.
C_2	Two-fold rotation about axis bisecting H-C-H angle.
i	Inversion operation.
C_2'	Two-fold rotation about axis normal to skeletal plane.

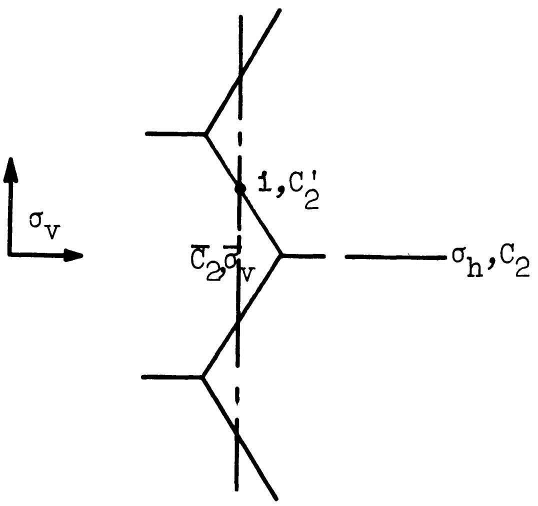


Fig. 4.3. Single-chain polyethylene symmetry operations.

Of these eight elements, only T, $\bar{\sigma}_V$, $\bar{C}_2$, and σ_V leave q_c invariant, and so these four elements form the star group.[30] The multiplication table for the star group is given in Table IV.

TABLE IV

STAR GROUP MULTIPLICATION TABLE
FOR SINGLE-CHAIN POLYETHYLENE

	T	$\bar{\sigma}_V$	$\bar{C}_2$	σ_V
T	T	$\bar{\sigma}_V$	$\bar{C}_2$	σ_V
$\bar{\sigma}_V$	$\bar{\sigma}_V$	T	σ_V	$\bar{C}_2$
$\bar{C}_2$	$\bar{C}_2$	σ_V	T	$\bar{\sigma}_V$
σ_V	σ_V	$\bar{C}_2$	$\bar{\sigma}_V$	T

The number of classes in the group, which is equal to the number of irreducible representations, is known if the class to which each element belongs is determined. Elements in the same class are conjugate. That is, the element R and X R X^{-1} are in the same class.[31] For example, if R is chosen to be $\bar{\sigma}_V$, then all conjugate elements are given by:

$$X_1 \; R \; X_1^{-1} = E\bar{\sigma}_V E^{-1} = \bar{\sigma}_V$$

$$\bar{C}_2\bar{\sigma}_V\bar{C}_2^{-1} = \bar{C}_2\bar{\sigma}_V\bar{C}_2 = \bar{C}_2\sigma_V = \bar{\sigma}_V$$

$$\sigma_V\bar{\sigma}_V\sigma_V^{-1} = \sigma_V\bar{\sigma}_V\sigma_V = \sigma_V\bar{C}_2 = \bar{\sigma}_V \quad .$$

So $\bar{\sigma}_V$ is in a class by itself.

The same is found to be true for E, $\bar{C}_2$, and σ_V, so there are four irreducible representations. The representations symmetric to $\bar{C}_2$ are labelled the A species and those antisymmetric to $\bar{C}_2$ are labelled the B species.[32] The representations symmetric to σ_V, are labelled with a subscript one and those antisymmetric to σ_V, are given a subscript two. The character table[30] for these one-dimensional representations of elements in the $\{q_c\}$ subgroup, the star group, is given in Table V. The character of a matrix operator in any representation is just the trace of the matrix.

TABLE V

STAR GROUP CHARACTER TABLE
FOR SINGLE-CHAIN POLYETHYLENE

	T	$\bar{\sigma}_V$	$\bar{C}_2$	σ_V
A_1	e^{iqd}	$e^{iqc/2}$	$e^{iqc/2}$	1
A_2	e^{iqd}	$-e^{iqc/2}$	$e^{iqc/2}$	-1
B_1	e^{iqd}	$-e^{iqc/2}$	$-e^{iqc/2}$	1
B_2	e^{iqd}	$e^{iqc/2}$	$-e^{iqc/2}$	-1

The term d is equal to any multiple of the unit cell dimension c, for

$$d = \ell c$$

and

$$o \leq \ell \leq N-1 \ .$$

Note that the orthogonality relation is obeyed[33]

$$\sum_{R} \chi^{*(\gamma)}(R)\chi^{(\gamma')}(R) = h\delta_{\gamma\gamma'}$$

where h = 4. The number of times each irreducible representation occurs in the reducible representation is[34]:

$$n^{(\gamma)} = \frac{1}{h} \sum \chi^{*(\gamma)}(R)\chi(R) \qquad (4.5)$$

where $\chi(R)$ is the character of the reducible representation for the operation R. The importance of this number, $n^{(\gamma)}$, for the γth representation is that it also represents the number of symmetry coordinates required for that representation.

TABLE VI

REDUCIBLE REPRESENTATION CHARACTERS FOR SINGLE-CHAIN POLYETHYLENE

$\chi(E)$ = 6(atoms) x 3 = 18

$\chi(\bar{\sigma}_v)$ = 0(atoms) x 3 = 0

$\chi(\bar{C}_2)$ = 0(atoms) x 3 = 0

$\chi(\sigma_v)$ = 2(atoms) x (1-1+1) = 2

These results, may be inferred from the following comments. The translation operation, T, leaves all displacements for the 6 atoms in a unit cell unchanged,* while σ_V leaves carbon displacements both in the chain axis direction (z) and in the x direction unchanged but reverses the sign of the carbon y displacements. The operation $\overline{\sigma}_V$ exchanges H^1 and H^2 atoms so has zero diagonal elements for the hydrogen atoms. Of course $\chi(\overline{\sigma}_V) = \chi(\overline{C}_2) = 0$, since no atoms are left undisturbed by these fractional translations.

Therefore, the number of times each irreducible representation appears in the reducible representation is found from Eq. (4.5) to be the following:

$$n^{(A_1)} = 1/4 \{(1 \times 18) + (1 \times 2)\} = 5$$

$$n^{(A_2)} = 1/4 \{(1 \times 18) - (1 \times 2)\} = 4$$

$$n^{(B_1)} = 1/4 \{18 + 2\} = 5$$

$$n^{(B_2)} = 1/4 \{18 - 2\} = 4$$

D. CARTESIAN SYMMETRY COORDINATES

In addition to the δ_c phase dependent symmetry coordinates referred to in Chapter 3, which consist of linear combinations of displacements of atoms in adjacent chemical repeat units, additional symmetry coordinates may be written. That is, nine local cartesian symmetry coordinates for the nth chemical repeat unit may be obtained. This is possible because the CH_2 unit itself has internal symmetry due to the σ_V mirror operation. The local symmetry coordinate vector is:

$$\underline{S}_n = \underline{\underline{U}}_n(\sigma_V)\underline{X}_n \quad . \tag{4.6}$$

---

*Considering a translation T equivalent to E for a single unit cell.

The components for the γth irreducible representation are given by[35]:

$$S_i^{(\gamma)} = \eta \sum_R \chi^{(\gamma)}(R) R \xi_i \quad . \qquad (4.7)$$

The first five rows in $\underline{S}_n$ for the A_1 species are symmetric to σ_v, and the last four rows for the A_2 species are antisymmetric to σ_v. ξ_i is a generating coordinate, as for example an x, y or z displacement of a hydrogen or carbon atom.

The results are shown in Eq. (4.8).

$$\left.\begin{aligned} S_{1n} &= \Delta X_n^C \\ S_{2n} &= \Delta Z_n^C \\ S_{3n} &= \frac{\Delta X_n^{H^1} + \Delta X_n^{H^2}}{\sqrt{2}} \\ S_{4n} &= \frac{\Delta Y_n^{H^1} - \Delta Y_n^{H^2}}{\sqrt{2}} \\ S_{5n} &= \frac{\Delta Z_n^{H^1} + \Delta Z_n^{H^2}}{\sqrt{2}} \end{aligned}\right\} \begin{array}{c}\text{Symmetric} \\ \text{to} \\ \sigma_v\end{array}$$

$$\left.\begin{aligned} S_{6n} &= \Delta Y_n^C \\ S_{7n} &= \frac{\Delta X_n^{H^1} - \Delta X_n^{H^2}}{\sqrt{2}} \\ S_{8n} &= \frac{\Delta Y_n^{H^1} + \Delta Y_n^{H^2}}{\sqrt{2}} \\ S_{9n} &= \frac{\Delta Z_n^{H^1} - \Delta Z_n^{H^2}}{\sqrt{2}} \end{aligned}\right\} \begin{array}{c}\text{Antisymmetric} \\ \text{to} \\ \sigma_v\end{array} \qquad (4.8)$$

These happen to be mutually orthogonal, although in general the prescription in Eq. (4.7) does not guarantee this.[35]

The transformation matrix is given in Eq. (4.9), as follows:

$$\underline{\underline{U}}_n(\sigma_v) = \begin{array}{c|ccc|ccc|ccc|} & \Delta X^c & \Delta Y^c & \Delta Z^c & \Delta X^{H1} & \Delta Y^{H1} & \Delta Z^{H1} & \Delta X^{H2} & \Delta Y^{H2} & \Delta Z^{H2} \\ S_{1n} & 1 & & & & & & & & \\ S_{2n} & & & 1 & & & & & & \\ S_{3n} & & & & 1/\sqrt{2} & & & 1/\sqrt{2} & & \\ \hline S_{4n} & & & & & 1/\sqrt{2} & & & -1/\sqrt{2} & \\ S_{5n} & & & & & & 1/\sqrt{2} & & & 1/\sqrt{2} \\ S_{6n} & & 1 & & & & & & & \\ \hline S_{7n} & & & & 1/\sqrt{2} & & & -1/\sqrt{2} & & \\ S_{8n} & & 1/\sqrt{2} & & & & & & 1/\sqrt{2} & \\ S_{9n} & & & & & & 1/\sqrt{2} & & & -1/\sqrt{2} \end{array} \qquad (4.9)$$

The screw-translation symmetry coordinates may now be obtained from the local coordinates, since

$$\underline{X}_s^{(\gamma)}(\delta_c) = \eta \sum_R \chi^{(\gamma)}(R) R \, \underline{S}_n(\sigma_v) \qquad (4.10)$$

for

$$R = E, \bar{c}_2, \bar{c}_2^2, \bar{c}_2^3, \ldots, \bar{c}_2^{(2N-1)}$$

where the phase is defined as $\delta_c = qc/2 = \Theta/2$. Then

$$\underline{X}_s^{(A)}(\delta_c) = \eta \{ \underline{S}_n(\sigma_v) + e^{iqc/2} \, \underline{S}_{n+1}(\sigma_v) + e^{iqc} \, \underline{S}_{n+2}(\sigma_v) + \ldots \} \qquad (4.11)$$

or[36]

$$\underline{X}_s^{(A)}(\delta_c) = \frac{1}{\sqrt{2N}} \sum_{m=0}^{2N-1} e^{im\delta_c} \, \underline{S}_m(\sigma_v) \qquad (4.12)$$

and

$$\underline{X}_s^{(B)}(\delta_c) = \frac{1}{\sqrt{2N}} \sum_{m=0}^{2N-1} e^{im\pi} e^{im\delta_c} \underline{S}_m(\sigma_v) \qquad (4.13)$$

where N is the number of unit cells along the c axis direction. The real and imaginary parts of these symmetry coordinates may be obtained.[37]

$$\begin{aligned} \mathrm{Re}\{\underline{X}_s^{(\gamma)}(\delta_c)\} &= \frac{1}{\sqrt{2}} [\underline{X}_s^{(\gamma)} + \underline{X}_s^{*(\gamma)}] \\ \mathrm{Im}\{\underline{X}_s^{(\gamma)}(\delta_c)\} &= \frac{1}{i\sqrt{2}} [\underline{X}_s^{(\gamma)} - \underline{X}_s^{*(\gamma)}] \end{aligned} \qquad (4.14)$$

so

$$\begin{aligned} \mathrm{Re}\{\underline{X}_s^{(A)}(\delta_c)\} &= \left(\frac{1}{N}\right)^{1/2} \sum_{m=0}^{2N-1} \cos m\delta_c \, \underline{S}_m(\sigma_v) \\ \mathrm{Im}\{\underline{X}_s^{(A)}(\delta_c)\} &= \left(\frac{1}{N}\right)^{1/2} \sum_{m=0}^{2N-1} \sin m\delta_c \, \underline{S}_m(\sigma_v) \end{aligned} \qquad (4.15)$$

where

2N = the number of chemical repeat units in the chain.

Also

$$\begin{aligned} \mathrm{Re}\{\underline{X}_s^{(B)}(\delta_c)\} &= \left(\frac{1}{N}\right)^{1/2} \sum_{m=0}^{2N-1} \cos m(\delta_c+\pi) \underline{S}_m(\sigma_v) \\ \mathrm{Im}\{\underline{X}_s^{(B)}(\delta_c)\} &= \left(\frac{1}{N}\right)^{1/2} \sum_{m=0}^{2N-1} \sin m(\delta_c+\pi) \underline{S}_m(\sigma_v) \quad . \end{aligned} \qquad (4.16)$$

There are now 36 real symmetry coordinates in place of the 18 complex coordinates. The order of these 18 will be altered so that the first nine A species coordinates are symmetric to the C_2 operation, which in reciprocal space takes $+q_c$ into $-q_c$, and the next nine A species coordinates are antisymmetric to C_2. The same is done for the 18 real B coordinates. The usefulness of doing this will be made clear in the next section. Nine real A species phase dependent coordinates, which are symmetric to C_2, are shown in Eq. (4.17).*

$$\begin{aligned}
X_1^{(A_1)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m=0}^{2N-1} \Delta X_m^c \cos m\delta_c \\
X_2^{(A_1)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m} \Delta Z_m^c \sin m\delta_c \\
X_3^{(A_1)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m} \frac{(\Delta X_m^{H^1} + \Delta X_m^{H^2})}{\sqrt{2}} \cos m\delta_c \\
X_4^{(A_1)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m} \frac{(\Delta Y_m^{H^1} - \Delta Y_m^{H^2})}{\sqrt{2}} \cos m\delta_c \\
X_5^{(A_1)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m} \frac{(\Delta Z_m^{H^1} + \Delta Z_m^{H^2})}{\sqrt{2}} \sin m\delta_c \qquad (4.17) \\
X_6^{(A_2)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m} \Delta Y_m^c \sin m\delta_c \\
X_7^{(A_2)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m} \frac{(\Delta X_m^{H^1} - \Delta X_m^{H^2})}{\sqrt{2}} \sin m\delta_c \\
X_8^{(A_2)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m} \frac{(\Delta Y_m^{H^1} + \Delta Y_m^{H^2})}{\sqrt{2}} \sin m\delta_c \\
X_9^{(A_2)}(\delta_c) &= \left(\frac{1}{N}\right)^{1/2} \sum_{m} \frac{(\Delta Z_m^{H^1} - \Delta Z_m^{H^2})}{\sqrt{2}} \cos m\delta_c \quad .
\end{aligned}$$

---

*Recall that Eq. (3.31) or the alternating coordinate systems are used for the phase independent transformation, so no $(-1)^m$ terms are shown here for the x and y displacements.

The nine A' coordinates which are antisymmetric to C_2 may be obtained from those above by simply replacing all cos $m\delta_c$ by sin $m\delta_c$ and all sin $m\delta_c$ by -cos $m\delta_c$.

The 18 B coordinates differ from the above coordinates only in a term $(-1)^m$ or cos $m\pi$ which appears in each coordinate, since

$$\cos m(\delta_c+\pi) = \cos m\delta_c \cos m\pi$$

$$\sin m(\delta_c+\pi) = \sin m\delta_c \cos m\pi \ .$$

E. PHASE DEPENDENT DYNAMICAL MATRICES

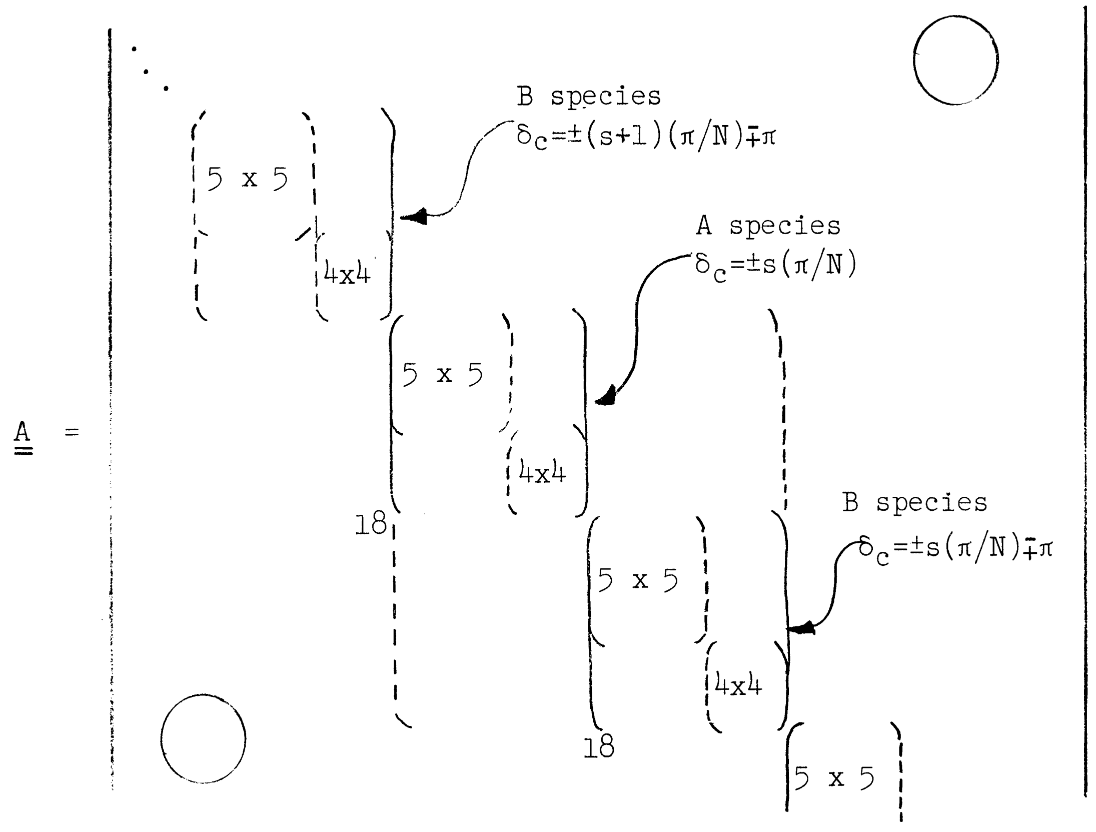
The 9 x 9 submatrices $\underline{\underline{A}}_{m,n}$ of the intramolecular cartesian force constant matrix $\underline{\underline{A}}$ may each be factored using the local symmetry coordinate transformation matrices, one of which is given in Eq. (4.9). Then

$$\underline{\underline{A}}_{m,n}(\sigma_v) = \underline{\underline{U}}_m(\sigma_v)\underline{\underline{A}}_{m,n}\underline{\underline{U}}_n(\sigma_v) \qquad (4.18)$$

where now

$$\underline{\underline{A}}_{m,n}(\sigma_v) = \left(\begin{array}{c|c} \begin{matrix} A_1 \\ 5 \times 5 \end{matrix} & \\ \hline & \begin{matrix} A_2 \\ 4 \times 4 \end{matrix} \end{array}\right) . \qquad (4.19)$$

The translational and screw translational symmetry is also utilized to block diagonalize the 18N x 18N cartesian force constant matrix $\underline{\underline{A}}$ into 9 x 9 blocks, each of which is factored as shown above. By using the complex symmetry coordinates from Eqs. (4.12) and (4.13) the following is obtained.



(4.20)

There are 2N complex (9 x 9) blocks and $0 \le s \le (N-1)/2$, since the Born cyclic boundary condition requires for

$$e^{iqr} = e^{iqn'c} = e^{i\Theta n'} = e^{i\frac{\Theta}{2}m} = e^{i\delta m} \qquad (4.21)$$

that the Nth unit cell be in phase with the first, or that

$$e^{iqx0} = e^{iqNc} = e^{i\delta 2N} = 1$$

for N an even number.

The values shown in Eq. (4.20) for δ_c in the B species blocks result from the fact that the B species symmetry coordinates differ from those of the A species only in a π phase factor. Also see Fig. 4.4, which follows.

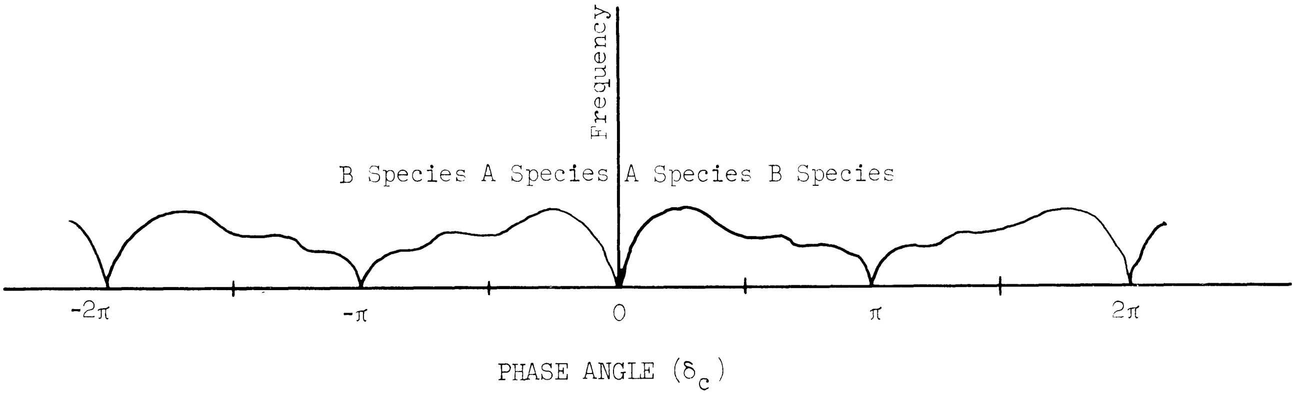


Fig. 4.4. Dispersion curve branches for symmetric and anti-symmetric species.

Instead of using complex symmetry coordinates however, real coordinates such as those given in Eq. (4.17) for the A species are used. Then each (18 x 18) block for a given δ_c value becomes a (36 x 36) block as:

$$\begin{array}{cc} & 18 \\ 18 & \left(\begin{array}{c|c} A & 0 \\ \hline 0 & B \end{array}\right) \end{array} \longrightarrow \begin{array}{cc} \left(\begin{array}{cccc} A & & & \\ & A' & & \\ & & B & \\ & & & B' \end{array}\right) & 36 \\ 36 & \end{array} \qquad (4.22)$$

where the primed species are anti-symmetric to C_2 and the unprimed species are symmetric to C_2. A somewhat different complex to real transformation is discussed in Chapter 7 for polyvinylchloride, since PVC lacks the symmetry operation $\bar{C}_2$ which simplifies the transformation here.[37]

The A and A' blocks are identical and the B and B' blocks are also identical in this case. The proof, which is not difficult, will be given now.

For the A' species cartesian symmetry coordinates which are antisymmetric to C_2, the phase dependent submatrix of coefficients, $\underline{\underline{U}}^{(A')}_{o,\alpha}(\delta_c)$ is:

$$\underline{\underline{U}}^{(A')}_{o,\alpha}(\delta_c) = \left(\frac{1}{N}\right)^{1/2} \times \begin{array}{c|ccccccccc|} X_1^{A'}(\delta_c) & \sin\alpha\delta_c & & & & & & & & \\ X_2^{A'}(\delta_c) & & -\cos\alpha\delta_c & & & & & & & \\ X_3^{A'}(\delta_c) & & & \sin\alpha\delta_c & & & & & & \\ X_4^{A'}(\delta_c) & & & & \sin\alpha\delta_c & & & & & \\ X_5^{A'}(\delta_c) & & & & & -\cos\alpha\delta_c & & & & \\ X_6^{A'}(\delta_c) & & & & & & -\cos\alpha\delta_c & & & \\ X_7^{A'}(\delta_c) & & & & & & & -\cos\alpha\delta_c & & \\ X_8^{A'}(\delta_c) & & & & & & & & -\cos\alpha\delta_c & \\ X_9^{A'}(\delta_c) & & & & & & & & & \sin\alpha\delta_c \\ & S_{1\alpha} & S_{2\alpha} & S_{3\alpha} & S_{4\alpha} & S_{5\alpha} & S_{6\alpha} & S_{7\alpha} & S_{8\alpha} & S_{9\alpha} \end{array} \tag{4.23}$$

where the 18N component screw translational symmetry coordinate vector is

$$\underline{X}^{(A')}(\delta) = \underline{\underline{U}}^{(A')}(\delta)\underline{S}(\sigma_V)$$

and the symmetry coordinate vector for the zeroeth chemical repeat unit is

$$\underline{X}_o^{(A')}(\delta) = \sum_{\alpha} \underline{\underline{U}}^{(A')}_{o,\alpha}(\delta)\underline{S}_{\alpha}(\sigma_V) \tag{4.24}$$

which is a nine component vector.

An A' species submatrix on the diagonal of $\underline{\underline{A}}(\delta_c)$ is shown by Eq. (3.42) to be:

$$\underline{\underline{A}}^{(A')}_{o,o}(\delta) = \sum_{\alpha,\gamma} \underline{\underline{U}}^{(A')}_{o,\alpha}(\delta)\underline{\underline{A}}_{o,\gamma}(\sigma_V)\underline{\underline{U}}^{(A')}_{o,\gamma+\alpha} \tag{4.25}$$

A given $\underline{\underline{A}}_{o,\gamma}(\sigma_V)$ matrix element is multiplied by a factor, the value of which depends on the element's row and column indices, as shown below for the A' species.

$$\begin{array}{ll|ll}
 & & \multicolumn{2}{c}{\text{Column}} \\
 & & j = 1,3,4,9 & j = 2,5,6,7,8 \\ \hline
 & i = 1,3,4,9 & \frac{1}{N}\sum\limits_{\alpha=0} +\sin \alpha\delta_c \sin(\alpha+\gamma)\delta_c & \frac{1}{N}\sum\limits_{\alpha=0} -\sin \alpha\delta_c \cos(\alpha+\gamma)\delta_c \\
\text{Row} & & & \\
 & i = 2,5,6,7,8 & \frac{1}{N}\sum\limits_{\alpha=0}^{2N-1} -\cos \alpha\delta_c \sin(\alpha+\gamma)\delta_c & \frac{1}{N}\sum\limits_{\alpha=0}^{2N-1} +\cos \alpha\delta_c \cos(\alpha+\gamma)\delta_c
\end{array}$$

For large N:

$$\frac{1}{N}\sum_{\alpha=0}^{2N-1} \cos \alpha\delta_c \cos(\alpha+\gamma)\delta_c = \frac{1}{N}\sum_{\alpha}\left(\frac{e^{i\alpha\delta}+e^{-i\alpha\delta}}{2}\right)\left(\frac{e^{i(\alpha+\gamma)\delta}+e^{-i(\alpha+\gamma)\delta}}{2}\right)$$

$$= \frac{1}{4N}\sum_{\alpha=0}^{2N-1} e^{i\gamma\delta}[e^{i2\alpha\delta}+1] + e^{-i\gamma\delta}[e^{-i2\alpha\delta}+1]$$

$$= \frac{1}{4N}\,2N[e^{i\gamma\delta}+e^{-i\gamma\delta}] = \cos\gamma\delta_c \quad .$$

The other sums are also reduced, to obtain a factor for the A' species (i,j)th element:

$$\begin{array}{ll|ll}
 & & \multicolumn{2}{c}{\text{Column}} \\
 & & j = 1,3,4,9 & j = 2,5,6,7,8 \\ \hline
 & i = 1,3,4,9 & \cos\gamma\delta_c & \sin\gamma\delta_c \\
\text{Row} & & & \\
 & i = 2,5,6,7,8 & -\sin\gamma\delta_c & \cos\gamma\delta_c
\end{array}$$

for a given $\underline{\underline{A}}_{o,\gamma}(\sigma_v)$. This is identical to the result for the A species, symmetric to C_2, which is given on page 59.

This result, that the A and A' species blocks are identical, is a simple statement that the dispersion curve (frequency solution for q) is the same for $+q_c$ as for $-q_c$. Recall that the C_2 operation in reciprocal space takes $+q_c$ into $-q_c$, but as seen above this does not alter the dynamical matrix.

Furthermore, elements in the B species block, $\underline{\underline{A}}^{(B)}_{o,o}(\delta_c)$, differ from those in the A species block only in the π phase term which appears in the B species cosine or sine arguments, as $\cos \gamma(\delta+\pi)$ or $\sin \gamma(\delta+\pi)$.

The significance of these observations is that only the A species (9×9), $(5 \times 5) \oplus (4 \times 4)$, δ_c dependent block need be used in the computer calculations. All B species solutions are obtained by simply allowing δ_c, which has range $0 \leq \delta \leq \pi/2$, to take on values between $\pi/2$ and π. This unfolding of the dispersion curves is shown in Fig. 4.4. See also page 117, Ref. 31. As already described by Eq. (4.25), each of the phase dependent $\underline{\underline{A}}_{o,o}(\delta_c)$ submatrices is assembled from a sum of cartesian force constant matrices to which the mass weighting is then applied by the $\underline{\underline{G}}^{1/2}_{c}$ submatrices according to Eq.(3.41) to obtain the phase dependent dynamical submatrix. An A species phase dependent force constant matrix is

$$\underline{\underline{A}}^{(A)}_{o,m}(\delta_c) = \sum_{\alpha,\beta} \underline{\underline{U}}^{(A)}_{o,\alpha}(\delta_c)\underline{\underline{A}}_{\alpha,\beta}(\sigma_v) \; (\tilde{\underline{\underline{U}}}^{(A)}(\delta_c))_{\beta,m} \qquad (4.26)$$

where from Eq. (4.17):

$$\underline{\underline{U}}^{(A)}_{o,\alpha}(\delta_c) = \left(\frac{1}{N}\right)^{1/2} \times \begin{array}{c|ccccccccc} & S_{1\alpha} & S_{2\alpha} & S_{3\alpha} & S_{4\alpha} & S_{5\alpha} & S_{6\alpha} & S_{7\alpha} & S_{8\alpha} & S_{9\alpha} \\ \hline X_1^{A_1}(\delta_c) & \cos\alpha\delta_c & & & & & & & & \\ X_2^{A_1}(\delta_c) & & \sin\alpha\delta_c & & & & & & & \\ X_3^{A_1}(\delta_c) & & & \cos\alpha\delta_c & & & & & & \\ X_4^{A_1}(\delta_c) & & & & \cos\alpha\delta_c & & & & & \\ X_5^{A_1}(\delta_c) & & & & & \sin\alpha\delta_c & & & & \\ X_6^{A_2}(\delta_c) & & & & & & \sin\alpha\delta_c & & & \\ X_7^{A_2}(\delta_c) & & & & & & & \sin\alpha\delta_c & & \\ X_8^{A_2}(\delta_c) & & & & & & & & \sin\alpha\delta_c & \\ X_9^{A_2}(\delta_c) & & & & & & & & & \cos\alpha\delta_c \end{array} \tag{4.27}$$

Since only diagonal blocks of the block diagonalized A matrix are nonzero, only m = 0 is needed, and

$$(\underline{\underline{G}}_c^{1/2})_{o,o}\underline{\underline{A}}^{(A)}_{o,o}(\delta_c)(\underline{\underline{G}}_c^{1/2})_{o,o} = \underline{\underline{C}}^{s(A)}_{o,o}(\delta_c) \tag{4.28}$$

where

$$\underline{\underline{A}}^{(A)}_{o,o}(\delta_c) = \sum_{\alpha,\gamma} \underline{\underline{U}}^{(A)}_{o,\alpha}(\delta_c)\underline{\underline{A}}_{o,\gamma}(\sigma_v)\underline{\underline{U}}^{(A)}_{o,\gamma+\alpha}(\delta_c) \tag{4.29}$$

since

$$(\underline{\underline{\tilde{U}}}(\delta_c))_{\gamma+\alpha,o} = \underline{\underline{U}}_{o,\gamma+\alpha}(\delta_c)$$

and $\gamma = \beta-\alpha$. Of course Eq. (4.28) actually represents all 2N diagonal blocks of $\underline{\underline{C}}^s$, since δ_c takes on 2N values.

From

$$\sum_{\alpha,\gamma} \underline{\underline{U}}^{(A)}_{o,\alpha}(\delta)\underline{\underline{A}}_{o,\gamma}(\sigma_V)\underline{\underline{U}}^{(A)}_{o,\gamma+\alpha}(\delta)$$

in Eq. (4.29), one sees that matrix elements of a given $\underline{\underline{A}}_{o,\gamma}(\sigma_V)$ matrix are multiplied by a sum of terms involving cos ($\alpha\delta$) and sin ($\alpha\delta$). For a given row and column element of $\underline{\underline{A}}_{o,\gamma}(\sigma_V)$, the A species multiplication factor is:

$$\begin{array}{ll|ll}
 & & \multicolumn{2}{c}{\text{Column}} \\
 & & j = 1,3,4,9 & j = 2,5,6,7,8 \\
\hline
\text{Row} & i = 1,3,4,9 & \frac{1}{N}\sum_{\alpha=0}^{2N-1} \cos\alpha\delta\,\cos(\alpha+\gamma)\delta & \frac{1}{N}\sum_{\alpha} \cos\alpha\delta\,\sin(\alpha+\gamma)\delta \\
 & i = 2,5,6,7,8 & \frac{1}{N}\sum_{\alpha} \sin\alpha\delta\,\cos(\alpha+\gamma)\delta & \frac{1}{N}\sum_{\alpha} \sin\alpha\delta\,\sin(\alpha+\gamma)\delta
\end{array}$$

For large N, certainly the factor for $\begin{Bmatrix} i = 1,3,4,9 \\ j = 1,3,4,9 \end{Bmatrix}$ and $\begin{Bmatrix} i = 2,5,6,7,8 \\ j = 2,5,6,7,8 \end{Bmatrix}$ is identical to the corresponding factor shown previously for the A' species on page 56. The $\begin{Bmatrix} i = 1,3,4,9 \\ j = 2,5,6,7,8 \end{Bmatrix}$ factor shown above is also the same as the $\begin{Bmatrix} i = 2,5,6,7,8 \\ j = 1,3,4,9 \end{Bmatrix}$ A' species factor shown on page 56, but with opposite sign.

Therefore the result is that the phase terms to be applied to the $\underline{\underline{A}}_{o,\gamma}(\sigma_V)$ matrix elements to obtain the A species, $\underline{\underline{A}}^{(A)}_{o,o}(\delta_c)$, block are:

$$\begin{array}{ll|ll}
 & & \multicolumn{2}{c}{\text{Column}} \\
 & & j = 1,3,4,9 & j = 2,5,6,7,8 \\
\hline
\text{Row} & i = 1,3,4,9 & \cos\gamma\delta_c & \sin\gamma\delta_c \\
 & i = 2,5,6,7,8 & -\sin\gamma\delta_c & \cos\gamma\delta_c
\end{array}$$

Finally then:

$$(\underline{\underline{A}}^{(A)}_{o,o})_{i,j} = \sum_{\gamma} (\underline{\underline{A}}_{o,\gamma}(\sigma_V))_{i,j} \cos \gamma\delta_c \qquad \begin{cases} i = 1,3,4,9 \\ j = 1,3,4,9 \end{cases} \quad \begin{cases} i = 2,5,6,7,8 \\ j = 2,5,6,7,8 \end{cases}$$

$$(\underline{\underline{A}}^{(A)}_{o,o})_{i,j} = \sum_{\gamma} (\underline{\underline{A}}_{o,\gamma}(\sigma_V))_{i,j} \sin \gamma\delta_c \qquad \begin{cases} i = 1,3,4,9 \\ j = 2,5,6,7,8 \end{cases} \qquad (4.30)$$

$$(\underline{\underline{A}}^{(A)}_{o,o})_{i,j} = \sum_{\gamma} -(\underline{\underline{A}}_{o,\gamma}(\sigma_V))_{i,j} \sin \gamma\delta_c \qquad \begin{cases} i = 2,5,6,7,8 \\ j = 1,3,4,9 \end{cases}$$

for $-2 \leq \gamma \leq +2$. In this way, one (5 x 5) and one (4 x 4) matrix is obtained for each value of δ_c for $0 \leq \delta_c \leq \pi$. The diagonal $\underline{\underline{G}}_c^{1/2}$ submatrices are then applied to the (5 x 5) A_1 and the (4 x 4) A_2 matrices to obtain the dynamical matrices as indicated in Eq. (4.28).

The solutions to the block diagonalized dynamical matrix Eq. (3.25),

$$\underline{\underline{C}}^s \, \underline{\underline{\Gamma}}^s_c = \underline{\underline{\Gamma}}^s_c \, \underline{\underline{\Lambda}}$$

for which each phase dependent diagonal block of $\underline{\underline{C}}^s$ is given by Eq. (4.28), are displayed in the following section.

F. DISPERSION CURVES AND ONE-PHONON FREQUENCY FUNCTIONS

The frequency solutions for single-chain normal polyethylene which were obtained from Eq. (3.25) are displayed in Fig. 4.5. The labels on branches

ν_1 to ν_9 match the notation of Tasumi, Shimanouchi, and Miyazawa.[24]

The corresponding frequency solutions for single-chain deuterated polyethylene are shown in Fig. 4.6. The labels in the latter figure match those of Tasumi and Krimm for the deuterated crystalline polyethylene results.[40]

These results match the published frequencies well enough to provide confirmation that the methods used in this analysis are essentially correct.

The eigenvectors corresponding to these frequency solutions are used to construct the longitudinal and transverse G-functions for single-chain polyethylene as described by Eqs. (2.1), (2.28), and (2.29). These directional frequency functions are shown in Figs. 4.7 and 4.8.

The force field will now be augmented by including intermolecular forces and the modified frequency solutions and eigenvectors will be obtained for a lattice of extended polyethylene molecules.

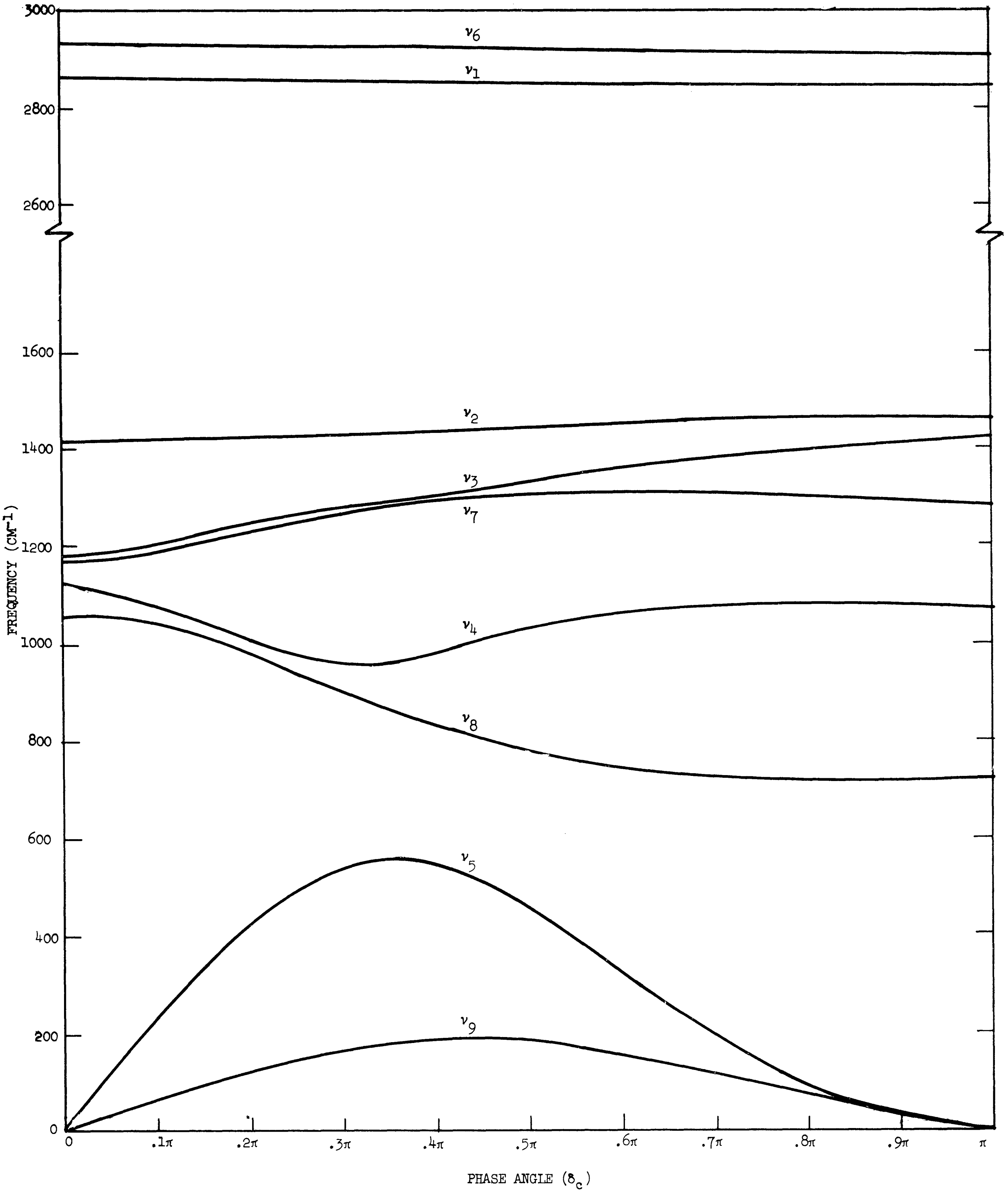


Fig. 4.5. Single-chain polyethylene dispersion curves.

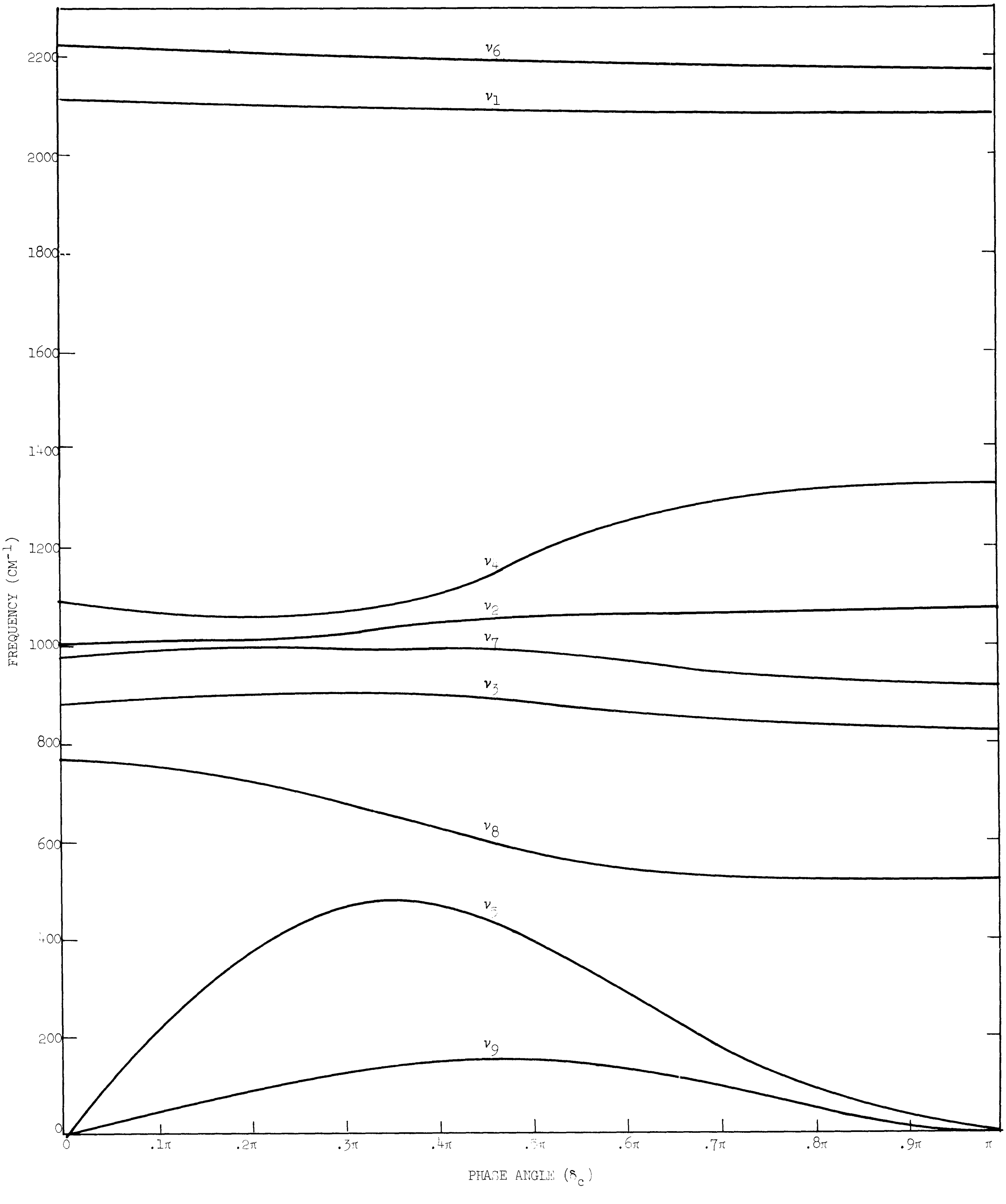


Fig. 4.6. Deuterated single-chain polyethylene dispersion curves.

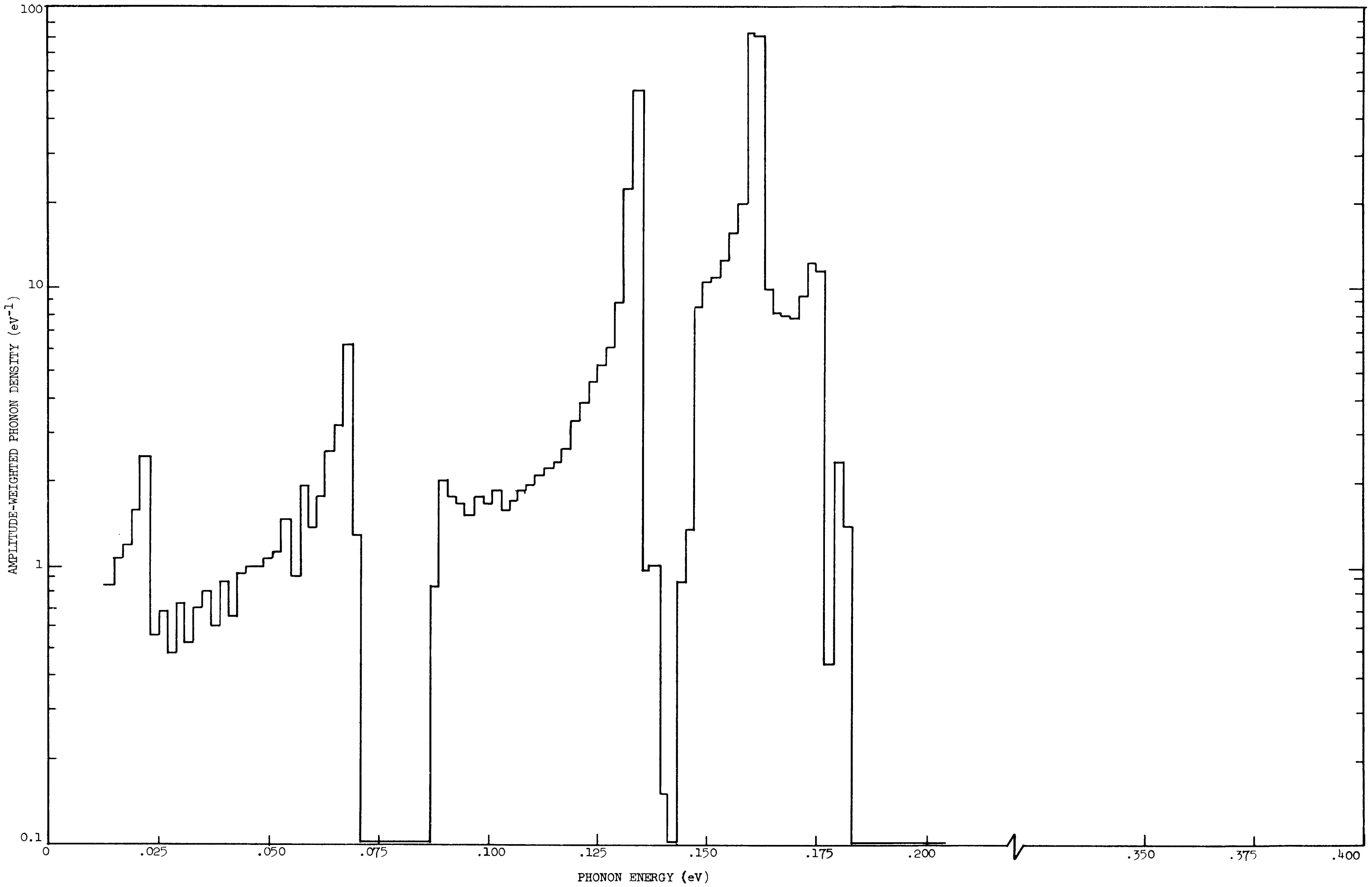


Fig. 4.7. Single-chain polyethylene longitudinal one-phonon G-function, $G_L^I(\epsilon)$.

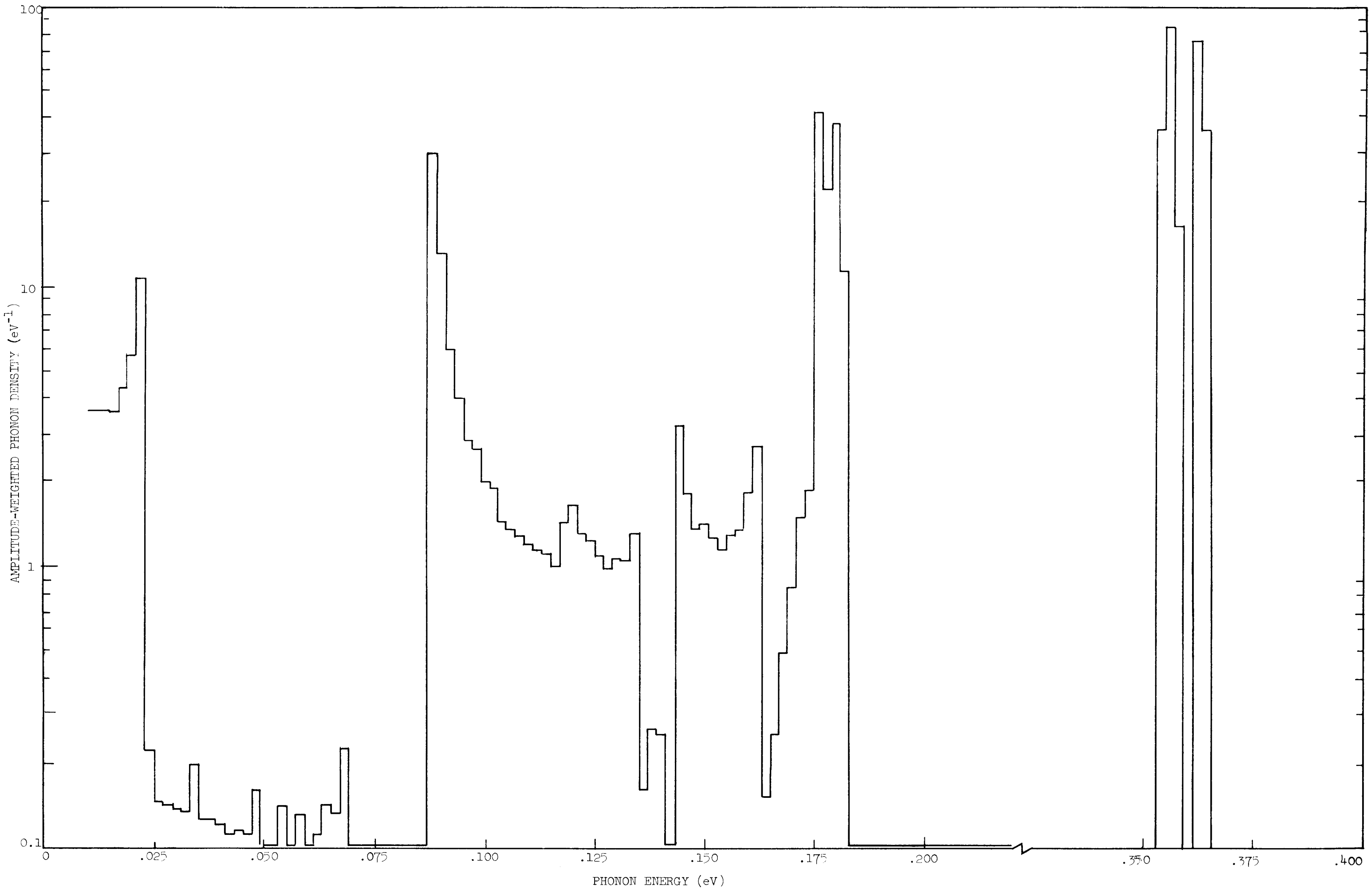


Fig. 4.8. Single-chain polyethylene transverse one-phonon G-function, $G_T^I(\epsilon)$.

CHAPTER 5

CRYSTALLINE POLYETHYLENE

The following development owes much to the published works in which the normal mode frequency solutions for crystalline polyethylene are described.[39,40]

In this chapter, the methods for calculating both the frequencies and cartesian polarization vectors required for construction of the directional frequency functions of crystalline polyethylene are described in some detail.

A. CRYSTAL STRUCTURE AND COORDINATES

The polyethylene unit cell is orthorhombic, with dimensions:

$$a = 7.155\text{Å}$$

$$b = 4.899\text{Å}$$

at liquid nitrogen temperature.[41] The unit cell contains four CH_2 chemical repeat units in the two molecular chains, as shown in Fig. 5.1.

The chain setting angle, θ, is assumed to be 48°.[23] Tasumi and Krimm have studied the dependence of the CH_2 frequencies on this angle[40] for the range

$$38° \leq \theta \leq 52°.$$

However, their intermolecular force constants which are used in this analysis are determined for $\theta = 48°$.

The CH_2 units denoted by dashed lines are those at a distance c/2 above or below the units shown with full lines. For bookkeeping purposes, the atoms identified with circled numbers are either in the nth or (n + 1) 'st units while the uncircled numbers refer to atoms in the lower (n - 1) 'st unit, looking down the chain axes.

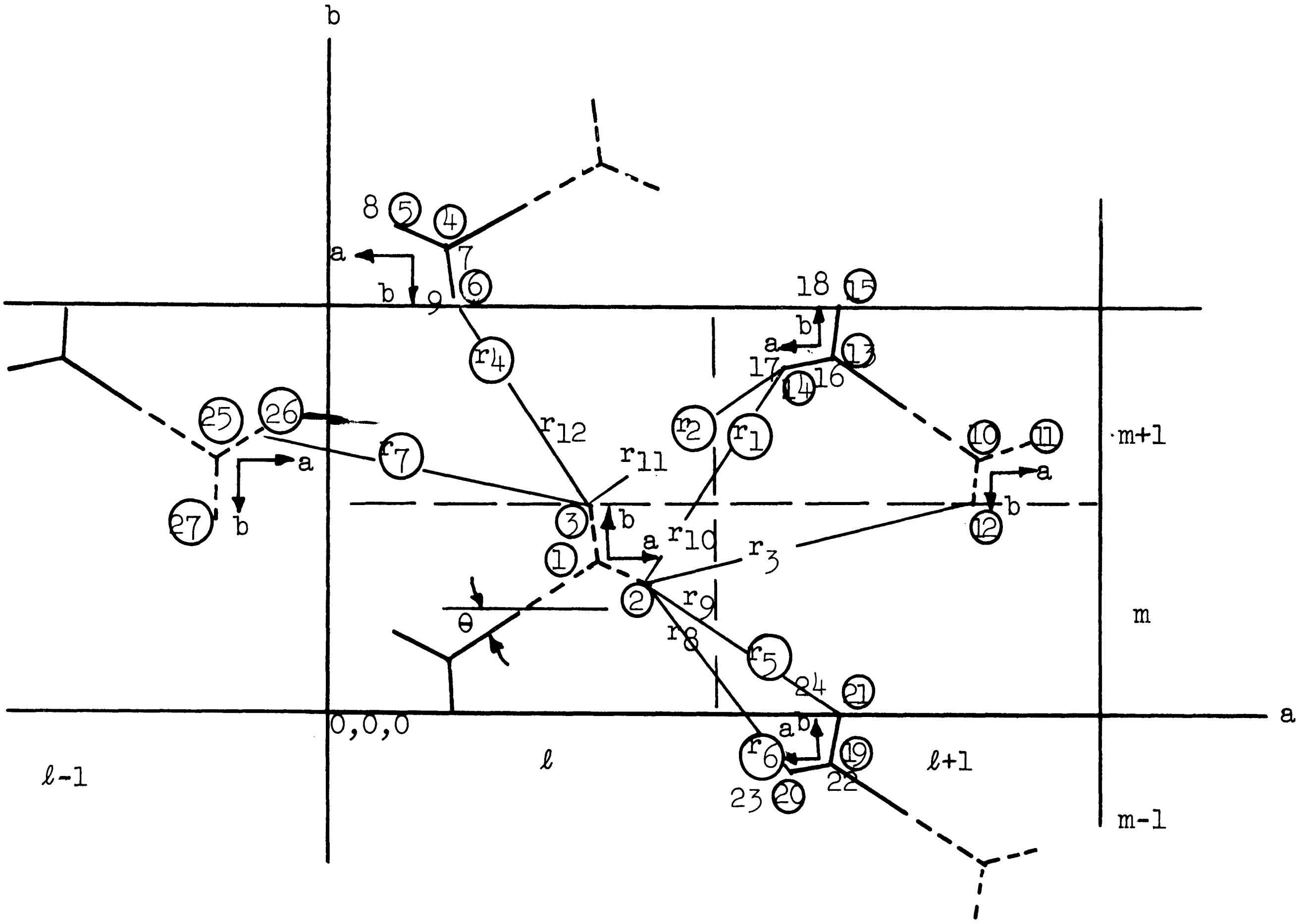


Fig. 5.1. Polyethylene crystal structure and intermolecular "Internal" coordinates.

Twelve intermolecular hydrogen-hydrogen distances are identified. Again, a circled distance is for the upper of two distances which have identical projections on the horizontal (a, b) plane. For example, the "internal" intermolecular stretching coordinate, Δr_1, corresponds to relative displacements of atoms numbered ② and ⑭ along the line joining their centers.

The number twelve is dictated by the choice of intermolecular force field which limits the range of the forces considered to $r \leq 3.0\text{Å}$.[39,40]

The coordinate system chosen for each CH_2 chemical repeat unit is shown also. Recall that using these alternating cartesian coordinate systems to calculate the $\underline{\underline{B}}^S$ matrix elements is equivalent to first calculating $\underline{\underline{B}}$ elements and then obtaining $\underline{\underline{B}}^S = \underline{\underline{B}}\ \underline{\underline{U}}\ (\underline{+})^{\dagger}$ from Eq. (3.31).

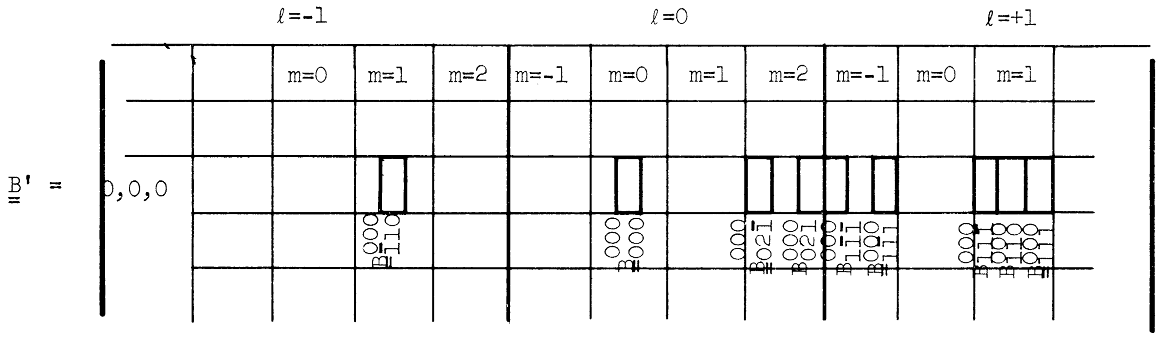
The individual chemical repeat units are identified by using the l,m,n indices for locations along the respective a,b,c, axes. The relationship between these "internal coordinates" and the cartesian coordinates is:

$$\underline{R}' = \underline{\underline{B}}' \, \underline{X}$$

from Eq. (3.35), where the only nonzero submatrices of $\underline{\underline{B}}'$ related to the "internal" coordinates of the (0,0,0) chemical repeat unit are:

$$\begin{array}{ccc} \underline{\underline{B}}^{0,0,0}_{0,0,0} & \underline{\underline{B}}^{0,0,0}_{1,1,0} & \underline{\underline{B}}^{0,0,0}_{1,\bar{1},1} \\ \underline{\underline{B}}^{0,0,0}_{0,2,1} & \underline{\underline{B}}^{0,0,0}_{1,1,1} & \underline{\underline{B}}^{0,0,0}_{1,\bar{1},\bar{1}} \\ \underline{\underline{B}}^{0,0,0}_{0,2,\bar{1}} & \underline{\underline{B}}^{0,0,0}_{1,1,\bar{1}} & \underline{\underline{B}}^{0,0,0}_{\bar{1},1,0} \end{array}$$

and these 12 x 9 submatrices of the $\underline{\underline{B}}'$ matrix appear in the 0, 0, 0 row as shown below.



(5.1)

The cartesian intermolecular force constants may now be determined.

B. INTERMOLECULAR FORCE CONSTANTS

The intermolecular forces acting on the hydrogen atoms in the l,m,nth CH_2 chemical repeat unit are indicated in Fig. (5.2).

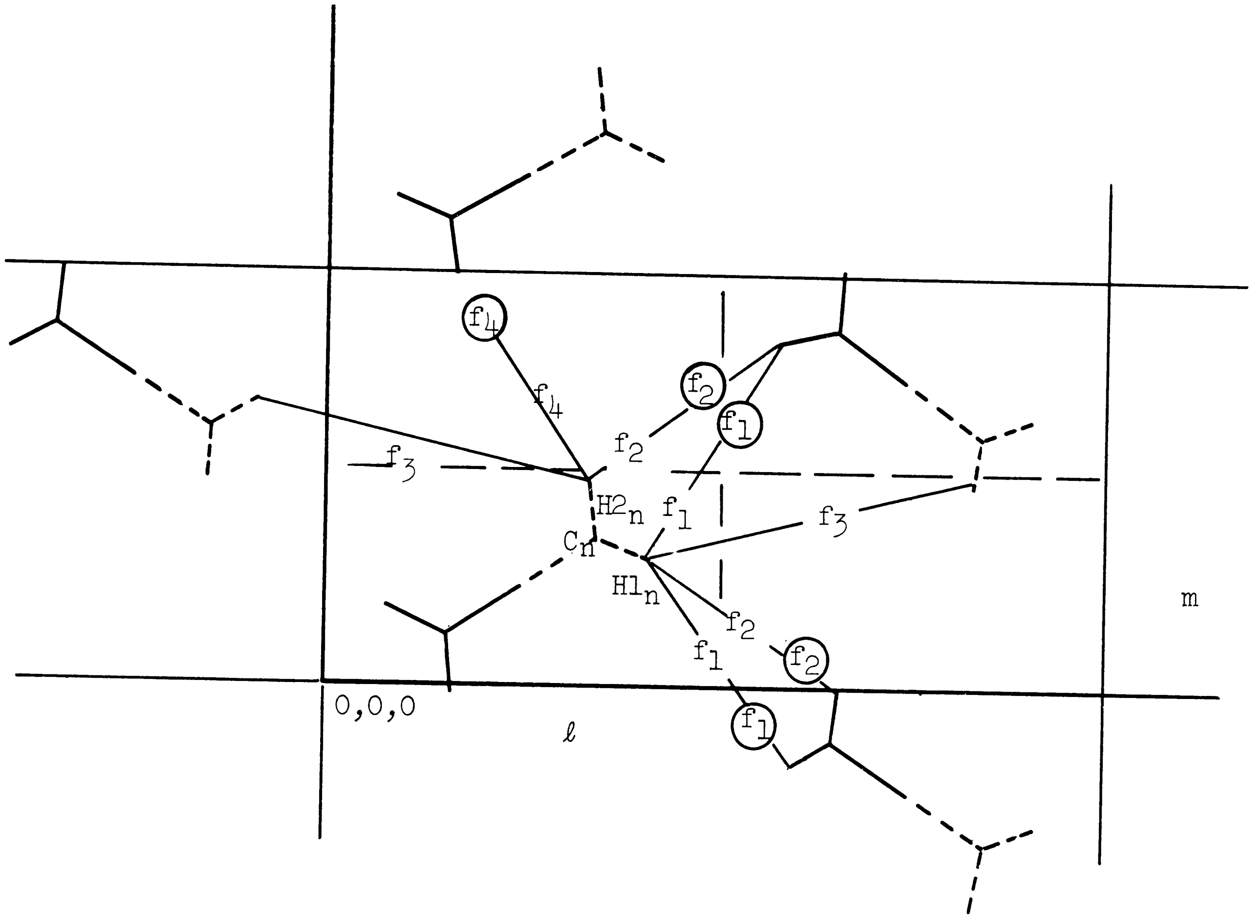


Fig. 5.2. Intermolecular forces on hydrogen atoms in a CH_2 unit of crystalline polyethylene.

The force constants chosen are those of Tasumi and Krimm.[40] This results in an "internal coordinate" force constant submatrix:

$$\underline{F}'^{000}_{000} = \begin{array}{c|cccccccccccc|} & \Delta r_1 & \Delta r_2 & \Delta r_3 & \Delta r_4 & \Delta r_5 & \Delta r_6 & \Delta r_7 & \Delta r_8 & \Delta r_9 & \Delta r_{10} & \Delta r_{11} & \Delta r_{12} \\ \Delta r_1 & f_1 & & & & & & & & & & & \\ \Delta r_2 & & f_2 & & & & & & & & & & \\ \Delta r_3 & & & f_3 & & & & & & & & & \\ \Delta r_4 & & & & f_4 & & & & \bigcirc & & & & \\ \Delta r_5 & & & & & f_2 & & & & & & & \\ \Delta r_6 & & & & & & f_1 & & & & & & \\ \Delta r_7 & & & & & & & f_3 & & & & & \\ \Delta r_8 & & \bigcirc & & & & & & f_1 & & & & \\ \Delta r_9 & & & & & & & & & f_2 & & & \\ \Delta r_{10} & & & & & & & & & & f_1 & & \\ \Delta r_{11} & & & & & & & & & & & f_2 & \\ \Delta r_{12} & & & & & & & & & & & & f_4 \end{array} \qquad (5.2)$$

where:

$f_1 = .0048$ md/Å

$f_2 = .0125$

$f_3 = .0142$

$f_4 = .0205$

at liquid nitrogen temperatures. It is important to also mention that in these crystalline calculations, the intramolecular torsion force constant, F_T, was taken to be 0.05 mdyne-A°/rad^2 whereas the value 0.107 mdyne-A°/rad^2 was used in the single-chain calculation.

An intermolecular force constant matrix in cartesian coordinates is obtained from:

$$\overset{9\times 9}{\underline{\underline{A}}'^{\,0,0,0}_{\,\ell,m,n}} = \sum_{\alpha,\beta,\gamma;\alpha',\beta',\gamma'} \overset{9\times 12}{(\tilde{\underline{\underline{B}}}')^{0,0,0}_{\alpha,\beta,\gamma}} \; \overset{12\times 12}{\underline{\underline{F}}'^{\,\alpha,\beta,\gamma}_{\,\alpha',\beta',\gamma'}} \; \overset{12\times 9}{\underline{\underline{B}}'^{\,\alpha',\beta',\gamma'}_{\,\ell,m,n}} \quad . \tag{5.3}$$

But:

$$\underline{\underline{F}}'^{\,\alpha,\beta,\gamma}_{\,\alpha',\beta',\gamma'} \quad \underline{\underline{F}}'^{\,0,0,0}_{\,\alpha'-\alpha,\beta'-\beta,\gamma'-\gamma} = \underline{\underline{F}}'^{\,0,0,0}_{\,\alpha'',\beta'',\gamma''} \quad . \tag{5.4}$$

Due to the choice of 12 internal coordinates which "belong" to the (0,0,0) unit, all possible intermolecular forces on hydrogen atoms in unit (0,0,0) are given by $\underline{\underline{F}}'^{\,0,0,0}_{\,0,0,0}$, and:

$$\underline{\underline{F}}'^{\,0,0,0}_{\,\alpha'',\beta'',\gamma''} = \underline{\underline{F}}'^{\,\alpha'',\beta'',\gamma''}_{\,0,0,0} = 0$$

for $\alpha'',\beta'',\gamma''$ not equal to zero.
Therefore:

$$\underline{\underline{A}}'^{\,0,0,0}_{\,\ell,m,n,} = (\tilde{\underline{\underline{B}}}')^{0,0,0}_{0,0,0} \; \underline{\underline{F}}'^{\,0,0,0}_{\,0,0,0} \; \underline{\underline{B}}'^{\,0,0,0}_{\,\ell,m,n} \quad . \tag{5.5}$$

Note that the intermolecular $\underline{\underline{B}}'$ submatrices are of order 12 x 9 and the intermolecular $\underline{\underline{F}}'$ force constant submatrices are of order 12 x 12. Recall that the intramolecular $\underline{\underline{B}}$ matrix is partitioned into 10 x 9 blocks and the intramolecular $\underline{\underline{F}}$ force constant submatrices are 10 x 10. In both cases of course the resulting cartesian force constant submatrices of $\underline{\underline{A}}$ and $\underline{\underline{A}}'$ are of order 9 x 9.

C. SPACE GROUP SYMMETRY ANALYSIS

The factor group theory analysis of crystalline polyethylene for $q_c = 0$, has been published.[42] The present discussion considers primarily those symmetry operations which leave q_c invariant, for all values of q_c, when:

$$-\pi/c \leq q_c \leq \pi/c.$$

The polyethylene crystal has $P\,\frac{(2_1}{n}\,\frac{2_1}{a}\,\frac{2_1)}{m}$ space group symmetry, which is also referred to as P nam symmetry. It is also referred to as D_{2h}^{16} space group symmetry in the Schoenflies notation.

The symbols have the following meanings in the Herman Maugin notation[43]:

P - Primitive lattice

$\frac{2_1}{n}$ - 2 refers to the order of the screw-rotation axis in the a direction. Subscript 1 divided by 2, or 1/2, refers to the fraction of the unit cell over which the translation occurs. Symbol n refers to a diagonal glide plane perpendicular to the a axis with a translation of magnitude $(b + c)/2$.

$\frac{2_1}{a}$ - Symbol 2_1 refers to a twofold screw-rotation axis in the b direction with a fractional translation of $1/2 \times b$. Symbol a indicates a glide plane perpendicular to the b axis with a fractional translation of magnitude $a/2$.

$\frac{2_1}{m}$ - Symbol 2_1 refers to a twofold screw-rotation axis along the c direction with a fractional translation of magnitude $c/2$. Symbol m refers to a mirror plane perpendicular to the c axis.

Those operations in the subgroup of this space group which leave q_c invariant are shown in Fig. 5.3. This subgroup is referred to as the star group or $\{q_c\}$ wave vector group.[30]

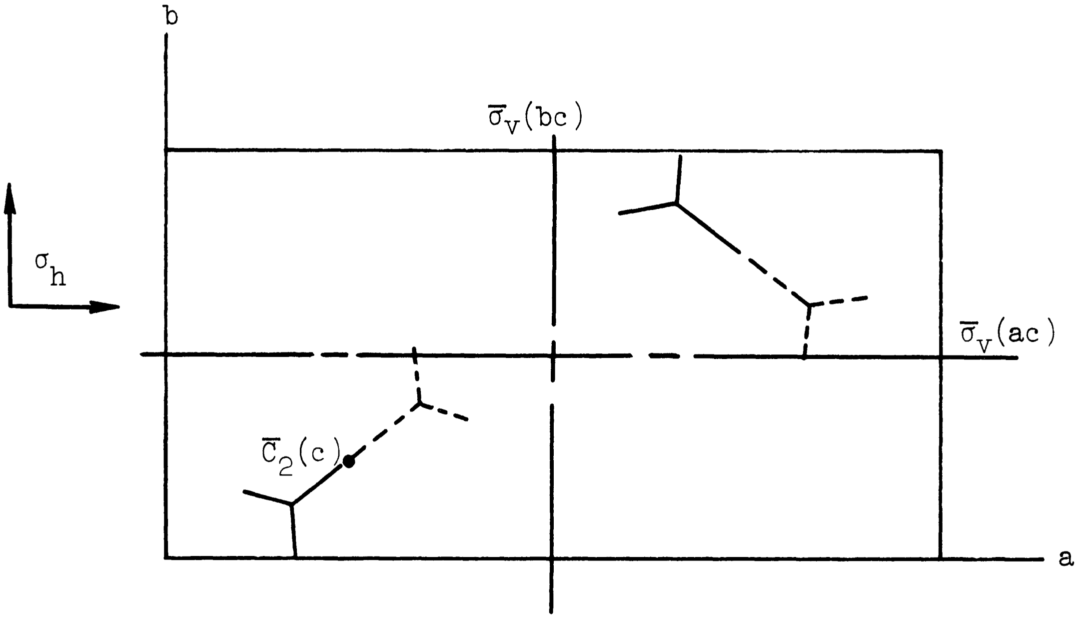


Fig. 5.3. Star group symmetry operations for crystalline polyethylene.

These operations are identified in Table VII.

TABLE VII

STAR SPACE GROUP ELEMENTS FOR CRYSTALLINE POLYETHYLENE

T - Translation by an integer multiple of a unit cell dimension.

$\bar{\sigma}_{v(ac)}$ - Mirror reflection in an ac plane, followed by a fractional translation of magnitude a/2 along the a axis direction.

$\bar{\sigma}_{v(bc)}$ - Mirror reflection in the bc plane, followed by a glide of (b/2 + c/2) in the bc plane.

$\bar{C}_2(c)$ - Rotation about the c axis through a chain, followed by a glide of magnitude c/2 along the c axis direction.

In addition to these four elements, the σ_h mirror in a CH_2 plane is also shown in Fig. 5.3. The latter element is used in obtaining real symmetry coordinates from the complex symmetry coordinates. This element takes $+q_c$ into $-q_c$, which does not alter the frequency solutions. This is seen in the symmetry of the dispersion curves about $q_c = 0$.

The number of nonequivalent irreducible representations is equal to the number of classes in the star group, $\{q_c\}$, while elements in the same class are conjugate to each other. In an abelian group, every element forms a class by itself and has a one dimensional representation.[31] Keeping this in mind, the multiplication table is formed and the number of classes is determined.

TABLE VIII

STAR SPACE GROUP MULTIPLICATION TABLE
FOR CRYSTALLINE POLYETHYLENE

	T_c	$\bar{\sigma}_v(ac)$	$\bar{\sigma}_v(bc)$	$\bar{C}_2(c)$
T_c	T_c	$\bar{\sigma}_v(ac)$	$\bar{\sigma}_v(bc)$	$\bar{C}_2(c)$
$\bar{\sigma}_v(ac)$	$\bar{\sigma}_v(ac)$	T_c	$\bar{C}_2(c)$	$\bar{\sigma}_v(bc)$
$\bar{\sigma}_v(bc)$	$\bar{\sigma}_v(bc)$	$\bar{C}_2(c)$	T_c	$\bar{\sigma}_v(ac)$
$\bar{C}_2(c)$	$\bar{C}_2(c)$	$\bar{\sigma}_v(bc)$	$\bar{\sigma}_v(ac)$	T_c

Elements in a class with $\bar{\sigma}_v(ac)$ are:

$$E\,\bar{\sigma}_v(ac)\,E^{-1} = \bar{\sigma}_v(ac)$$

$$\bar{\sigma}_v(bc)\,\bar{\sigma}_v(ac)\,\bar{\sigma}_v^{-1}(bc) = \bar{\sigma}_v(bc)\,\bar{\sigma}_v(ac)\,\bar{\sigma}_v(bc) = \bar{\sigma}_v(bc)\,\bar{C}_2(c) = \bar{\sigma}_v(ac)$$

$$\bar{C}_2(c)\,\bar{\sigma}_v(ac)\,\bar{C}_2^{-1}(c) = \bar{C}_2(c)\,\bar{\sigma}_v(ac)\,\bar{C}_2(c) = \bar{C}_2(c)\,\bar{\sigma}_v(bc) = \bar{\sigma}_v(ac)$$

Therefore $\bar{\sigma}_V(ac)$ forms a class by itself. The same is true of $\bar{\sigma}_V(bc)$ and $\bar{C}_2(c)$.

There are therefore four one-dimensional irreducible representations in the $\{q_c\}$ subgroup of Pnam.

Those irreducible representations (species) which are symmetric to $\bar{C}_2(c)$ are labelled the A species and those which are antisymmetric to $\bar{C}_2(c)$ are labelled the B species. Those symmetric to the $\bar{\sigma}_V(ac)$ mirror are labelled with a subscript 1 and those anti-symmetric to $\bar{\sigma}_V(ac)$ are labelled with a subscript 2.

The character table for these representations, when $q_a = q_b = 0$, is:

TABLE IX

STAR GROUP CHARACTER TABLE
FOR CRYSTALLINE POLYETHYLENE

	T_c	$\bar{\sigma}_V(ac)$	$\bar{\sigma}_V(bc)$	$\bar{C}_2(c)$
A_1	$e^{iqn'c}$	$+1$	$+ e^{iqc/2}$	$+ e^{iqc/2}$
A_2	$e^{iqn'c}$	-1	$- e^{iqc/2}$	$+ e^{iqc/2}$
B_1	$e^{iqn'c}$	$+1$	$- e^{iqc/2}$	$- e^{iqc/2}$
B_2	$e^{iqn'c}$	-1	$+ e^{iqc/2}$	$- e^{iqc/2}$

In T_c above, the character is $e^{iq\,n'c} = e^{iq\,2n'\frac{c}{2}} = e^{iq\,nc/2} = e^{in\delta}$, where n labels the chemical repeat units, n' labels the unit cells, and $\delta = qc/2$.

Note that the character $\chi\,[\bar{C}_2(c)]$ in the B representations is $-e^{iqc/2} = + e^{i(q_c c/2 + \pi)}$ which is the product of $e^{i\pi}$ and the character for the A representation. This relationship will be used later to simplify the procedure for obtaining the dynamical matrices in the B representations.

Note also that the characters for the γth representation obey the orthogonality relation[33]:

$$\sum_R \chi^{*(\gamma)}(R)\ \chi^{(\gamma')}(R) = 4\delta_{\gamma\gamma'} \quad . \qquad (5.6)$$

In order to determine the number of symmetry coordinates required for each representation, it is necessary to know the number of times each irreducible representation appears in the reducible representation for a symmetry element. This number is[34]:

$$n^{(\gamma)} = \frac{1}{4} \sum_R \chi^{*(\gamma)}(R)\ \chi(R) \qquad (5.7)$$

where $\chi(R)$ is the character in the reducible representation. $\chi(E) = 36$, as there are 12 atoms in a unit cell, and $\chi(\overline{\sigma}_v(ac)) = \chi(\overline{\sigma}_v(bc)) = \chi(\overline{C}_2(c)) = 0$, since these operations leave no atom displacements unchanged. The number of times each irreducible representation appears therefore is:

$$n^{(A_1)} = \frac{1}{4}[1 \times 36] = 9$$

$$n^{(A_2)} = 9$$

$$n^{(B_1)} = 9$$

$$n^{(B_2)} = 9$$

This means that each irreducible representation requires 9 symmetry coordinates and that 9 x 9 dynamical matrices will appear in the block diagonalized dynamical matrix.

D. CARTESIAN SYMMETRY COORDINATES

Since there are four one dimensional irreducible representations, each of which appears nine times in the reducible representation, there must be four sets of symmetry coordinates. Each set contains nine components. A given component or symmetry coordinate may be obtained from[35]:

$$S^{(\gamma)} = \eta \sum_{R} \chi(R)\, R\, \xi \qquad (5.8)$$

where the sum is taken over all symmetry operations, R, of the subgroup of the space group $P \frac{2_1}{n} \frac{2_1}{a} \frac{2_1}{m}$, which leave the phonon wave vector q_c invariant. Recall that only the phase shifts along the q_c axis are being considered here.

By operating on each of the cartesian displacement coordinates of the zeroeth CH_2 repeat unit atoms and applying the appropriate character, a set of symmetry coordinates may be obtained. The symmetry operations are:

$$R = E,\ \overline{C}_2\,(c),\ \overline{\sigma}_v(ac),\ \overline{\sigma}_v(bc);\ \overline{C}_2^2(c),\ \overline{\sigma}_v(ac)\ \overline{C}_2^2(c),\ \ldots$$

which includes all products of the four elements of the $\{q_c\}$ group and the translational subgroup of the space group. In this way, the first nine coordinates, which are labelled the A_1 species to indicate that they are symmetric to both the $\overline{C}_2(c)$ and the $\overline{\sigma}_v(ac)$ operations, are found to be:

$$S_1^{(A_1)}(\delta_c) = \eta \sum_{\ell mn}^{2N_a-1,2N_b-1,2N_c-1} (-1)^n\ \Delta a^c_{\ell mn}\ e^{in\delta_c}$$

$$S_2^{(A_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{m+n}\ \Delta b^c_{\ell mn}\ e^{in\delta_c}$$

$$S_3^{(A_1)}(\delta_c) = \eta \sum_{\ell mn} \Delta c^{c}_{\ell mn}\, e^{in\delta_c}$$

$$S_4^{(A_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{n}\, \Delta a^{H^1}_{\ell mn}\, e^{in\delta_c}$$

$$S_5^{(A_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{m+n}\, \Delta b^{H^1}_{\ell mn}\, e^{in\delta_c}$$

$$S_6^{(A_1)}(\delta_c) = \eta \sum_{\ell mn} \Delta c^{H^1}_{\ell mn}\, e^{in\delta_c}$$

$$S_7^{(A_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{n}\, \Delta a^{H^2}_{\ell mn}\, e^{in\delta_c}$$

$$S_8^{(A_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{m+n}\, \Delta b^{H^2}_{\ell mn}\, e^{in\delta_c}$$

$$S_9^{(A_1)}(\delta_c) = \eta \sum_{\ell mn} \Delta c^{H^2}_{\ell mn}\, e^{in\delta_c} \quad . \qquad (5.9)$$

rmalization factor is $\eta = \left(\frac{1}{N_{abc}}\right)^{1/2}$, where N_{abc} is the number of repeat units in the crystal. $N_{abc} = 2N_a\, 2N_b\, 2N_c$, where N_a, N_b, N_c are respectively the number of unit cells in the a, b, and c directions.

If now the characters for the A_2 species are used, the nine coordinates which are symmetric to $\bar{C}_2(c)$ but antisymmetric to $\bar{\sigma}_v(ac)$ are found to be the following:

$$S_1^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{m+n}\, \Delta a^{c}_{\ell mn}\, e^{in\delta_c}$$

$$S_2^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{n}\, \Delta b^{c}_{\ell mn}\, e^{in\delta_c}$$

$$S_3^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{m}\, \Delta c^{c}_{\ell mn}\, e^{in\delta_c}$$

$$S_4^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{m+n}\, \Delta a^{H^1}_{\ell mn}\, e^{in\delta_c}$$

$$S_5^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^n \, \Delta b^{H^1}_{\ell mn} \, e^{in\delta_c}$$

$$S_6^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^m \, \Delta c^{H^1}_{\ell mn} \, e^{in\delta_c}$$

$$S_7^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^{m+n} \, \Delta a^{H^2}_{\ell mn} \, e^{in\delta_c}$$

$$S_8^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^n \, \Delta b^{H^2}_{\ell mn} \, e^{in\delta_c}$$

$$S_9^{(A_2)}(\delta_c) = \eta \sum_{\ell mn} (-1)^m \, \Delta c^{H^2}_{\ell mn} \, e^{in\delta_c} \quad . \qquad (5.10)$$

The nine B_1 species coordinates which are antisymmetric to $\overline{C}_2(c)$, but symmetric to $\overline{\sigma}_v(ac)$ are:

$$S_1^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} \Delta a^{c}_{\ell mn} \, e^{in\delta_c}$$

$$S_2^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^m \, \Delta b^{c}_{\ell mn} \, e^{in\delta_c}$$

$$S_3^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^n \, \Delta c^{c}_{\ell mn} \, e^{in\delta_c}$$

$$S_4^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} \Delta a^{H^1}_{\ell mn} \, e^{in\delta_c}$$

$$S_5^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^m \, \Delta b^{H^1}_{\ell mn} \, e^{in\delta_c}$$

$$S_6^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^n \, \Delta c^{H^1}_{\ell mn} \, e^{in\delta_c}$$

$$S_7^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} \Delta a^{H^2}_{\ell mn} \, e^{in\delta_c}$$

$$S_8^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^m \, \Delta b^{H^2}_{\ell mn} \, e^{in\delta_c}$$

$$S_9^{(B_1)}(\delta_c) = \eta \sum_{\ell mn} (-1)^n \, \Delta c^{H^2}_{\ell mn} \, e^{in\delta_c} \quad . \qquad (5.11)$$

The nine B_2 species coordinates which are antisymmetric to both $\bar{C}_2(c)$ and $\bar{\sigma}_v(ac)$ are:

$$
\begin{aligned}
S_1^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} (-1)^m \, \Delta a^c_{\ell mn} \, e^{in\delta_c} \\
S_2^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} \Delta b^c_{\ell mn} \, e^{in\delta_c} \\
S_3^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} (-1)^{m+n} \, \Delta c^c_{\ell mn} \, e^{in\delta_c} \\
S_4^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} (-1)^m \, \Delta a^{H^1}_{\ell mn} \, e^{in\delta_c} \\
S_5^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} \Delta b^{H^1}_{\ell mn} \, e^{in\delta_c} \\
S_6^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} (-1)^{m+n} \, \Delta c^{H^1}_{\ell mn} \, e^{in\delta_c} \\
S_7^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} (-1)^m \, \Delta a^{H^2}_{\ell mn} \, e^{in\delta_c} \\
S_8^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} \Delta b^{H^2}_{\ell mn} \, e^{in\delta_c} \\
S_9^{(B_2)}(\delta_c) &= \eta \sum_{\ell mn} (-1)^{m+n} \, \Delta c^{H^2}_{\ell mn} \, e^{in\delta_c} \quad .
\end{aligned}
\tag{5.12}
$$

Notice that each term in the sum for a given B_1 symmetry coordinate differs from the corresponding term in an A_1 coordinate only by a factor $e^{in\pi} = (-1)^n$. Each B_2 symmetry coordinate also differs from the corresponding A_2 coordinate by this factor. This relationship will be used subsequently to good advantage.

Now the real and imaginary parts of the thirty-six complex coordinates may be obtained.[27] In vector notation:

$$\mathrm{Re}\{\underline{S}^{(\gamma)}(\delta_c)\} = \frac{1}{\sqrt{2}}\,[\underline{S}^{(\gamma)}(\delta_c) + \underline{S}^{(\gamma)}(\delta_c)^*]$$

$$\mathrm{Im}\{\underline{S}^{(\gamma)}(\delta_c)\} = \frac{1}{i\sqrt{2}}\,[\underline{S}^{(\gamma)}(\delta_c) - \underline{S}^{(\gamma)}(\delta_c)^*] \qquad (5.13)$$

in which case:

$$\mathrm{Re}\{\underline{S}^{(\gamma)}(\delta_c)\} = \sqrt{2}\,\eta \sum_{\ell mn} e^{-in\delta_c}\ \underline{S}^{(\gamma)}_{\ell mn} \cos n\delta_c$$

$$\mathrm{Im}\{\underline{S}^{(\gamma)}(\delta_c)\} = \sqrt{2}\,\eta \sum_{\ell mn} e^{-in\delta_c}\ \underline{S}^{(\gamma)}_{\ell mn} \sin n\delta_c \qquad (5.14)$$

for:

$$\gamma = A_1, A_2.$$

For the B species coordinates:

$$\mathrm{Re}\{\underline{S}^{(B_j)}(\delta_c)\} = \sqrt{2}\,\eta \sum_{\ell mn} e^{-in\delta_c} S^{(A_j)}_{\ell mn} \cos\,(\delta_c + \pi)n$$

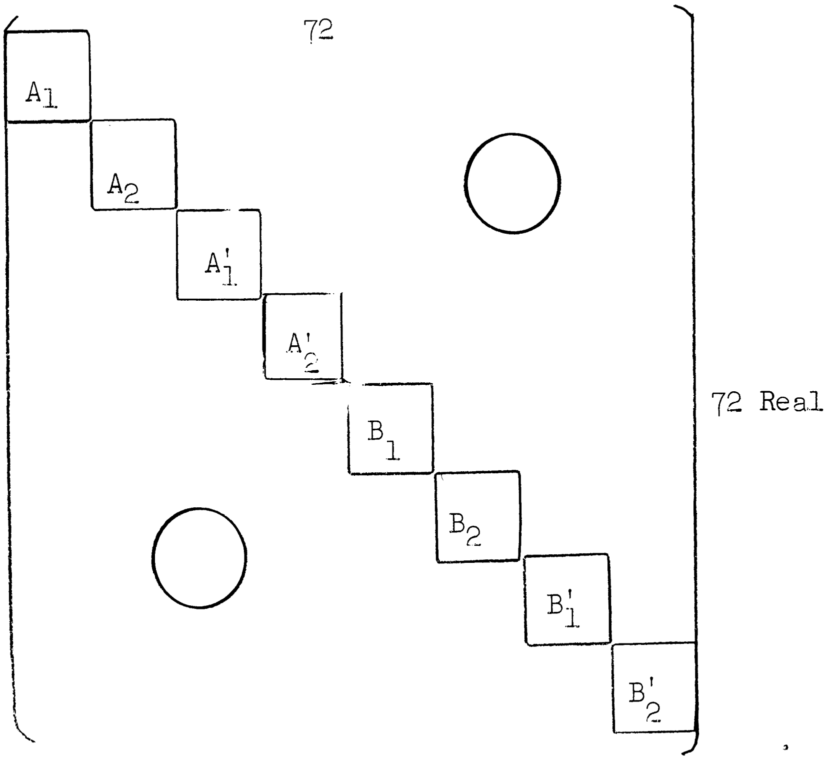
$$\mathrm{Im}\{\underline{S}^{(B_j)}(\delta_c)\} = \sqrt{2}\,\eta \sum_{\ell mn} e^{-in\delta_c}\ S^{(A_j)}_{\ell mn} \sin\,(\delta_c + \pi)n \qquad (5.15)$$

where $j = 1,2$.

There are now (2 x 36) real symmetry coordinates in place of the original 36 complex coordinates. Further use of the crystal symmetry may be made by utilizing the horizontal mirror plane σ_h which passes through the CH_2 repeat units. Theorder of the A_1 and A_2 coordinates (36 in number) is rearranged so that the first nine are A_1 coordinates symmetric to σ_h, the second nine are A_2 coordinates symmetric to σ_h, the third nine are A_1 coordinates antisymmetric to σ_h and the last nine are A_2 coordinates antisymmetric to σ_h. The same rearrangement is performed for the 36 B species coordinates.

Use of these seventy-two real phase dependent coordinates makes it possible to obtain the block diagonalized real phase dependent dynamical matrix so that, for each δ_c value, the following set of 9 x 9 submatrices is obtained:

$\underline{\underline{C}}^s(\delta_c) =$



, (5.16)

The primed matrices are those which have coordinates antisymmetric to σ_h.

The real symmetry coordinates which make this factorization possible are:

$$S_1^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} [(-1)^n]\, \Delta a^c_{\ell mn} \cos n\delta_c$$

$$S_2^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} [(-1)^{m+n}]\, \Delta b^c_{\ell mn} \cos n\delta_c$$

$$S_3^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} \Delta c^c_{\ell mn} \sin n\delta_c$$

$$S_4^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} [(-1)^n]\, \Delta a^{H_1}_{\ell mn} \cos n\delta_c$$

$$S_5^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} [(-1)^{m+n}]\, \Delta b^{H_1}_{\ell mn} \cos n\delta_c$$

$$S_6^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} \Delta c_{\ell mn}^{H_1} \sin n\delta_c$$

$$S_7^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} [(-1)^n]\, \Delta a_{\ell mn}^{H_2} \cos n\delta_c$$

$$S_8^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} [(-1)^{m+n}]\, \Delta b_{\ell mn}^{H_2} \cos n\delta_c$$

$$S_9^{(A_1)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} \Delta c_{\ell mn}^{H_2} \sin n\delta_c \quad . \qquad (5.17)$$

The terms shown in brackets [] are diagonal elements of $[\underline{\underline{U}}^{(A_1)}(\underline{+})]_{\ell mn}^{\ell mn}$, where:

$$\underline{S}^{(A_1)}(\delta_c) = \underline{\underline{U}}^{(A)}(\delta\ )\ \underline{\underline{U}}^{(A_1)}(\pm)\ \underline{X}$$

as described in chapter 3.

The A_2 species coordinates are:

$$S_1^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{m+n}\, \Delta a_{\ell mn}^{c} \cos n\delta_c$$

$$S_2^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{n}\, \Delta b_{\ell mn}^{c} \cos n\delta_c$$

$$S_3^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{m}\, \Delta c_{\ell mn}^{c} \sin n\delta c_c$$

$$S_4^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{m+n}\, \Delta a_{\ell mn}^{H_1} \cos n\delta_c$$

$$S_5^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{n}\, \Delta b_{\ell mn}^{H_1} \cos n\delta_c$$

$$S_6^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{m}\, \Delta c_{\ell mn}^{H_1} \sin n\delta_c$$

$$S_7^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{m+n}\, \Delta a_{\ell mn}^{H_2} \cos n\delta_c$$

$$S_8^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{n}\, \Delta b_{\ell mn}^{H_2} \cos n\delta_c$$

$$S_9^{(A_2)}(\delta_c) = \sqrt{2}\,\eta \sum_{\ell mn} (-1)^{m}\, \Delta c_{\ell mn}^{H_2} \sin n\delta_c \qquad (5.18)$$

The A_1' and A_2' symmetry coordinates, which are antisymmetric to the σ_h mirror, are obtained from Eqs. (5.17) and (5.18) by simply replacing cos $n\delta_c$ by sin $n\delta_c$ and by replacing sin $n\delta_c$ by - cos $n\delta_c$.

E. PHASE DEPENDENT DYNAMICAL MATRICES

The transformation of the cartesian coordinate force constant matrix, $\underline{\underline{A}}$, to real space group symmetry coordinates results in a block diagonal matrix for each δ_c value as shown in the previous section. According to Eq. (3.42), a given (9 x 9) A_1 species block is obtained from:

$$\begin{aligned}
\underline{\underline{A}}^{(A_1)0,0,0}_{(\delta_c)0,0,0} &= \sum_{\alpha\beta\gamma;\alpha'\beta'\gamma'} \underline{\underline{U}}^{(A)000}_{(\delta_c)\alpha\beta\gamma}\, \underline{\underline{A}}^{(A_1)\alpha\beta\gamma}_{\alpha'\beta'\gamma'} \left(\underline{\underline{U}}(\delta_c)\right)^{\widetilde{(A)}\ \alpha'\beta'\gamma'}_{000} \\
&= \sum_{\alpha\beta\gamma;\alpha'\beta'\gamma'} \underline{\underline{U}}^{(A)000}_{(\delta_c)\alpha\beta\gamma}\, \underline{\underline{A}}^{(A_1)000}_{\alpha'-\alpha,\beta'-\beta,\gamma'-\gamma}\, \underline{\underline{U}}^{(A)000}_{(\delta_c)\alpha'\beta'\gamma'} \\
&= \sum_{\alpha''\beta''\gamma'';\alpha\beta\gamma} \underline{\underline{U}}^{(A)000}_{(\delta_c)00\gamma}\, \underline{\underline{A}}^{(A_1)000}_{\alpha''\beta''\gamma''}\, \underline{\underline{U}}(\delta_c)^{(A)\,0,0,0}_{0,0,\gamma''+\gamma} \qquad (5.19)
\end{aligned}$$

since:

$$\begin{aligned}
\alpha'' &= \alpha' - \alpha \\
\beta'' &= \beta' - \beta \\
\gamma'' &= \gamma' - \gamma
\end{aligned}$$

and:

$$\underline{\underline{U}}^{0,0,0}_{\alpha''+\alpha,\beta''+\beta,\gamma''+\gamma} = \underline{\underline{U}}^{0,0,0}_{0,0,\gamma''+\gamma}$$

which is real and independent of $\alpha'' + \alpha$ and $\beta'' + \beta$ for $q_a = q_b = 0$.

As in the single-chain polyethylene analysis, the matrix elements of a given $\underline{\underline{A}}^{0,0,0}_{\alpha''\beta''\gamma''}$ matrix are multiplied by a sum of terms as shown below, since the transformation submatrix is:

$$\underline{\underline{U}}(\delta_c)^{(A_1)000}_{00\gamma} = \left(\frac{2}{N}\right)^{1/2}_{abc} \begin{array}{c|ccccccccc|} S_1^{(A_1)} & \cos\gamma\delta_c & & & & & & & & \\ S_2^{(A_1)} & & \cos\gamma\delta_c & & & & & & & \\ S_3^{(A_1)} & & & \sin\gamma\delta_c & & & & & & \\ S_4^{(A_1)} & & & & \cos\gamma\delta_c & & & & & \\ S_5^{(A_1)} & & & & & \cos\gamma\delta_c & & & & \\ S_6^{(A_1)} & & & & & & \sin\gamma\delta_c & & & \\ S_7^{(A_1)} & & & & & & & \cos\gamma\delta_c & & \\ S_8^{(A_1)} & & & & & & & & \cos\gamma\delta_c & \\ S_9^{(A_1)} & & & & & & & & & \sin\gamma\delta_c \\ & \Delta a^{c}_{00\gamma} & \Delta b^{c}_{00\gamma} & \Delta c^{c}_{00\gamma} & \Delta a^{H1}_{00\gamma} & \Delta b^{H1}_{00\gamma} & \Delta c^{H1}_{00\gamma} & \Delta a^{H2}_{00\gamma} & \Delta b^{H2}_{00\gamma} & \Delta c_{00\gamma} \end{array}$$

(5.20)

Recall that the $(-1)^n$ or $(-1)^{m+n}$ terms in the symmetry coordinates are introduced into the analysis by selecting coordinate systems for the different CH_2 units appropriately as shown in Fig. 5.1. This is effectively accomplished by changing the signs of $\underline{\underline{B}}'$ matrix elements in a corresponding manner to obtain the $\underline{\underline{B}}'^{S}$ matrix elements.

According to Eq. (5.19) and (5.20), a matrix element in a given row and column of $\underline{\underline{A}}^{000}_{\alpha''\beta''\gamma''}$ is multiplied by a factor shown below:

$$\begin{array}{ll|ll}
 & & \multicolumn{2}{c}{\text{Column of } \underline{\underline{A}}^{0,0,0}_{\alpha'',\beta'',\gamma''}} \\
 & & j = 1,2,4,5,7,8 & j = 3,6,9 \\
\hline
\text{Row of} & i = 1,2,4,5,7,8 & \frac{1}{N_c}\sum\limits_{\gamma} \cos\gamma\delta_c \cos(\gamma+\gamma'')\delta_c & \frac{1}{N_c}\sum\limits_{\gamma} \cos\gamma\delta_c \sin(\gamma+\gamma'')\delta_c \\
\underline{\underline{A}}^{0,0,0}_{\alpha''\beta''\gamma''} & i = 3,6,9 & \frac{1}{N_c}\sum\limits_{\gamma} \sin\gamma\delta_c \cos(\gamma+\gamma'')\delta_c & \frac{1}{N_c}\sum\limits_{\gamma} \sin\gamma\delta_c \sin(\gamma+\gamma'')\delta_c
\end{array}$$

Although the row-column indices here are different than in the single-chain polyethylene case, the sums are nearly the same and the results for the factors are:

$$\begin{array}{ll|ll}
 & & \multicolumn{2}{c}{\text{Column}} \\
 & & j = 1,2,4,5,7,8 & j = 3,6,9 \\
\hline
\text{Row} & i = 1,2,4,5,7,8 & \cos\gamma''\delta_c & \sin\gamma''\delta_c \\
 & i = 3,6,9 & -\sin\gamma''\delta_c & \cos\gamma''\delta_c
\end{array}$$

Therefore the matrix elements of $\underline{\underline{A}}(\delta_c)$ required to obtain the dynamical sub-matrix, $\underline{\underline{G}}_c^{1/2}\ \underline{\underline{A}}^{(A_1)\,0,0,0}_{\quad\ \ 0,0,0}\ \underline{\underline{G}}_c^{1/2} = \underline{\underline{C}}^{(A_1)}(\delta_c)$, are:

$$\left(\underline{\underline{A}}^{(A_1)\,000}_{\quad\ \ 000}\right)_{i,j} = \sum_{\alpha B\gamma} \left(\underline{\underline{A}}^{(A_1)\,000}_{\quad\ \ \alpha\beta\gamma}\right)_{i,j} \cos\gamma\delta_c\ ; \quad \text{for} \quad \begin{array}{l} i = \left\{1,2,4,5,7,8\right. \\ j = \left\{1,2,4,5,7,8\right. \\ i = \left\{3,6,9\right. \\ j = \left\{3,6,9\right. \end{array} \tag{5.21}$$

$$\left(\underline{\underline{A}}^{(A_1)\,000}_{\quad\ \ 000}\right)_{i,j} = \sum_{\alpha\beta\gamma} \left(\underline{\underline{A}}^{(A_1)\,000}_{\alpha\beta\gamma}\right)_{i,j} \sin\gamma\delta_c\ ; \quad \text{for} \quad \begin{array}{l} i = \left\{1,2,4,5,7,8\right. \\ j = \left\{3,6,9\right. \end{array} \tag{5.22}$$

$$\left(\underline{\underline{A}}^{(A_1)\,000}_{\quad\ \ 000}\right)_{i,j} = \sum_{\alpha\beta\gamma} -\left(\underline{\underline{A}}^{(A_1)\,000}_{\alpha\beta\gamma}\right)_{i,j} \sin\gamma\delta_c\ ; \quad \text{for} \quad \begin{array}{l} i = \left\{3,6,9\right. \\ j = \left\{1,2,4,5,7,8\right. \end{array} \tag{5.23}$$

As was true for the single chain, the A_1 and A_1' species (9 x 9) blocks are identical and the A_2 and A_2' species (9 x 9) blocks are identical. As was also true for the single chain, B species blocks differ from the A species blocks only in the factor cos $\gamma\pi$. Therefore only two (9 x 9) matrices need be obtained (A_1 and A_2 species) for each δ_c value. By again allowing δ_c to take on values, $\pi/2 \leq \delta_c \leq \pi$, the B_1 and B_2 species frequency solutions are obtained.

F. DISPERSION CURVES AND POLARIZATION VECTORS

Only the low frequency solutions for normal crystalline polyethylene are displayed in Fig. 5.4 as a function of the phase shift, δ_c, between adjacent chemical repeat units. The corresponding dispersion relations for deuterated polyethylene are given in Fig. 5.5.

The higher frequency solutions which were obtained differ in no essential respect from the published results.[39,40]

In Figs. 5.6 and 5.7 the squares of the hydrogen and carbon polarization vectors for normal crystalline polyethylene are plotted vs. δ_c for the ν_9 and ν_5 branches. For these curves:

$$(\gamma^{H}_{ab})^2 = \frac{1}{2}\left\{\left[\frac{\gamma^{2\,H1}_{a} + \gamma^{2\,H1}_{b}}{2}\right] + \left[\frac{\gamma^{2\,H2}_{a} + \gamma^{2\,H2}_{b}}{2}\right]\right\}$$

$$(\gamma^{H}_{c})^2 = \frac{1}{2}\{\gamma^{2\,H1}_{c} + \gamma^{2\,H2}_{c}\}$$

$$(\gamma^{c}_{ab})^2 = \frac{1}{2}\{\gamma^{c^2}_{a} + \gamma^{c^2}_{b}\}$$

$$(\gamma^{c}_{c})^2 = \gamma^{c^2}_{c} \quad .$$

In addition, the polarization vectors for deuterated crystalline polyethylene are displayed vs. δ_c in the Appendix.

It is important to point out that the required normalization for the polarization vectors, which is indicated in Eq. (2.3), is such that the sum

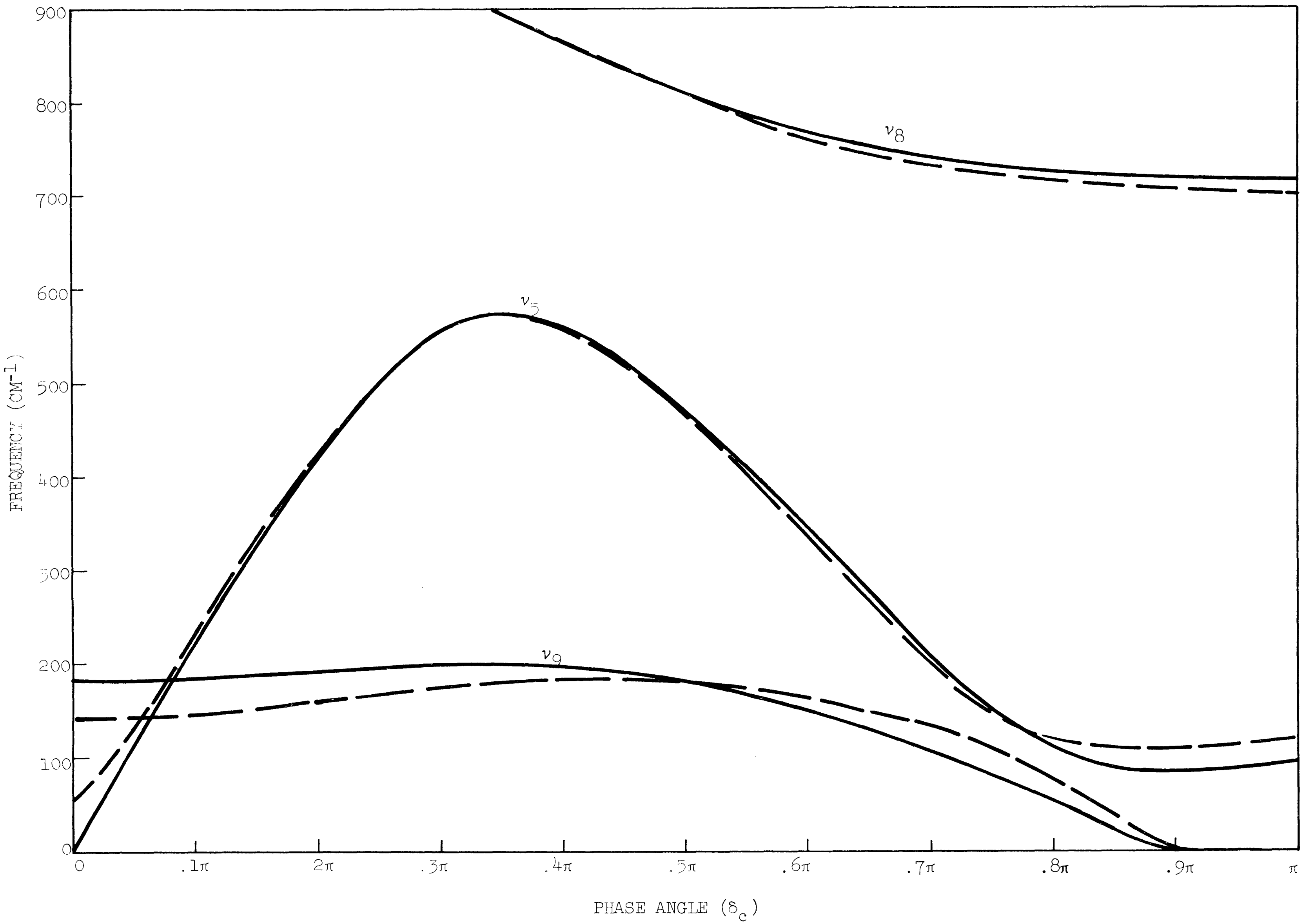


Fig. 5.4. Crystalline polyethylene low frequency dispersion curves (F_τ = .05 mdyne - Å/rad^2).

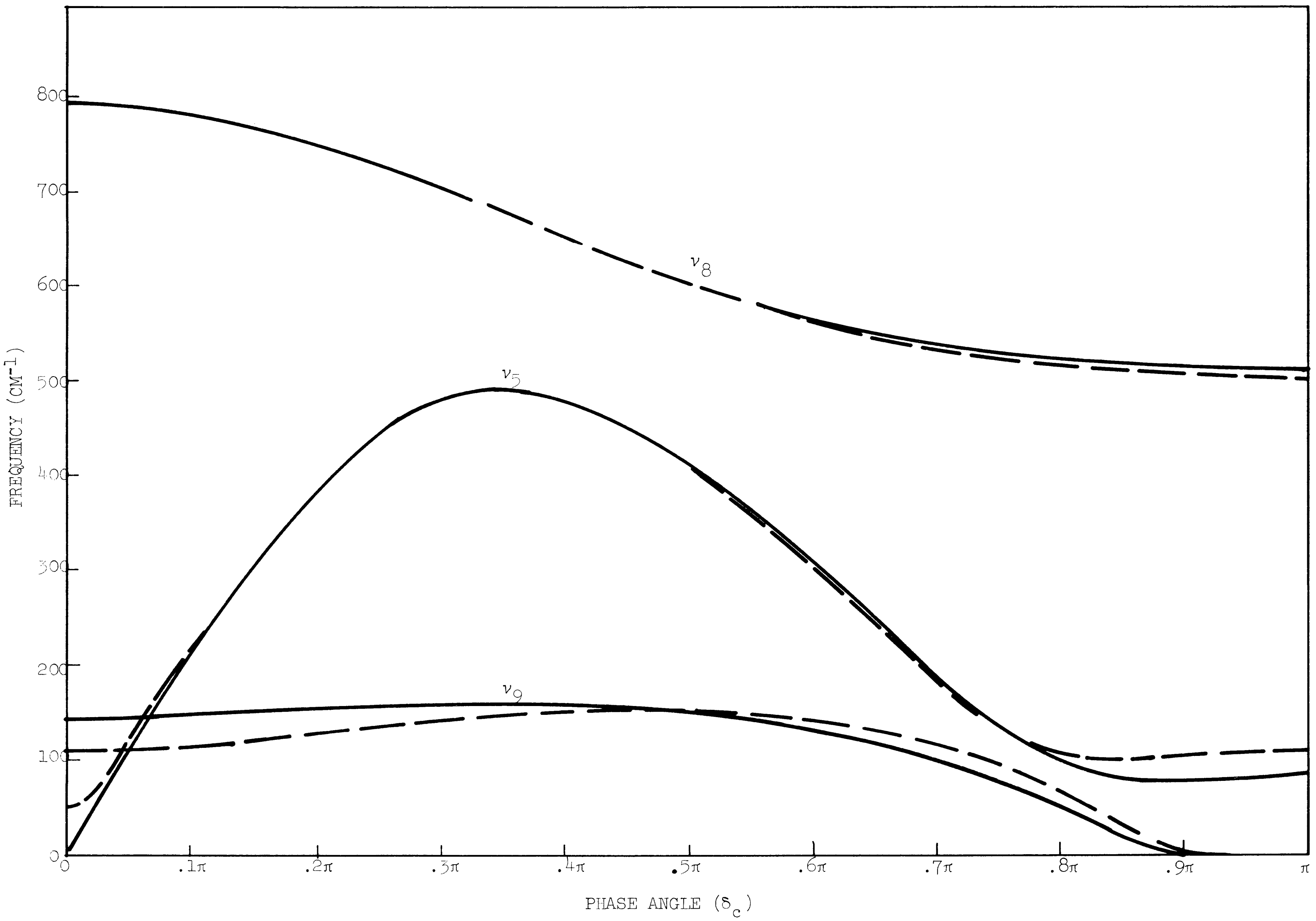


Fig. 5.5. Deuterated crystalline polyethylene low frequency dispersion curves (F_τ = .05 mdyne - Å/rad^2).

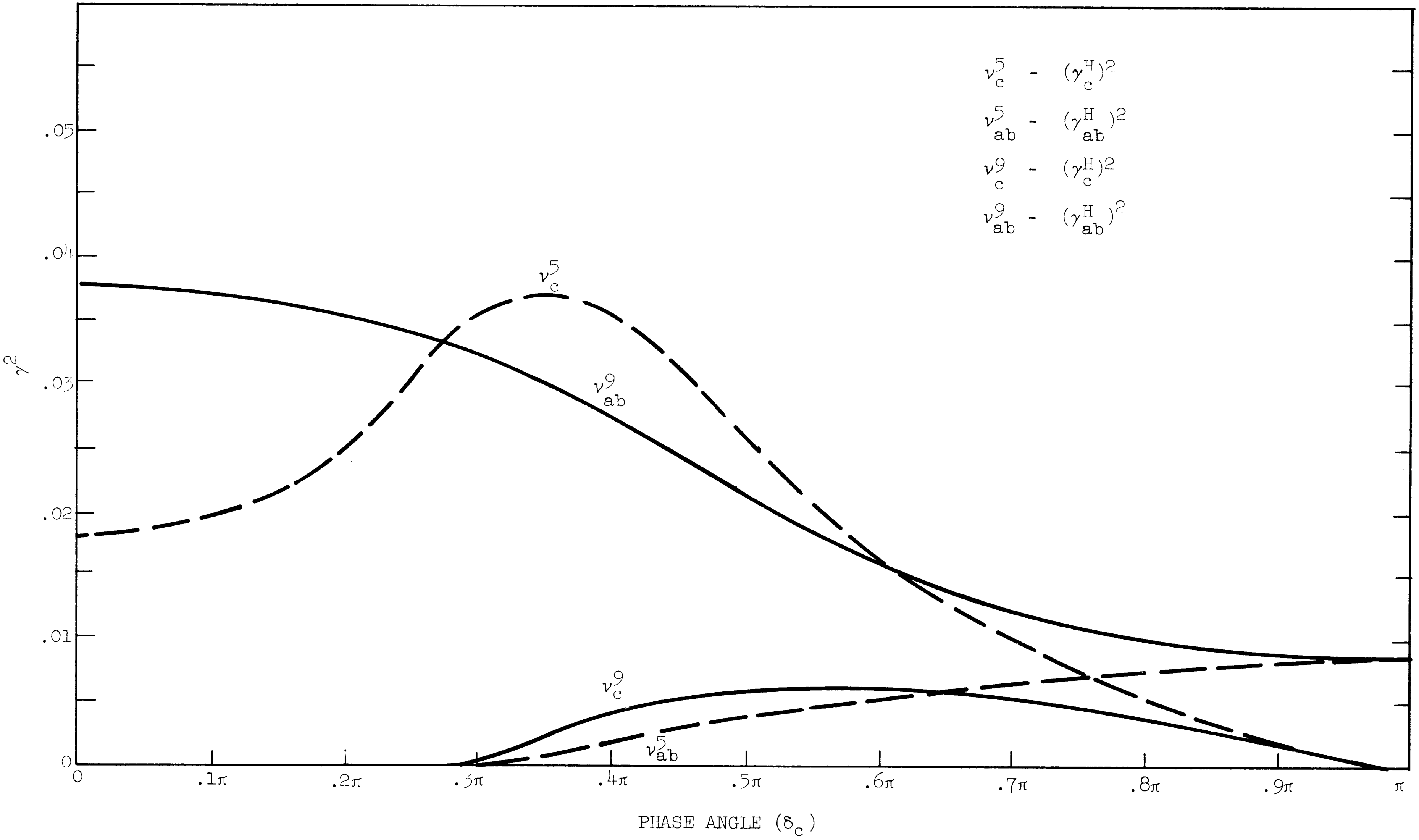


Fig. 5.6. Squares of the polarization vector magnitudes for ν_5 and ν_9 hydrogen motions in normal crystalline polyethylene vs. phase angle (δ_c).

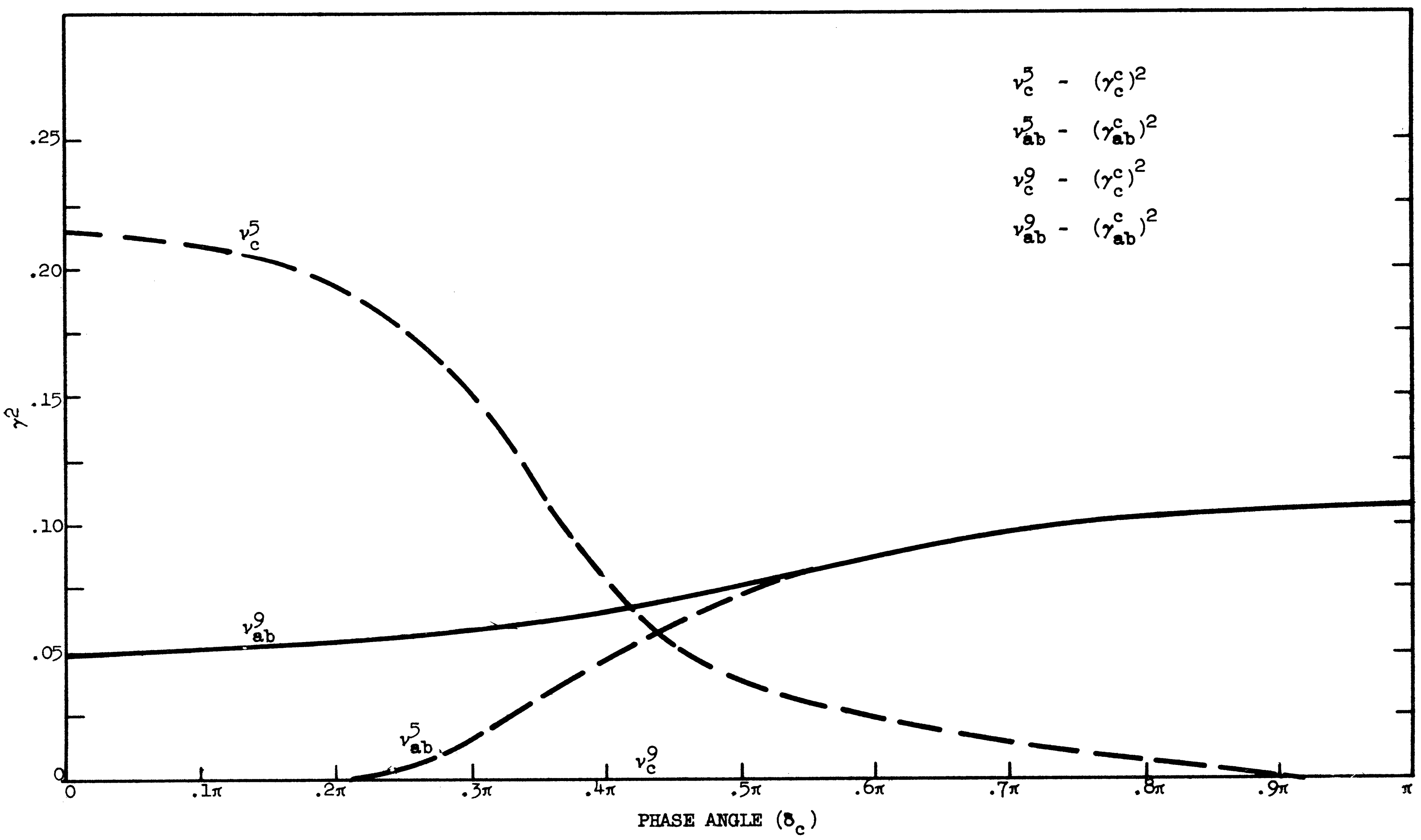


Fig. 5.7. Squares of the polarization vector magnitudes for ν_5 and ν_9 carbon motions in normal crystalline polyethylene vs. phase angle (δ_c).

on s is taken over all atoms in a unit cell. However, in the computer calculations the eigenvector solutions to the equations of motion are obtained from the (9 x 9) A_1 and A_2 species and the B_1 and B_2 species dynamical matrices. For each of these four dynamical matrices the eigenvectors are normalized to unity. Instead of obtaining the eigenvectors from one 36 x 36 matrix at each q value so that the total sum of squares for 36 polarization vectors is 1, the sum of squares from four nine component vectors is 4 at each q value. Therefore, the computed polarization vectors shown in the Appendix for deuterated crystalline polyethylene must be adjusted by a factor of 1/4 to obtain the desired normalization. The polarization vectors shown in Figs. 5.6 and 5.7 are already renormalized in this way.

G. ONE-PHONON FREQUENCY FUNCTIONS

The transverse and longitudinal one-phonon hydrogen frequency functions are shown in Figs. 5.8 and 5.9, respectively, for normal crystalline polyethylene. In Figs. 5.10 and 5.11, the transverse and longitudinal G-functions are shown for a deuterium atom in deuterated crystalline polyethylene. The "incoherent approximation" is invoked in plotting the frequency functions for deuterated polyethylene in this way, since $(CD_2)_n$ scatters neutrons primarily in coherent events. In addition to the arguments presented in Chapter 2 to justify this approximation, this approach is further justified by the very close similarity between experimental frequency spectra obtained for normal and deuterated polyethylene.[9]

H. TWO-PHONON FREQUENCY FUNCTIONS

The temperature dependent two-phonon transverse and longitudinal hydrogen frequency functions for normal crystalline polyethylene are shown in Figs. 5.12 and 5.13, respectively. Only the energy range from zero to 0.1 ev is shown. These functions are obtained from the relations for $G_T^{II}(\epsilon)$ and $G_L^{II}(\epsilon)$ in Eq. (2.59).

I. DIRECTIONAL DEBYE-WALLER FACTORS AND WEIGHTED FREQUENCY FUNCTIONS

The transverse and longitudinal Debye-Waller coefficients are first calculated using Eqs. (2.45) and (2.25), respectively. In these calculations, the frequency spectra are given a quadratic frequency dependence below .006 eV, in accord with specific heat requirements[50] and in order to guarantee a finite Debye-Waller coefficient and non-zero cross-section. The normal polyethylene results for $2W/\kappa^2$, on the temperature range from 0°K to 600°K, are shown in Fig. 5.14.

For the special case when neutrons are scattered through 90° with an initial and final neutron energy of .030 eV, the transverse and longitudinal Debye-Waller factors for normal polyethylene are as shown in Fig. 5.15, for the same temperature range. The ratios of e^{-2W_L}/e^{-2W_T} are given in Fig. 5.16. These are the calculated ratios between the longitudinal and transverse elastic peak magnitudes, each of which is given by Eq. (2.19).

The relative magnitudes of the transverse one- and two-phonon contributions, as a function of temperature, are seen quite clearly in Fig. 5.17. At the higher temperatures, for example, the height of the .022 eV peak relative to

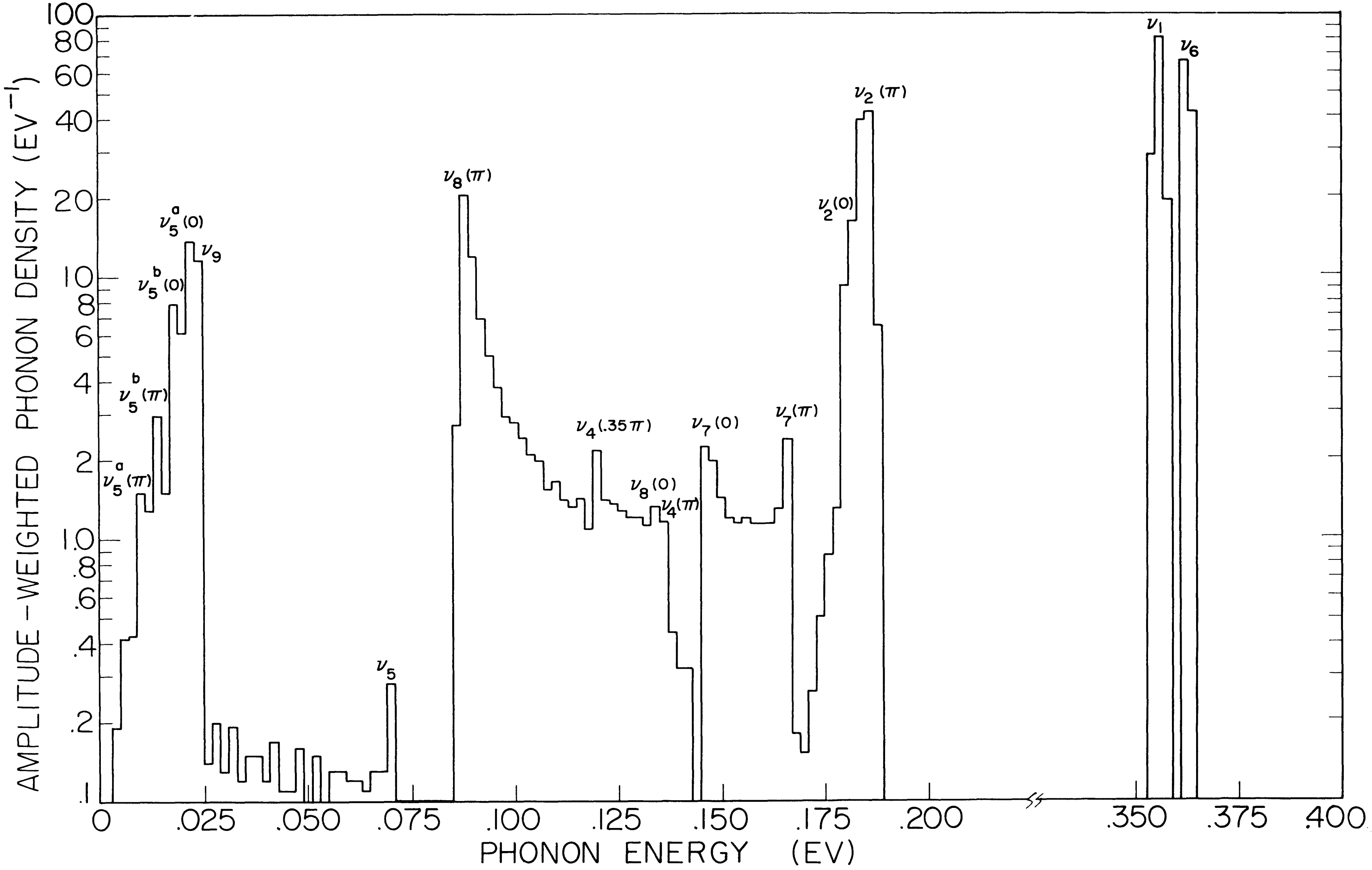


Fig. 5.8. Transverse one-phonon hydrogen G-function, $G_T^I(\epsilon)$, for normal crystalline polyethylene.

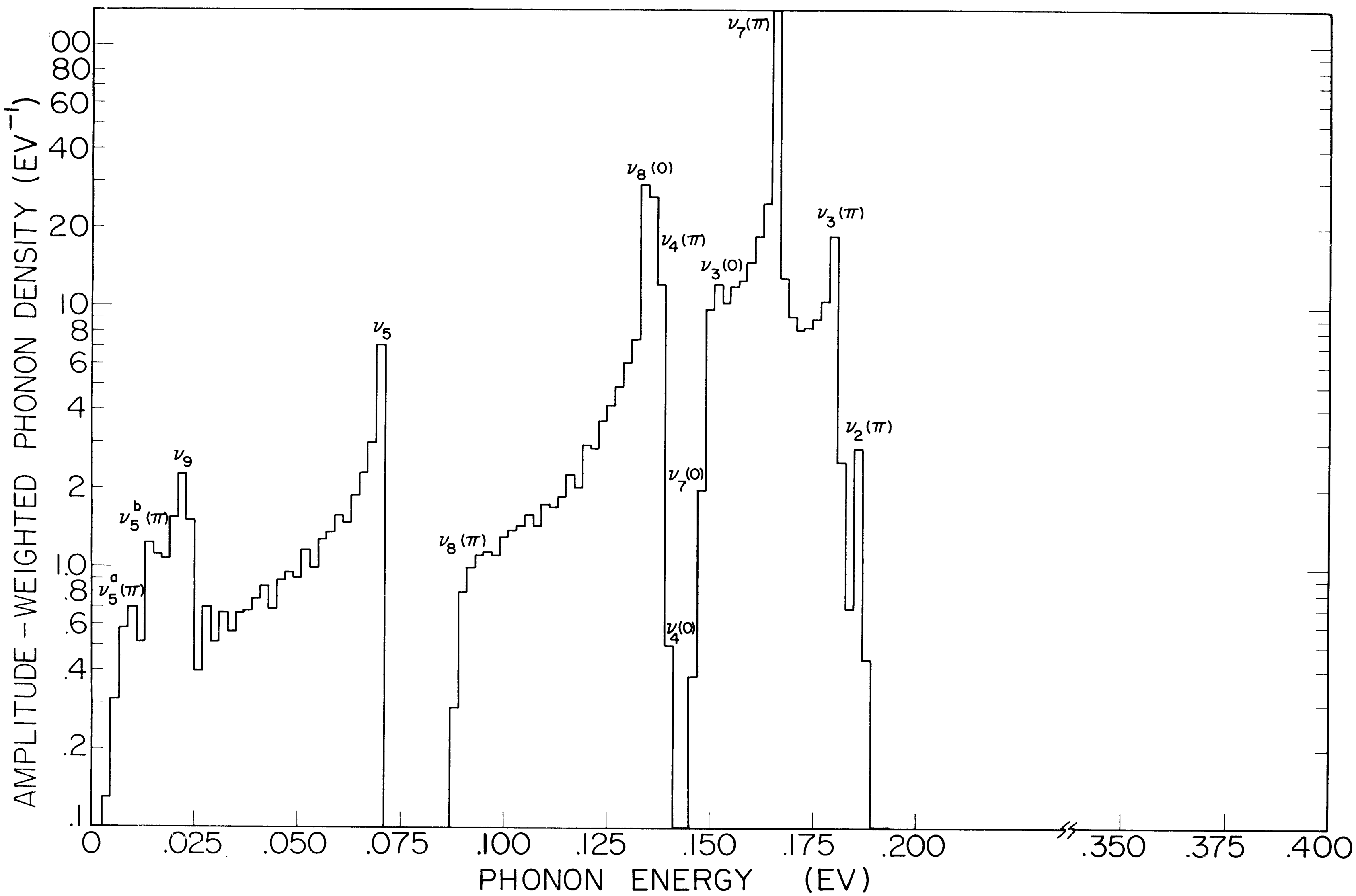


Fig. 5.9. Longitudinal one-phonon hydrogen G-function, $G_L^I(\epsilon)$, for normal crystalline polyethylene.

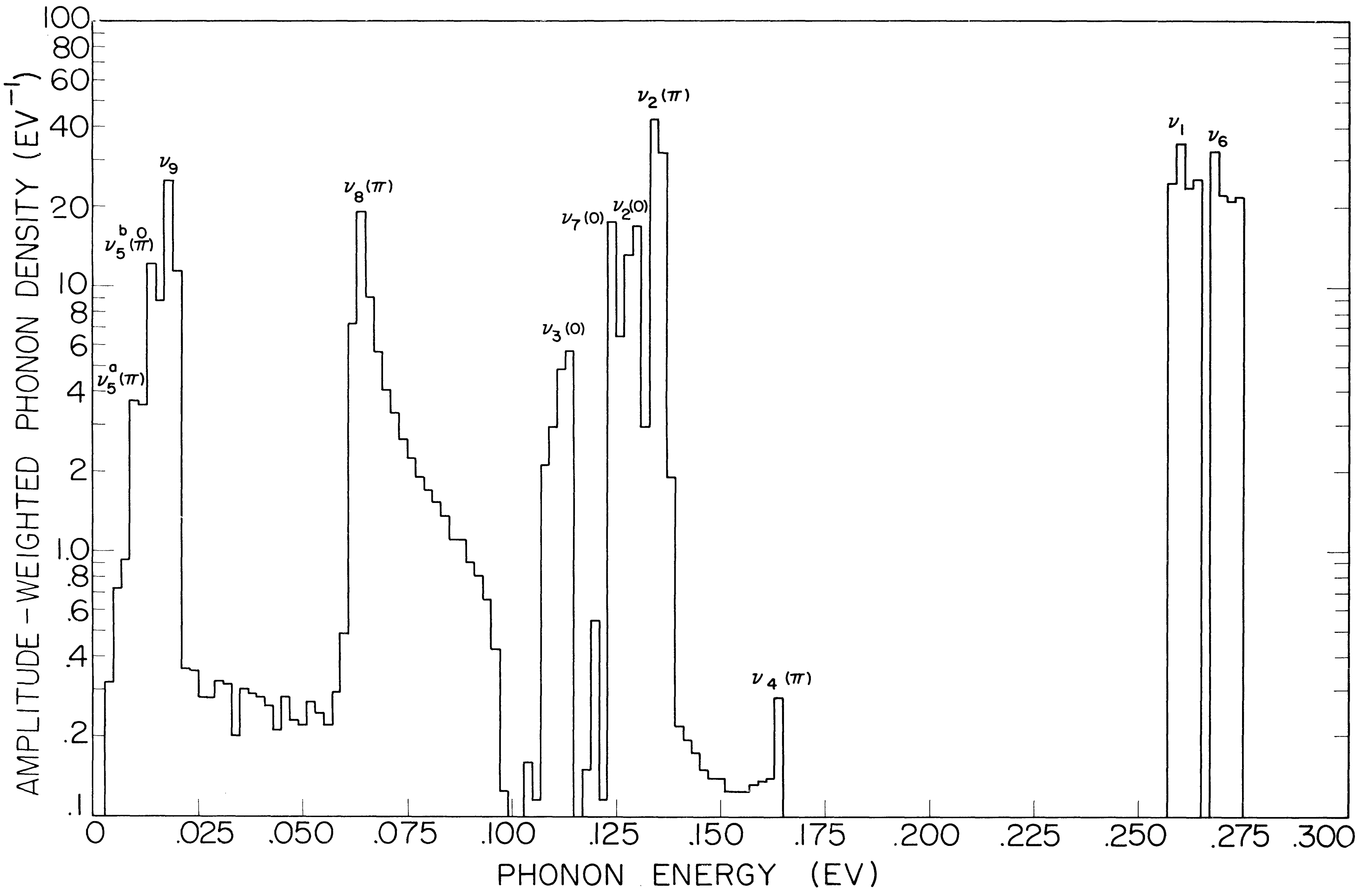


Fig. 5.10. Transverse one-phonon deuterium G-function, $G_T^I(\epsilon)$, for deuterated crystalline polyethylene.

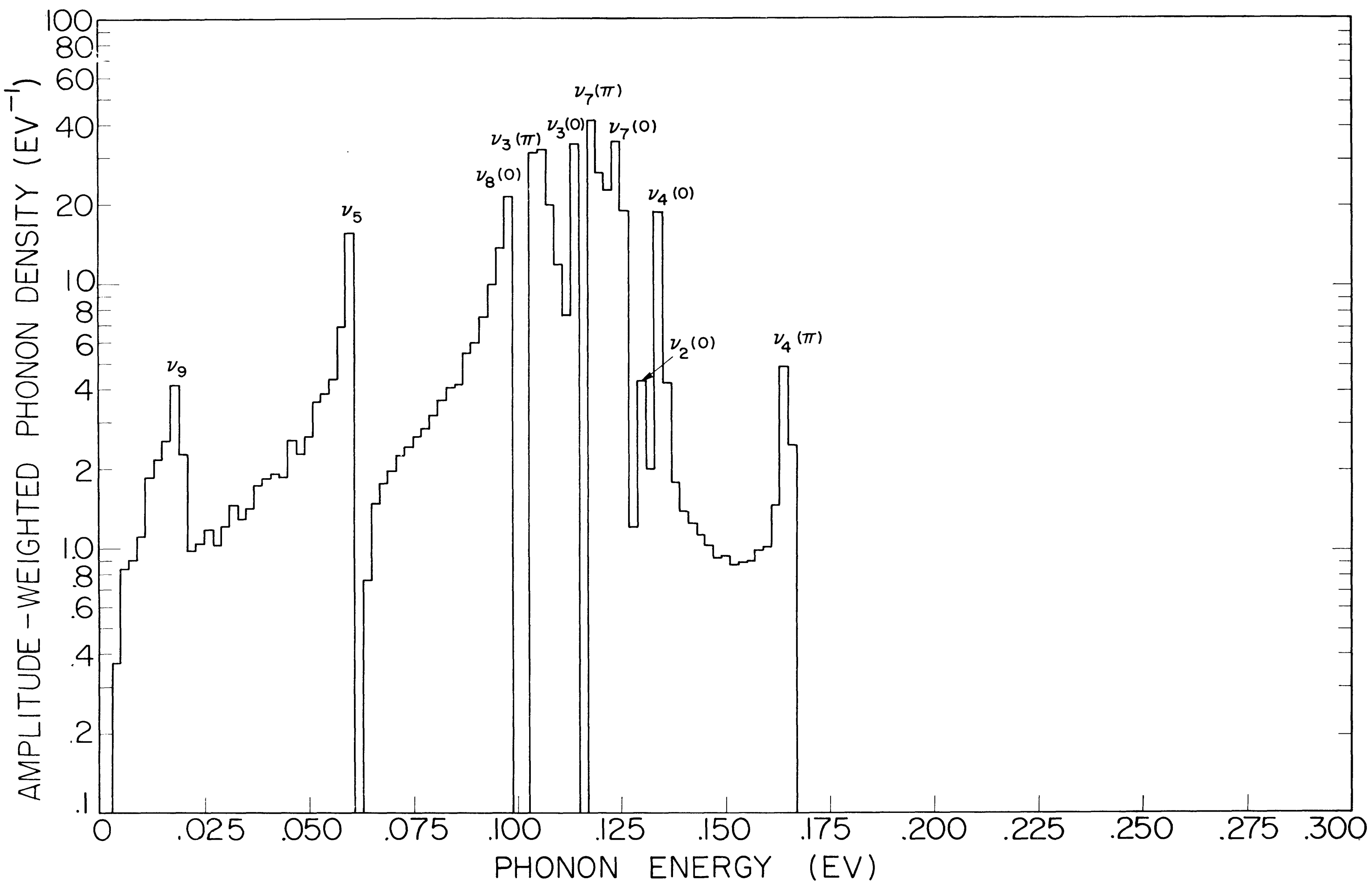


Fig. 5.11. Longitudinal one-phonon deuterium G-function, $G_L^I(\epsilon)$, for deuterated crystalline polyethylene.

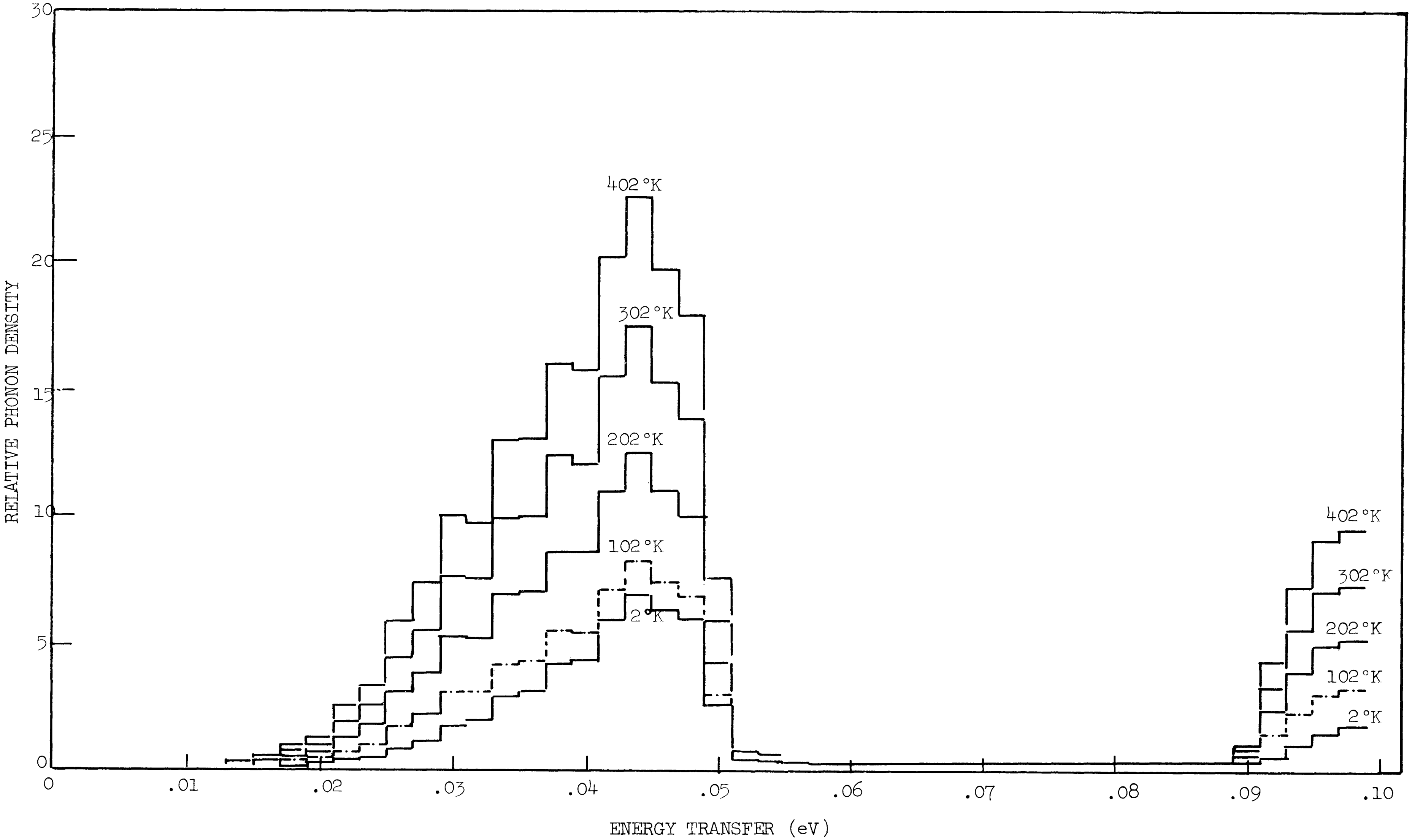


Fig. 5.12. Transverse two-phonon G-function, $G_T^{II}(\epsilon)$, for normal crystalline polyethylene as a function of temperature.

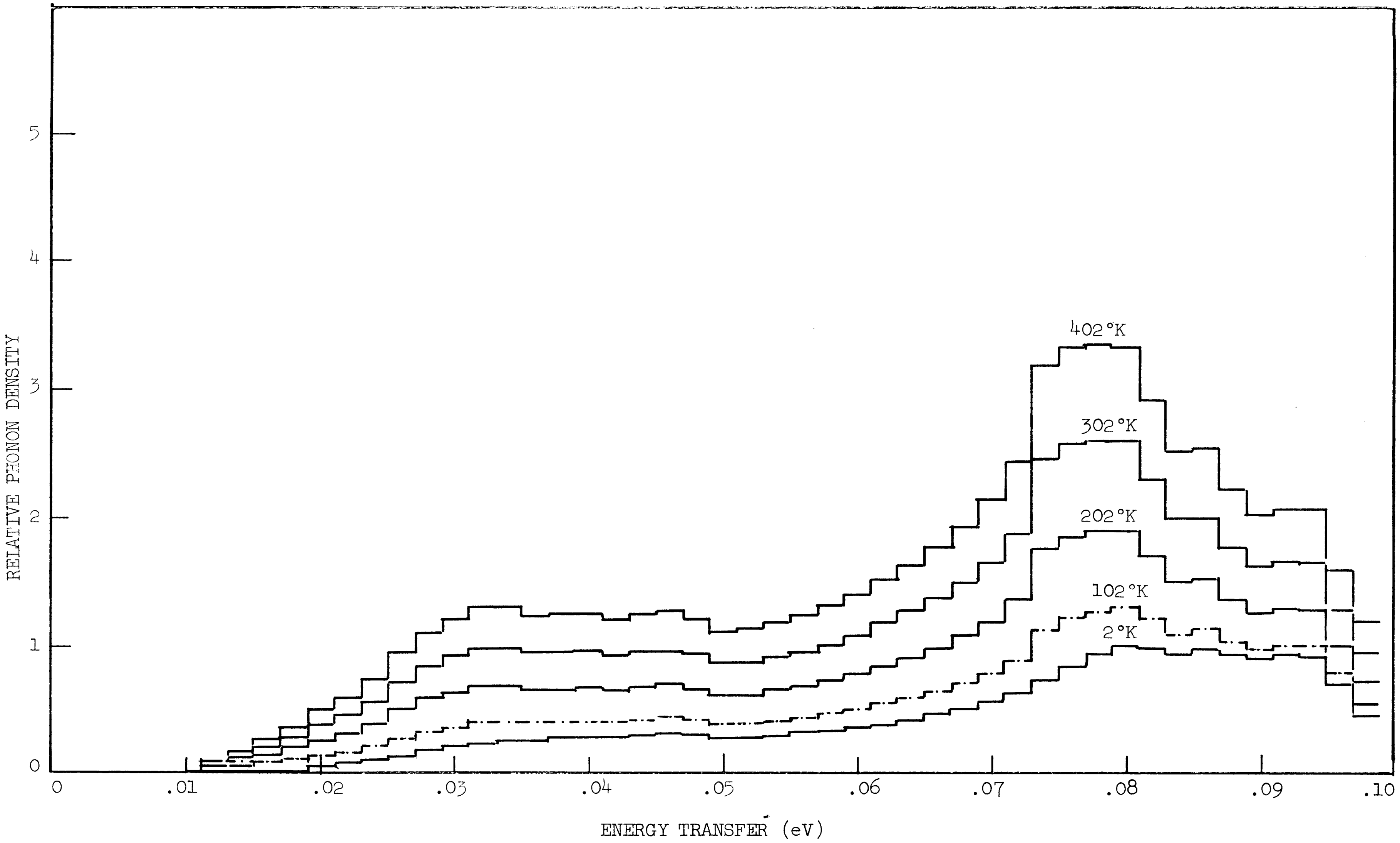


Fig. 5.13. Longitudinal two-phonon G-function, $G_L^{II}(\epsilon)$, for normal crystalline polyethylene as a function of temperature.

the two-phonon .044 eV peak is decreased considerably.

The longitudinal Debye-Waller weighted one- and two-phonon frequency functions are shown in Fig. 5.18 . The scale of Fig. 5.18 is expanded relative to that used for the transverse functions in Fig. 5.17, yet the temperature variations are less dramatic.

For deuterated polyethylene, the Debye-Waller coefficients at 93°K are calculated to be:

$$2W_L/\kappa^2 = .0166\ \text{Å}^2$$
$$2W_T/\kappa^2 = .0206\ \text{Å}^2 \quad ,$$

These may be compared to the values for normal polyethylene at 93°K, which are:

$$2W_L/\kappa^2 = .0205\ \text{Å}^2$$
$$2W_T/\kappa^2 = .0253\ \text{Å}^2 \quad .$$

The one- and two-phonon directional frequency functions for deuterated crystalline polyethylene are shown in Figs. 5.19 and 5.20. These functions are also weighted by the Debye-Waller factors, which are calculated for $E_f = .030$ ev. and $\theta_s = \pi/2$.

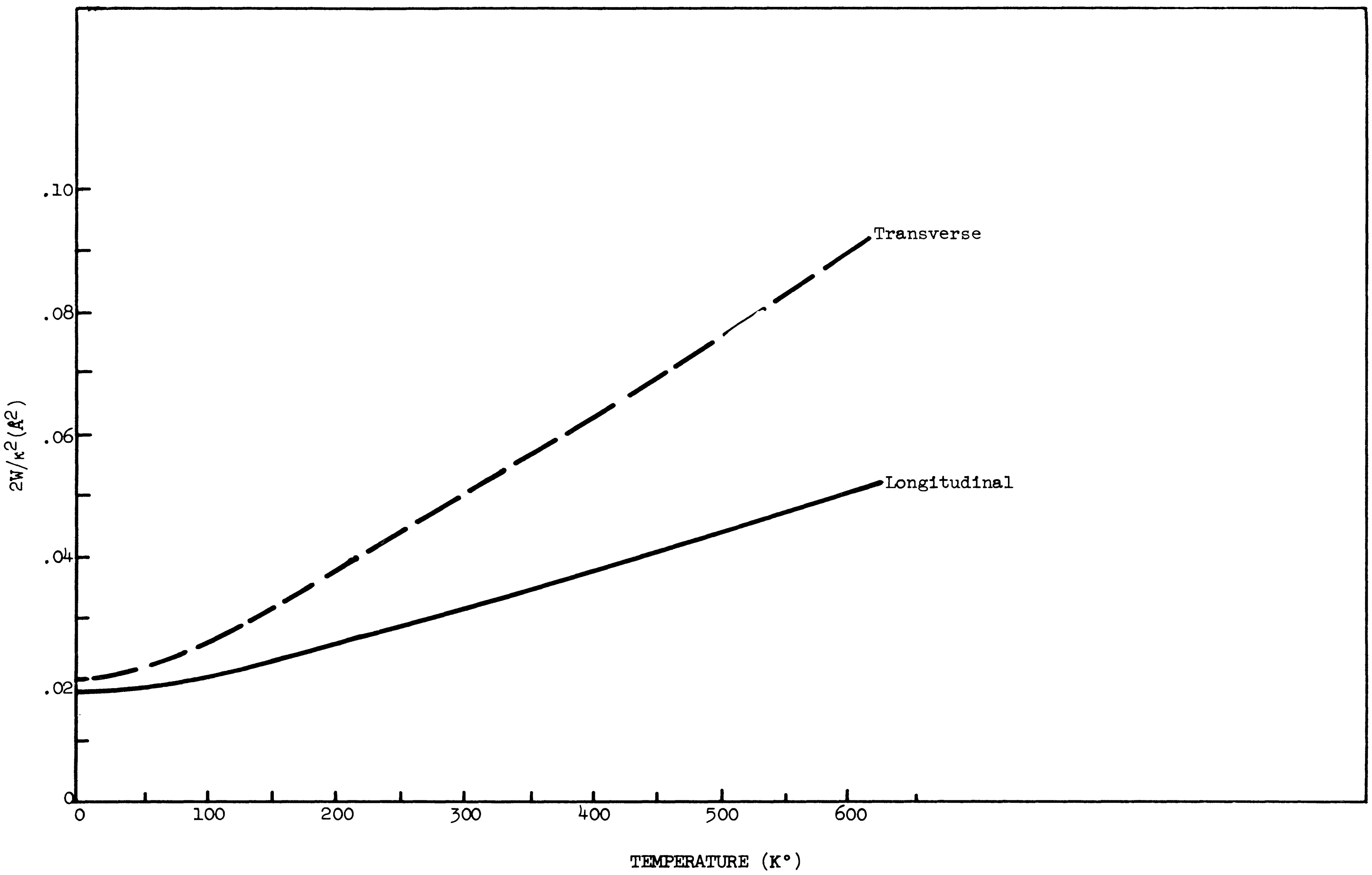


Fig. 5.14. Calculated directional Debye-Waller coefficients as a function of temperature, for crystalline polyethylene.

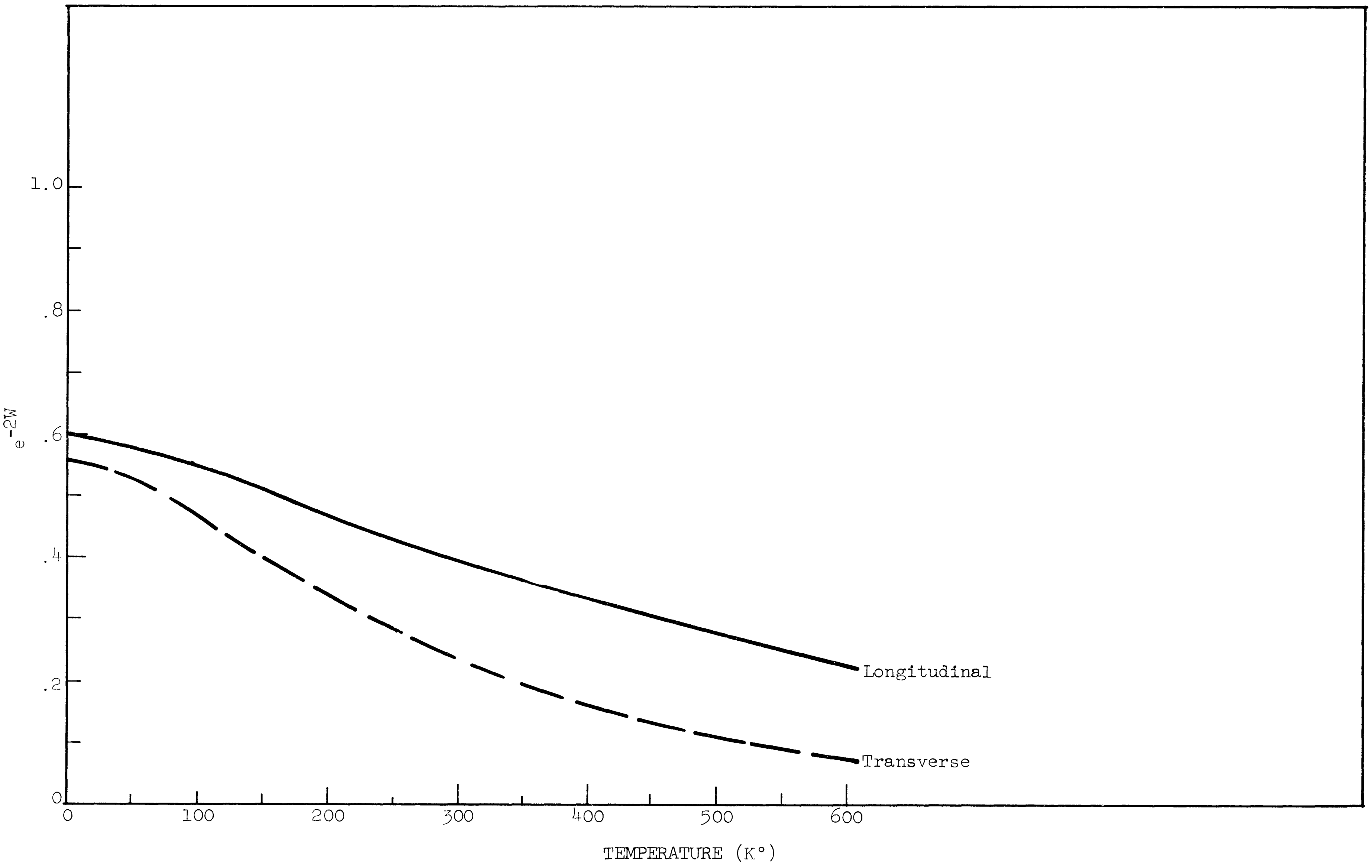


Fig. 5.15. Calculated directional Debye-Waller factors as a function of temperature, for crystalline polyethylene ($E_i = E_f = .030$ eV; $\Theta_s = \pi/2$).

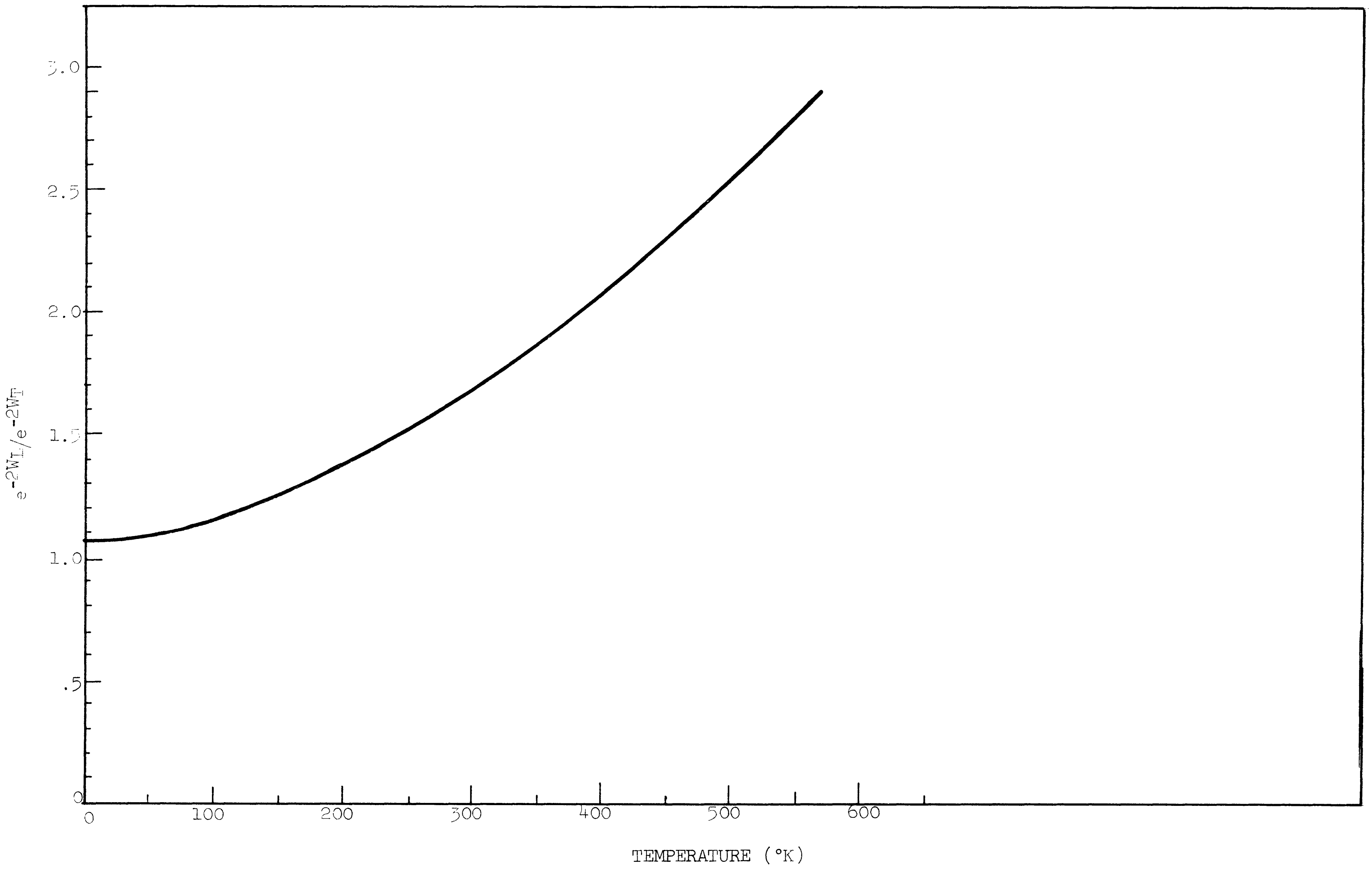


Fig. 5.16. Calculated longitudinal to transverse elastic peak ratios as a function of temperature, for crystalline polyethylene ($E_i = E_f = .030$ eV; $\Theta_s = \pi/2$).

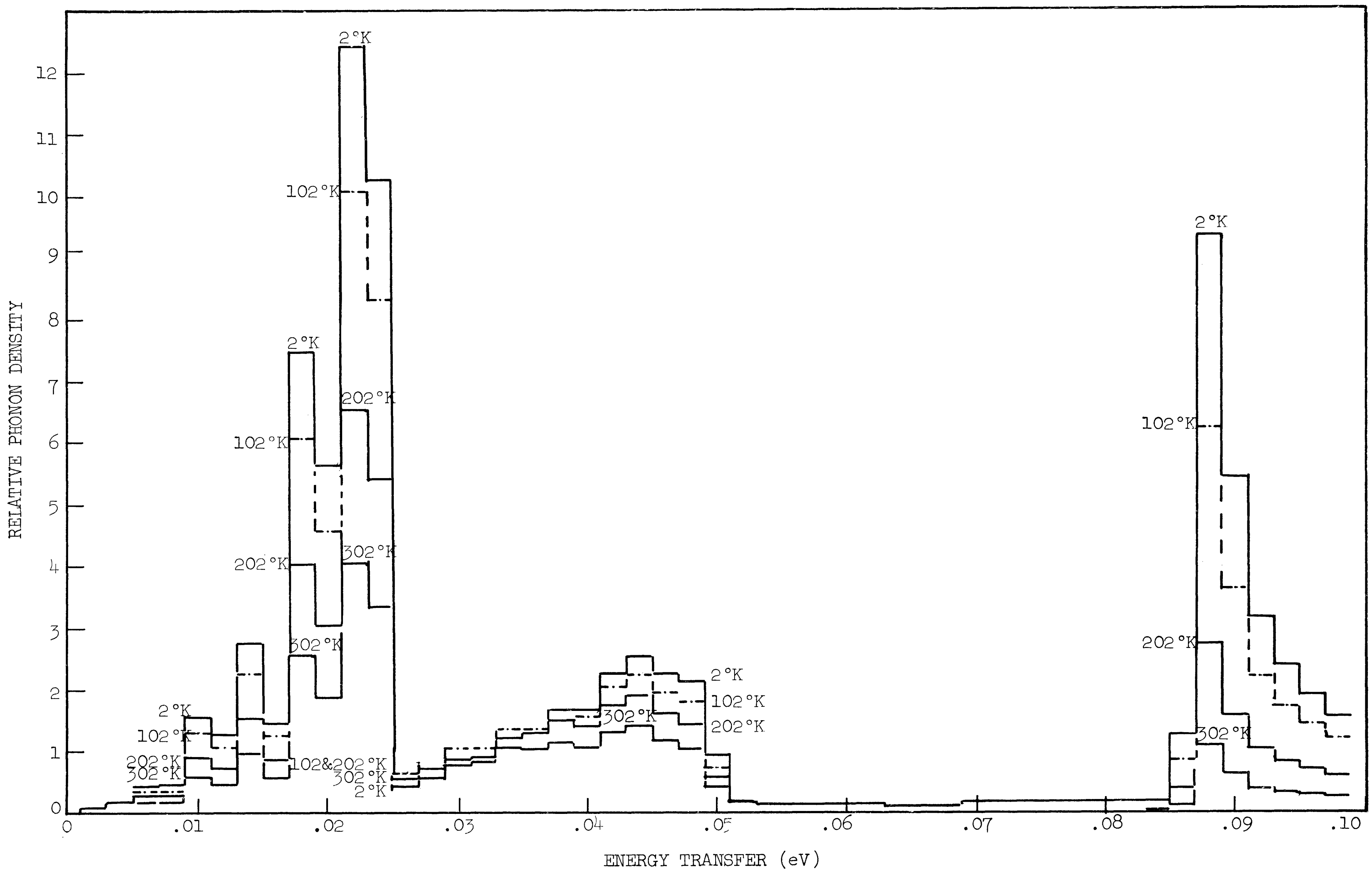


Fig. 5.17. Sum of transverse one- and two-phonon frequency functions for crystalline polyethylene weighted by the Debye-Waller factor (E_i = E_f = .030 eV; Θ_s = $\pi/2$, T = 93°K).

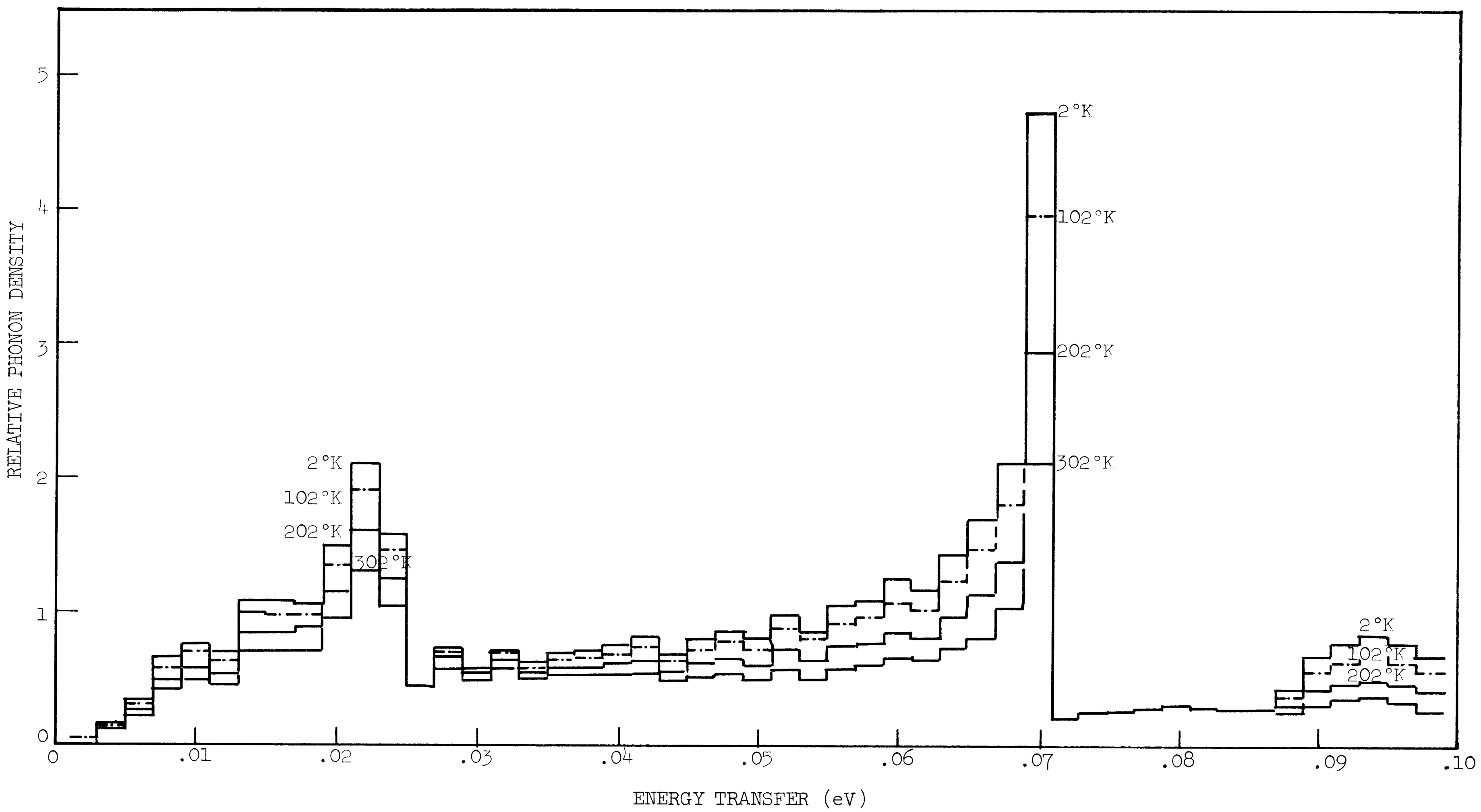


Fig. 5.18. Sum of longitudinal one- and two-phonon frequency functions for crystalline polyethylene weighted by the Debye-Waller factor ($E_i = E_f = .030$ eV; $\Theta_s = \pi/2$, $T = 93°K$).

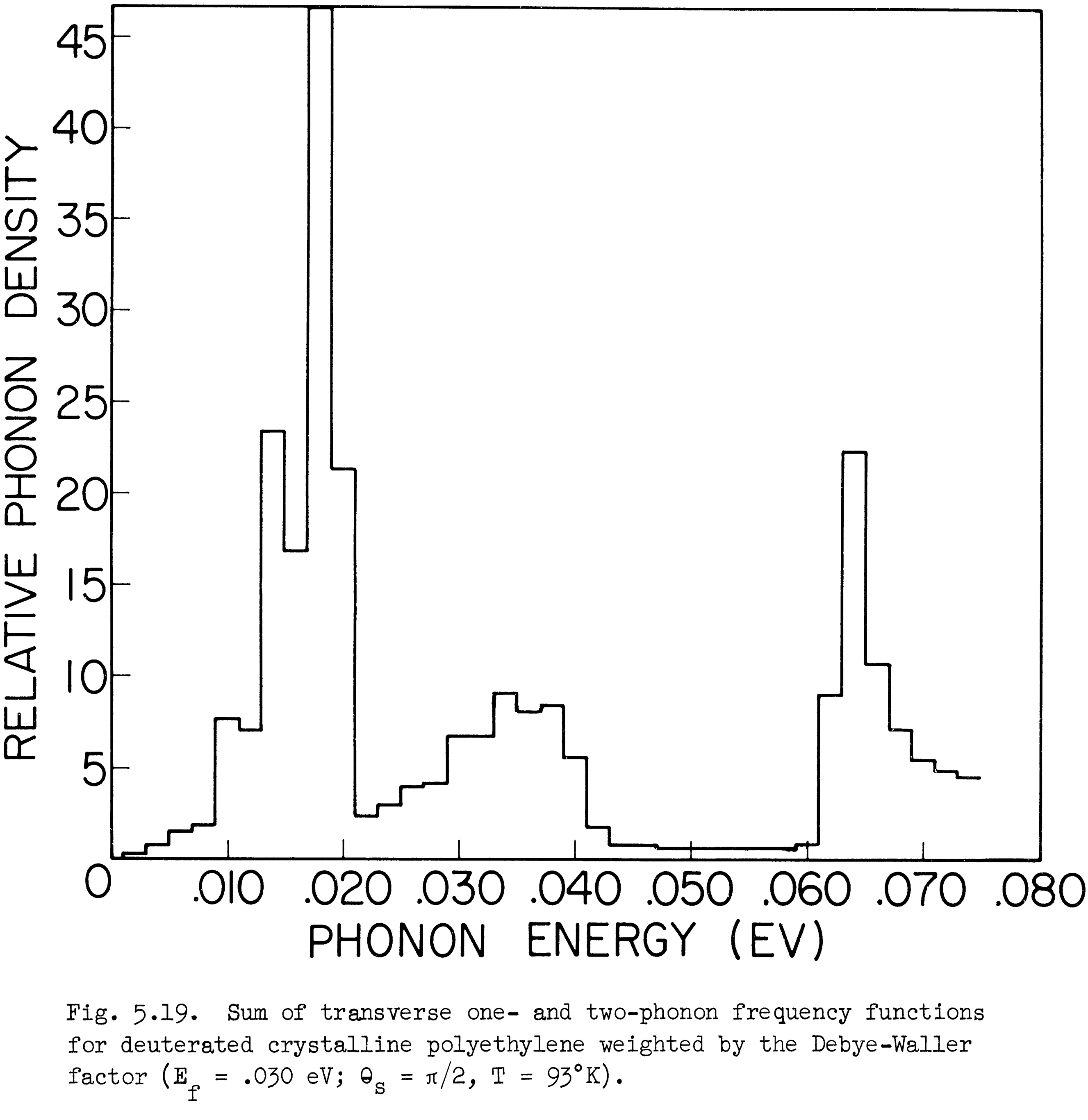


Fig. 5.19. Sum of transverse one- and two-phonon frequency functions for deuterated crystalline polyethylene weighted by the Debye-Waller factor (E_f = .030 eV; $\Theta_s = \pi/2$, T = 93°K).

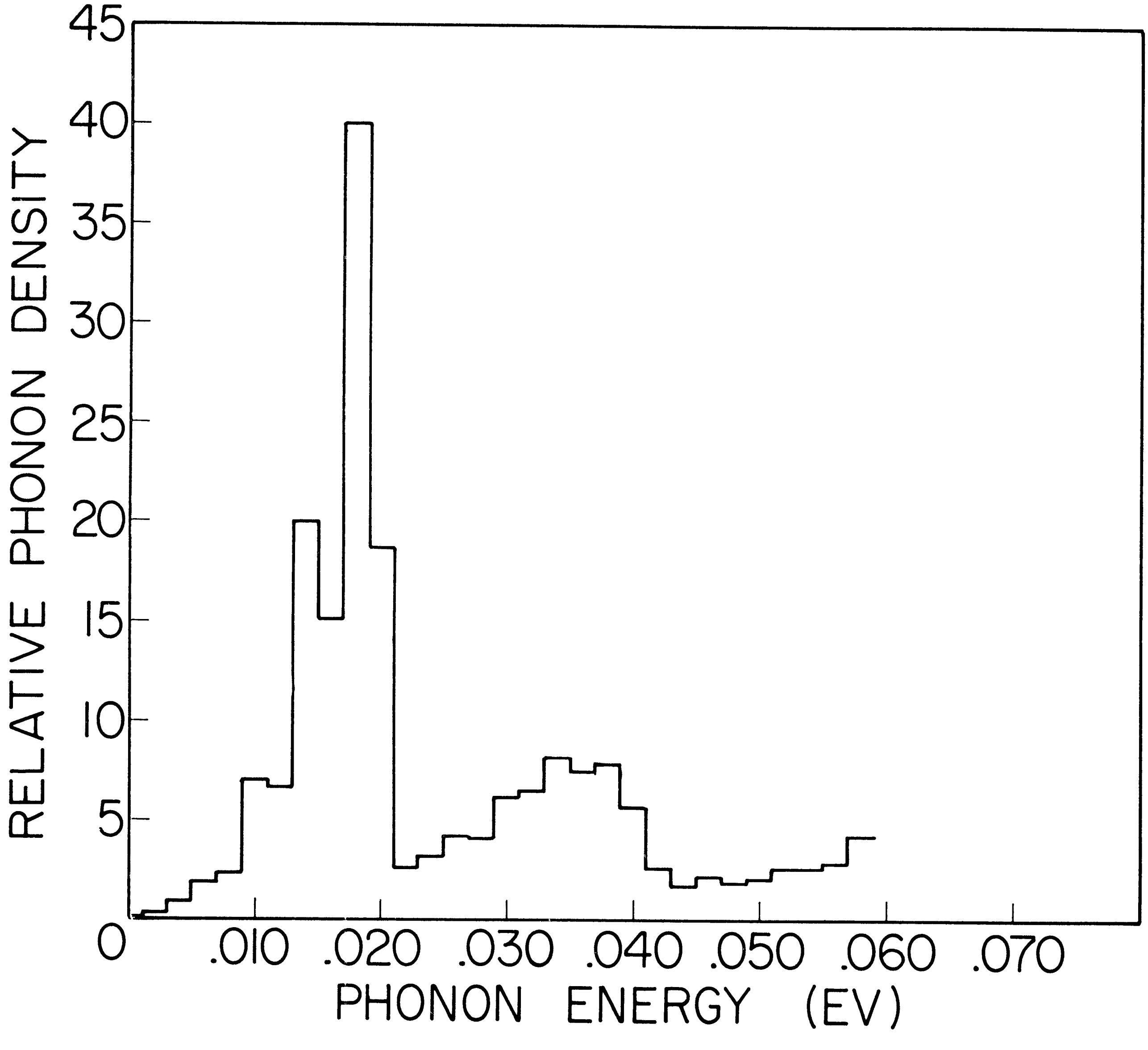


Fig. 5.20. Sum of one- and two-phonon frequency functions for unoriented deuterated crystalline polyethylene weighted by the Debye-Waller factor (E_f = .030 eV; $\Theta_s = \pi/2$, T = 93°K).

CHAPTER 6

POLYVINYLCHLORIDE

A. MOLECULAR STRUCTURE AND COORDINATES

The crystalline polyvinylchloride chain consists of ($CH_2CHC\ell$) units joined to form a planar zig-zag structure with chlorine atoms in adjacent repeat units located on opposite sides of this plane.[44,45] This syndiotactic conformation requires two chemical repeat units along the chain direction per unit cell, as shown in Fig. 6.1.

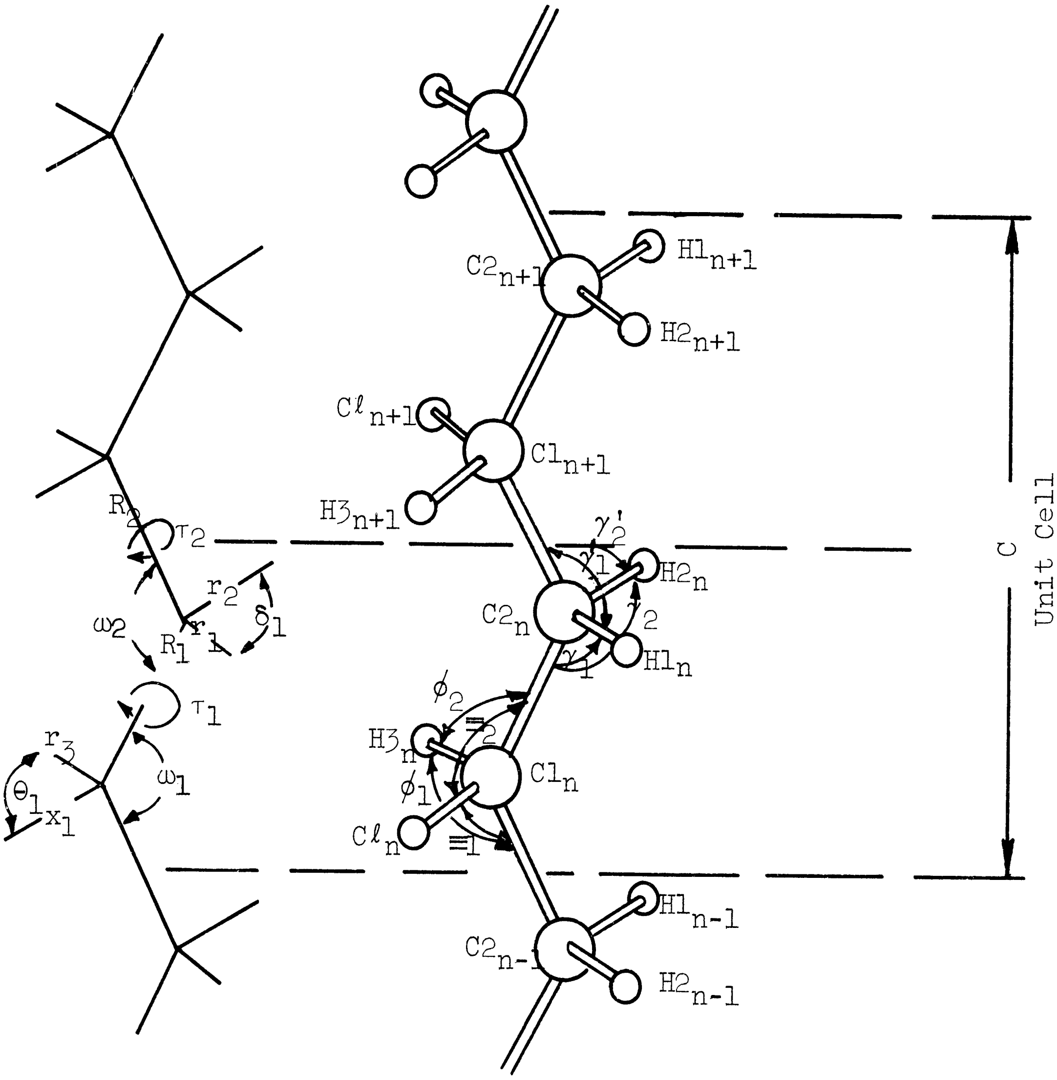


Fig. 6.1. Syndiotactic polyvinylchloride chain structure and internal coordinates.

Polyvinylchloride crystallizes with orthorhombic unit cells of dimension $a = 10.6 \pm .1\text{Å}$ and $b = 5.4 \pm .1\text{Å}$, each containing 4 molecular chains.[46] However this analysis considers only an isolated chain, on the assumption that the intermolecular forces are significantly weaker than the intramolecular forces. The unit cell dimension along the chain is $c = 5.1\text{Å}$[46] and the interatomic bond lengths and angles are as given in Table X.

TABLE X

POLYVINYLCHLORIDE REPEAT UNIT DIMENSIONS[45]

r_{c-H}	=	1.093Å
r_{c-c}	=	1.54A
r_{c-c_ℓ}	=	1.798A
Angles	=	109° 28'

These are the same as Schachtschneider and Snyders' polyethylene dimensions[28] except for the carbon-chlorine bond distance. Using Opaskar's notation, the internal coordinates for each chemical repeat unit are described in Table XI. One of the 20 x 18 submatrices of the partitioned $\underline{\underline{B}}^s$ matrix is shown in Eq. (6.1).

Only the row and column labels are shown, to aid in interpreting the computer output matrices in which the actual $\underline{\underline{B}}^s$ matrix elements are displayed. These matrices are given in the Appendix. The calculation of these elements proceeds as described previously, using $\underline{\underline{B}}^s = \underline{\underline{B}}\ \underline{\underline{U}}\ (\underline{+})^{\dagger}$ where in this case the equivalent alternating cartesian coordinate systems are as shown in Fig. 6.2. Notice that these are not right-handed systems.

TABLE XI

POLYVINYLCHLORIDE CHEMICAL REPEAT UNIT INTERNAL COORDINATES

R_1	$C1_n - C2_n$	Stretch
X_1	$C1_n - C\ell_n$	Stretch
r_3	$C1_n - H3_n$	Stretch
ω_1	$C2_{n-1} - C1_n - C2_n$	Bend
θ_1	$H3_n - C1_n - C\ell_n$	Bend
Ξ_1	$C\ell_n - C1_n - C2_{n-1}$	Bend
ϕ_1	$H3_n - C1_n - C2_{n-1}$	Bend
Ξ_2	$C\ell_n - C1_n - C2_n$	Bend
ϕ_2	$H3_n - C1_n - C2_n$	Bend
τ_1	$C1_n - C2_n$	Torsion
---	-----------------	-------
R_2	$C2_n - C1_{n+1}$	Stretch
r_1	$C2_n - H1_n$	Stretch
r_2	$C2_n - H2_n$	Stretch
ω_2	$C1_n - C2_n - C1_{n+1}$	Bend
δ_1	$H1_n - C2_n - H2_n$	Bend
γ_1	$C1_n - C2_n - H1_n$	Bend
γ_2	$C1_n - C2_n - H2_n$	Bend
γ'_1	$C1_{n+1} - C2_n - H1_n$	Bend
γ'_2	$C1_{n+1} - C2_n - H2_n$	Bend
τ_2	$C2_n - C1_{n+1}$	Torsion

$$
\begin{array}{c|ccccccccc|ccccccccc|}
 & X^{C1}_{n+1} & Y^{C1}_{n+1} & Z^{C1}_{n+1} & X^{C\ell}_{n+1} & Y^{C\ell}_{n+1} & Z^{C\ell}_{n+1} & X^{H3}_{n+1} & Y^{H3}_{n+1} & Z^{H3}_{n+1} & X^{C2}_{n+1} & Y^{C2}_{n+1} & Z^{C2}_{n+1} & X^{H1}_{n+1} & Y^{H1}_{n+1} & Z^{H1}_{n+1} & X^{H2}_{n+1} & Y^{H2}_{n+1} & Z^{H2}_{n+1} \\
\Delta R_1 &&&&&&&&&&&&&&&&&& \\
\Delta X_1 &&&&&&&&&&&&&&&&&& \\
\Delta r_3 &&&&&&&&&&&&&&&&&& \\
\Delta \omega_1 &&&&&&&&&&&&&&&&&& \\
\Delta \theta_1 &&&&&&&&&&&&&&&&&& \\
\Delta \Xi_1 &&&&&&&&&&&&&&&&&& \\
\Delta \phi_1 &&&&&&&&&&&&&&&&&& \\
\Delta \Xi_2 &&&&&&&&&&&&&&&&&& \\
\Delta \phi_2 &&&&&&&&&&&&&&&&&& \\
\Delta \tau_1 &&&&&&&&&&&&&&&&&& \\
\hline
\Delta R_2 &&&&&&&&&&&&&&&&&& \\
\Delta r_1 &&&&&&&&&&&&&&&&&& \\
\Delta r_2 &&&&&&&&&&&&&&&&&& \\
\Delta \omega_2 &&&&&&&&&&&&&&&&&& \\
\Delta \delta_1 &&&&&&&&&&&&&&&&&& \\
\Delta \gamma_1 &&&&&&&&&&&&&&&&&& \\
\Delta \gamma_2 &&&&&&&&&&&&&&&&&& \\
\Delta \gamma'_1 &&&&&&&&&&&&&&&&&& \\
\Delta \gamma'_2 &&&&&&&&&&&&&&&&&& \\
\Delta \tau_2 &&&&&&&&&&&&&&&&&&
\end{array}
= \underline{\underline{B}}^{s}_{n,n+1}
\qquad (6.1)
$$

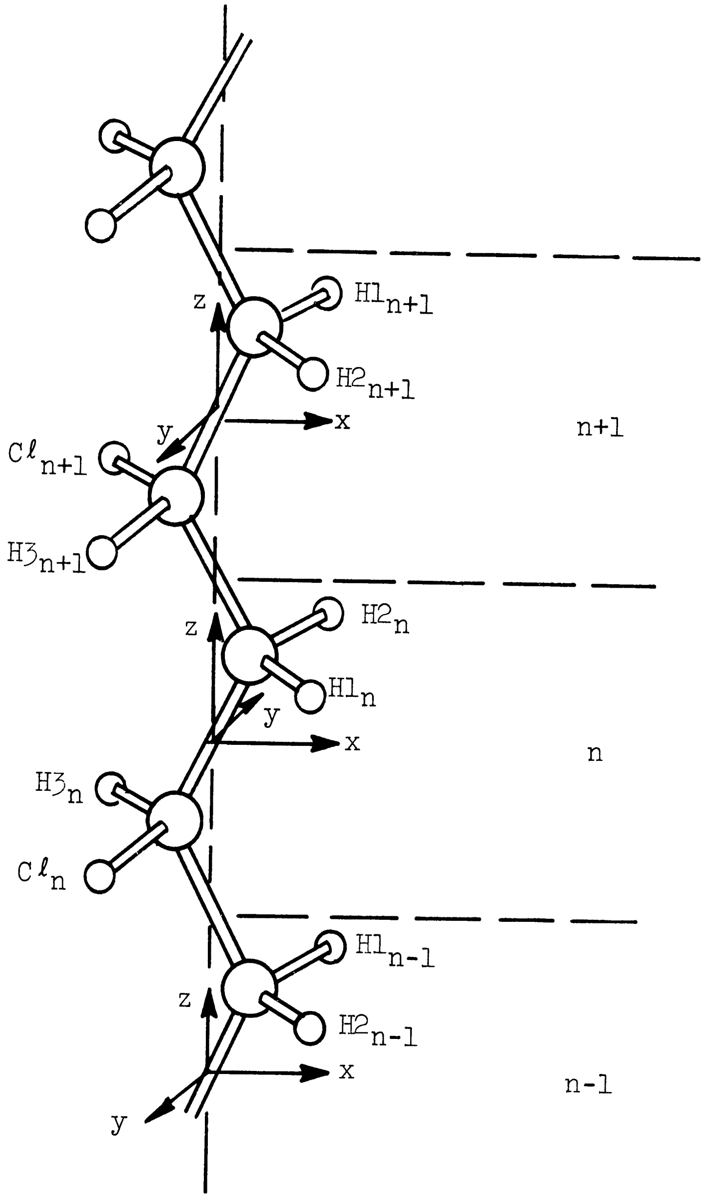


Fig. 6.2. Polyvinylchloride repeat unit coordinate systems.

As was true also in the polyethylene calculations, the torsion coordinate:[26,27]

$$\Delta\tau = \sum_i \Delta\tau_{i/9} \qquad (6.2)$$

is used:

B. INTRAMOLECULAR FORCE CONSTANTS

With the exception of the diagonal torsion force constant, all internal coordinate constants are taken from Opaskar's work.[45] His set of force constants is a modified version of Schachtschneider and Snyders' compilation for the saturated hydrocarbons, containing in addition several newly determined force constants.

The diagonal torsion force constant, $F_T = .06$ mdyne -Å/rad^2, has also been included in this analysis. This value is chosen after assuming that the torsion force constant for polyvinylchloride should not be greatly different from that of polyethylene.

The arrays of internal coordinate force constant matrix elements are given in the Appendix. One of these submatrices is labelled F2, which is $\underline{\underline{F}}_{0,\bar{1}}$, for forces on the zeroeth chemical repeat unit from internal coordinate displacements in unit (-1). The other submatrix is labelled F3, which is $\underline{\underline{F}}_{0,0}$, for forces on atoms in the zeroeth chemical repeat unit from displacements of atoms in this unit. Of course, forces on the zeroeth unit due to displacements in unit (+1) are given by $\tilde{\underline{\underline{F}}}_{0,\bar{1}}$. Displacements of atoms in cells beyond $n = \pm 1$ are assumed in this model to produce zero force on atoms in the zeroeth unit.

For each chemical repeat unit ($CH_2CHC\ell$) containing six atoms, a 20 x 20 internal coordinate force constant submatrix is utilized, with row and column labels for the internal coordinates as indicated in Eq. (6.3).

The cartesian force constant matrices are obtained by again using Eq. (3.51), which is:

$$\underline{\underline{A}}_{0,m} = \sum_{\alpha,\gamma} (\tilde{\underline{\underline{B}}}^{s}_{0,\alpha})\, \underline{\underline{F}}_{0,\gamma}\, \underline{\underline{B}}_{0,m-\gamma-\alpha} \quad .$$

The limits on the indices is this case however are:

$$-1 \geq m \leq +1 \qquad -1 \geq \gamma \leq +1$$

$$-1 \geq \alpha \leq +1 \qquad -1 \geq (m-\gamma-\alpha) \leq +1$$

Only the $\underline{\underline{A}}_{0,0}$ and $\underline{\underline{A}}_{0,\bar{1}}$ submatrices must be determined, since all others are then known from:

$$\underline{\underline{A}}_{0,m} = \tilde{\underline{\underline{A}}}_{0,\bar{m}}$$

and:

$$\underline{\underline{A}}_{n,m} = \underline{\underline{A}}_{0,m-n}$$

C. LINE GROUP SYMMETRY ANALYSIS

The extended syndiotactic polyvinylchloride chain has one-dimensional space group C_{2v} symmetry.[44] There are four elements in the group as shown in Fig. 6.3. These operations are described in Table XII.

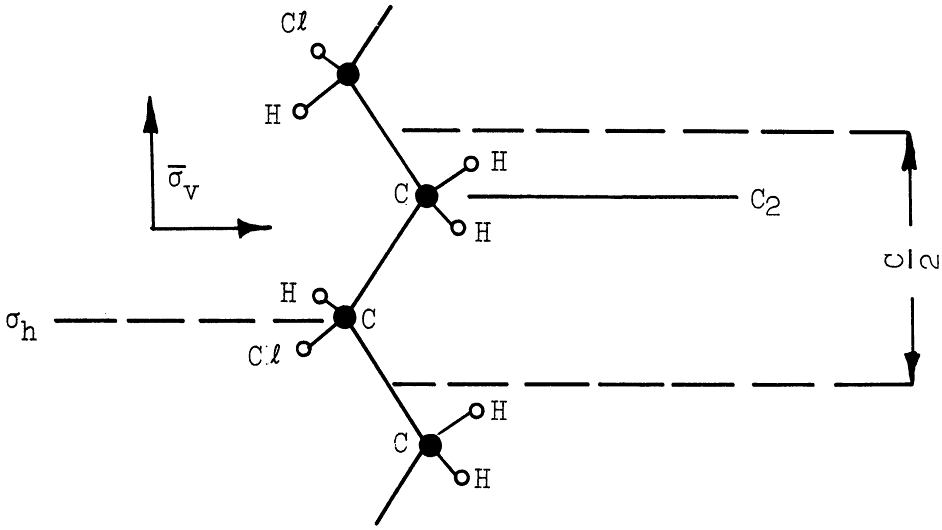


Fig. 6.3. Single-chain polyvinylchloride symmetry operations.

Unit m

$$\underline{F}_{0,m} = \begin{array}{c|cccccccccc|cccccccccc}
 & R_1 & X_1 & r_3 & \omega_1 & \Theta_1 & \Xi_1 & \phi_1 & \Xi_2 & \phi_2 & \tau_1 & R_2 & r_1 & r_2 & \omega_2 & \delta_1 & \gamma_1 & \gamma_2 & \gamma'_1 & \gamma'_2 & \tau_2 \\
\hline
R_1 & & & & & & & & & & & & & & & & & & & & \\
X_1 & & & & & & & & & & & & & & & & & & & & \\
r_3 & & & & & & & & & & & & & & & & & & & & \\
\omega_1 & & & & & & & & & & & & & & & & & & & & \\
\Theta_1 & & & & & & & & & & & & & & & & & & & & \\
\Xi_1 & & & & & & & & & & & & & & & & & & & & \\
\phi_1 & & & & & & & & & & & & & & & & & & & & \\
\Xi_2 & & & & & & & & & & & & & & & & & & & & \\
\phi_2 & & & & & & & & & & & & & & & & & & & & \\
\tau_1 & & & & & & & & & & & & & & & & & & & & \\
\hline
R_2 & & & & & & & & & & & & & & & & & & & & \\
r_1 & & & & & & & & & & & & & & & & & & & & \\
r_2 & & & & & & & & & & & & & & & & & & & & \\
\omega_2 & & & & & & & & & & & & & & & & & & & & \\
\delta_1 & & & & & & & & & & & & & & & & & & & & \\
\gamma_1 & & & & & & & & & & & & & & & & & & & & \\
\gamma_2 & & & & & & & & & & & & & & & & & & & & \\
\gamma'_1 & & & & & & & & & & & & & & & & & & & & \\
\gamma'_2 & & & & & & & & & & & & & & & & & & & & \\
\tau_2 & & & & & & & & & & & & & & & & & & & & \\
\hline
\end{array} \tag{6.3}$$

TABLE XII

POLYVINYLCHLORIDE LINE GROUP SYMMETRY ELEMENTS

Element	Description
T_n	pure translation along the chain axis of magnitude nc.
C_2	twofold rotation about an axis through a CH_2 unit, perpendicular to the chain axis.
$\bar{\sigma}_v$	mirror reflection in the skeletal plane followed by a fractional translation of magnitude c/2 along the chain.
σ_h	mirror reflection in the horizontal plane through a $HCC\ell$ group.

Only the operations T_n and $\bar{\sigma}_v$ leave the magnitude and direction of $\underline{q}_c$ unchanged in reciprocal space. The operations C_2 and σ_h take $+q_c$ into $-q_c$. Since the dispersion curves are symmetric about $q = 0$, these elements could also be used in writing symmetry coordinates for block diagonalizing the dynamical matrices. However only the $\{q_c\}$ star group elements are used here since the correct orientations for the repeat unit cartesian coordinate systems are dependent upon having subgroup elements which take the coordinate system of one repeat unit into that of the adjacent unit so that:

$$\underline{\underline{B}}^{s}_{r,c} = \underline{\underline{B}}^{s}_{0,c-r}$$

as required.

The multiplication table for this subgroup of the space group is very simple. It is:

TABLE XIII

C_{2v} STAR LINE GROUP MULTIPLICATION TABLE

	T	$\bar{\sigma}_v$
T	T	$\bar{\sigma}_v$
$\bar{\sigma}_v$	$\bar{\sigma}_v$	T

There are two irreducible representations, one of which is symmetric to the glide operation, $\overline{\sigma_v}$, and one of which is anti-symmetric to $\overline{\sigma_v}$. These are respectively labelled the A and B species. The character table for the $\{q_c\}$ star group is given in Table XIV.

TABLE XIV

C_{2v} STAR LINE GROUP CHARACTER TABLE

	T	$\bar{\sigma}_v$
A	1	$e^{iqc/2}$
B	1	$-e^{iqc/2}$

Note that the above species notation differs from that of Opaskar, where the A species in his work is symmetric to the C_2 operation and the B species is anti-symmetric to C_2. Each irreducible representation appears 18 times in the reducible representation since:

$$n^{(\gamma)} = \frac{1}{2}\sum_R \overset{*}{\chi}{}^{(\gamma)}(R)\ \chi^{(R)}$$

and:

$$n^{(A)} = 1/2\{1 \times 36 + e^{iqc/2} \times 0\} = 18$$

$$n^{(B)} = 1/2\{1 \times 36 - e^{iqc/2} \times 0\} = 18 .$$

As a consequence, there are 18 cartesian symmetry coordinates for each species.

D. CARTESIAN SYMMETRY COORDINATES

The 18 components of the cartesian symmetry coordinate vector:

$$\underline{S}^{(\gamma)} = \underline{\underline{U}}^{(\gamma)}\ \underline{X} = \underline{\underline{U}}^{(\gamma)}(\delta_c)\ \underline{\underline{U}}^{(\gamma)}(\pm)\ \underline{X}$$

for the γth irreducible representation, are obtained from:

$$S_i^{(\gamma)} = \eta \sum_R \chi^{(\gamma)}(R)\ \xi_i$$

The results are shown in Eq. (6.4) for the A species, where $\eta = 1/(2N_c)^{1/2}$.

$$S_1^{(A)} = \eta \sum_{n=0}^{2N-1} e^{in\delta_c}\ \Delta X_n^{C1}$$

$$S_2^{(A)} = \eta \sum_n (-1)^n\ e^{in\delta_c}\ \Delta Y_n^{C1}$$

$$S_3^{(A)} = \eta \sum_n e^{in\delta_c}\ \Delta Z_n^{C1}$$

$$S_4^{(A)} = \eta \sum_n e^{in\delta_c}\ \Delta X_n^{C\ell}$$

$$S_5^{(A)} = \eta \sum_n (-1)^n\ e^{in\delta_c}\ \Delta Y_n^{C\ell}$$

$$S_6^{(A)} = \eta \sum_n e^{in\delta_c}\ \Delta Z_n^{C\ell}$$

$$S_7^{(A)} = \eta \sum_n e^{in\delta_c}\ \Delta X_n^{H3}$$

$$S_8^{(A)} = \eta \sum_n (-1)^n\ e^{in\delta_c}\ \Delta Y_n^{H3}$$

$$S_9^{(A)} = \eta \sum_n e^{in\delta_c}\ \Delta Z_n^{H3}$$

$$S_{10}^{(A)} = \eta \sum_{n} e^{in\delta_c} \Delta X_n^{C2}$$

$$S_{11}^{(A)} = \eta \sum_{n} (-1)^n e^{in\delta_c} \Delta Y_n^{C2}$$

$$S_{12}^{(A)} = \eta \sum_{n} e^{in\delta_c} \Delta Z_n^{C2}$$

$$S_{13}^{(A)} = \eta \sum_{n} e^{in\delta_c} \Delta X_n^{H1}$$

$$S_{14}^{(A)} = \eta \sum_{n} (-1)^n e^{in\delta_c} \Delta Y_n^{H1}$$

$$S_{15}^{(A)} = \eta \sum_{n} e^{in\delta_c} \Delta Z_n^{H1}$$

$$S_{16}^{(A)} = \eta \sum_{n} e^{in\delta_c} \Delta X_n^{H2}$$

$$S_{17}^{(A)} = \eta \sum_{n} (-1)^n e^{in\delta_c} \Delta Y_n^{H2}$$

$$S_{18}^{(A)} = \eta \sum_{n=0}^{2N-1} e^{in\delta_c} \Delta Z_n^{H2} \qquad (6.4)$$

for $\delta_c = qC/2$.

For the B species, each term in the above coordinates is multiplied by $(-1)^n = e^{in\pi}$.

Unlike the case for polyethylene, for which real symmetry coordinates could be written[37] due to the combined presence of the $\bar{C}_2$ symmetry operation and an operation which takes +q into $-q_c$, this is not possible for polyvinylchloride. The line group for PVC does not include the $\bar{C}_2$ operation. This is evident from the fact that the molecule has a front and a back, which are defined by the positions of the chlorine atoms.

E. PHASE DEPENDENT DYNAMICAL MATRICES

The A and B species symmetry coordinates make it possible to block diagonalize the dynamical matrix $\underline{\underline{C}}$ to obtain $\underline{\underline{C}}^s$. There are N/2 (18 x 18) A species blocks for the N/2 values of δ_c where $0 \le \delta_c < \pi/2$ and there are N/2 (18 x 18) B species blocks for the N/2 values of δ_c where $\pi/2 \le \delta_c \le \pi$. The N(18 x 18)A and B species blocks for $-\pi \le \delta \le 0$ are identical to the N blocks for $0 \le \delta_c \le \pi$. However, in this case, all 18 x 18 phase dependent dynamical submatrices are complex valued.

To obtain real matrices in this case, the complex dynamical matrix equation, $\underline{\underline{C}}^s \underline{\underline{\Gamma}}_c{}^s = \underline{\underline{\Gamma}}_c{}^s \underline{\underline{\Lambda}}$, is first rewritten in row eigenvector form since the computer programs used for these calculations supply a row eigenvector for each branch j rather than a column eigenvector. It is then partitioned into real and imaginary submatrices. The complex matrix equation is then:

$$\tilde{\underline{\underline{\Gamma}}}_c^s \tilde{\underline{\underline{C}}}^s = \underline{\underline{\Lambda}}\, \tilde{\underline{\underline{\Gamma}}}_c^s . \qquad (6.5)$$

The jth row is:

$$\tilde{\underline{\gamma}}_j^s \tilde{\underline{\underline{C}}}^s = \omega_j^2 \tilde{\underline{\gamma}}_j^s \qquad (6.6)$$

which in real form is:

$$\left[\begin{array}{c|c} \tilde{\underline{\gamma}}_R^s & \tilde{\underline{\gamma}}_I^s \end{array}\right] \left[\begin{array}{c|c} \tilde{\underline{\underline{C}}}_R^s & \tilde{\underline{\underline{C}}}_I^s \\ \hline -\tilde{\underline{\underline{C}}}_I^s & \tilde{\underline{\underline{C}}}_R^s \end{array}\right] = \omega_j^2 \left[\begin{array}{c|c} \tilde{\underline{\gamma}}_R^s & \tilde{\underline{\gamma}}_I^s \end{array}\right] \qquad (6.7)$$

where $\underline{\underline{C}}_R^s = \tilde{\underline{\underline{C}}}_R^s$ and $-\underline{\underline{C}}_I^s = \tilde{\underline{\underline{C}}}_I^s$.

Therefore the real dynamical matrix is a symmetric matrix.

From Eq. (6.7),

$$\tilde{\underline{\gamma}}_R^s \tilde{\underline{\underline{C}}}_R^s - \tilde{\underline{\gamma}}_I^s \tilde{\underline{\underline{C}}}_I^s = \omega_j^2 \tilde{\underline{\gamma}}_R^s$$

and:

$$\tilde{\underline{\gamma}}_I^s \tilde{\underline{\underline{C}}}_R^s + \tilde{\underline{\gamma}}_R^s \tilde{\underline{\underline{C}}}_I^s = \omega_j^2 \tilde{\underline{\gamma}}_I^s \tag{6.8}$$

which added together becomes:

$$(\tilde{\underline{\gamma}}_R^s + i\tilde{\underline{\gamma}}_I^s)\tilde{\underline{\underline{C}}}_R^s + i(\tilde{\underline{\gamma}}_R^s + i\tilde{\underline{\gamma}}_I^s)\tilde{\underline{\underline{C}}}_I{}^s = \omega_j^2(\tilde{\underline{\gamma}}_R^s + i\tilde{\underline{\gamma}}_I^s)$$

or

$$(\tilde{\underline{\gamma}}_R^s + i\tilde{\underline{\gamma}}_I^s)(\tilde{\underline{\underline{C}}}{}^s_R + i\tilde{\underline{\underline{C}}}{}^s_I) = \omega_j^2(\tilde{\underline{\gamma}}_P^s + i\tilde{\underline{\gamma}}_I^s). \tag{6.9}$$

This agrees with Eq. (6.6), as required.

The preceding arguments, in terms of $\underline{\underline{C}}^s$, are extended to obtain the real (36 x 36) submatrix $\underline{\underline{A}}^{(A)}_{0,0}(\delta_c)$. For a diagonal block, Eq. (3.42) leads to the complex matrix:

$$\underline{\underline{A}}^{(A)}_{0,0}(\delta_c) = \sum_{\alpha,\gamma} \underline{\underline{U}}^{(A)}_{0,\alpha}(\delta_c)\ \underline{\underline{A}}_{0,\gamma}\ \underline{\underline{U}}^{(A)}_{0,\gamma+\alpha}(\delta_c)^*$$

since:

$$(\underline{\underline{U}}^{\dagger}(\delta_c))_{\gamma+\alpha,0} = \underline{\underline{U}}_{0,\gamma+\alpha}{}^*(\delta_c) .$$

The complex transformation matrix is:

$$\underline{\underline{U}}^{(A)}_{0,\alpha}(\delta_c) = \left(\frac{1}{2N_c}\right)^{\frac{1}{2}} \begin{array}{cc} 18 & \left[\begin{array}{ccc} \cos\alpha\delta_c + i\sin\alpha\delta_c & & \bigcirc \\ & \ddots & \\ \bigcirc & & \cos\alpha\delta_c + i\sin\alpha\delta_c \end{array}\right] \\ & 18 \end{array} \tag{6.10}$$

so that elements in a given $\underline{\underline{A}}_{0,\gamma}$ matrix are multiplied by a factor:

$$\frac{1}{2N}\sum_{\alpha=0}^{2N-1}[\cos\alpha\delta + i\sin\alpha\delta_c][\cos(\alpha+\gamma)\delta - i\sin(\alpha+\gamma)\delta] \qquad (6.11)$$

which is:

$$\frac{1}{2N}\sum_{\alpha=0}^{2N-1}[\cos\alpha\delta\cos(\alpha+\gamma)\delta + \sin\alpha\delta\sin(\alpha+\gamma)\delta] + i[\sin\alpha\delta\cos(\alpha+\gamma)\delta - \cos\alpha\delta\sin(\alpha+\gamma)\delta] \qquad (6.12)$$

or:

$$\frac{1}{2N}\sum_{\alpha=0}^{2N-1}[\cos\gamma\delta - i\sin\gamma\delta] \qquad (6.13)$$

which becomes:

$$\frac{1}{2N}\times 2N\,[\cos\gamma\delta - i\sin\gamma\delta_c] \qquad (6.14)$$

so that:

$$\underline{\underline{A}}^{(A)}_{0,0}(\delta_c) = \sum_{\gamma}[\cos\gamma\delta - i\sin\gamma\delta]\,\underline{\underline{A}}_{0,\gamma} \qquad (6.15)$$

$$= \underline{\underline{A}}_{0,0} + \underline{\underline{A}}_{0,1}(\cos\delta - i\sin\delta) + \underline{\underline{A}}_{0,\bar{1}}(\cos\delta + i\sin\delta) \qquad (6.16)$$

which is:

$$\underline{\underline{A}}_{0,0}(\delta_c) = \{\underline{\underline{A}}_{0,0} + [\underline{\underline{A}}_{0,1} + \underline{\underline{A}}_{0,\bar{1}}]\cos\delta_c + i\,[\underline{\underline{A}}_{0,\bar{1}} - \underline{\underline{A}}_{0,1}]\sin\delta_c\} \qquad (6.17)$$

Then the expanded real matrix is:

$$\underline{\underline{A}}^{(A)}_{0,0}(\delta_c) = \left[\begin{array}{c|c} \underline{\underline{A}}_{0,0}+[\underline{\underline{A}}_{0,1}+\underline{\underline{A}}_{0,\bar{1}}]\cos\delta_c & [\underline{\underline{A}}_{0,1}-\underline{\underline{A}}_{0,\bar{1}}]\sin\delta_c \\ \hline [\underline{\underline{A}}_{0,\bar{1}}-\underline{\underline{A}}_{0,1}]\sin\delta_c & \underline{\underline{A}}_{0,0}+[\underline{\underline{A}}_{0,1}+\underline{\underline{A}}_{0,\bar{1}}]\cos\delta_c \end{array}\right] \quad (6.18)$$

The real dynamical submatrix $\underline{\underline{C}}^{s}_{0,0}(\delta_c)$ is obtained finally from Eq. (3.41) where the intermolecular $\underline{\underline{A}}'(\delta_c)$ matrix is a zero matrix.

F. DISPERSION CURVES AND POLARIZATION VECTORS

The frequency solutions for the isolated syndiotactic polyvinylchloride chain, obtained in this study, are displayed in Fig. 6.4. (See also Ref. 45.) Due to the (36 x 36) expanded real form of the dynamical matrix equation, 18 degenerate pairs of frequency solutions are obtained at each δ_c value.

The squares of the real and imaginary components of the complex eigenvectors, as indicated in Eq. (6.7), are combined to yield the squared polarization vectors, which are given in the Appendix as a function of δ_c. Note that these vector terms are squared values unlike the case for deuterated crystalline polyethylene where the polarization vectors themselves are shown.

G. ONE-PHONON FREQUENCY FUNCTIONS

The directional amplitude weighted frequency functions for polyvinylchloride are given in Figs. 6.5 to 6.12. The labelling of the atoms, H_1, H_2, $C\ell$, H_3, C_1, C_2, matches that shown in Figs. 6.1 and 6.2. These spectra are also given the quadratic frequency dependence below .006 eV, in order to calculate the Debye-Waller coefficients.

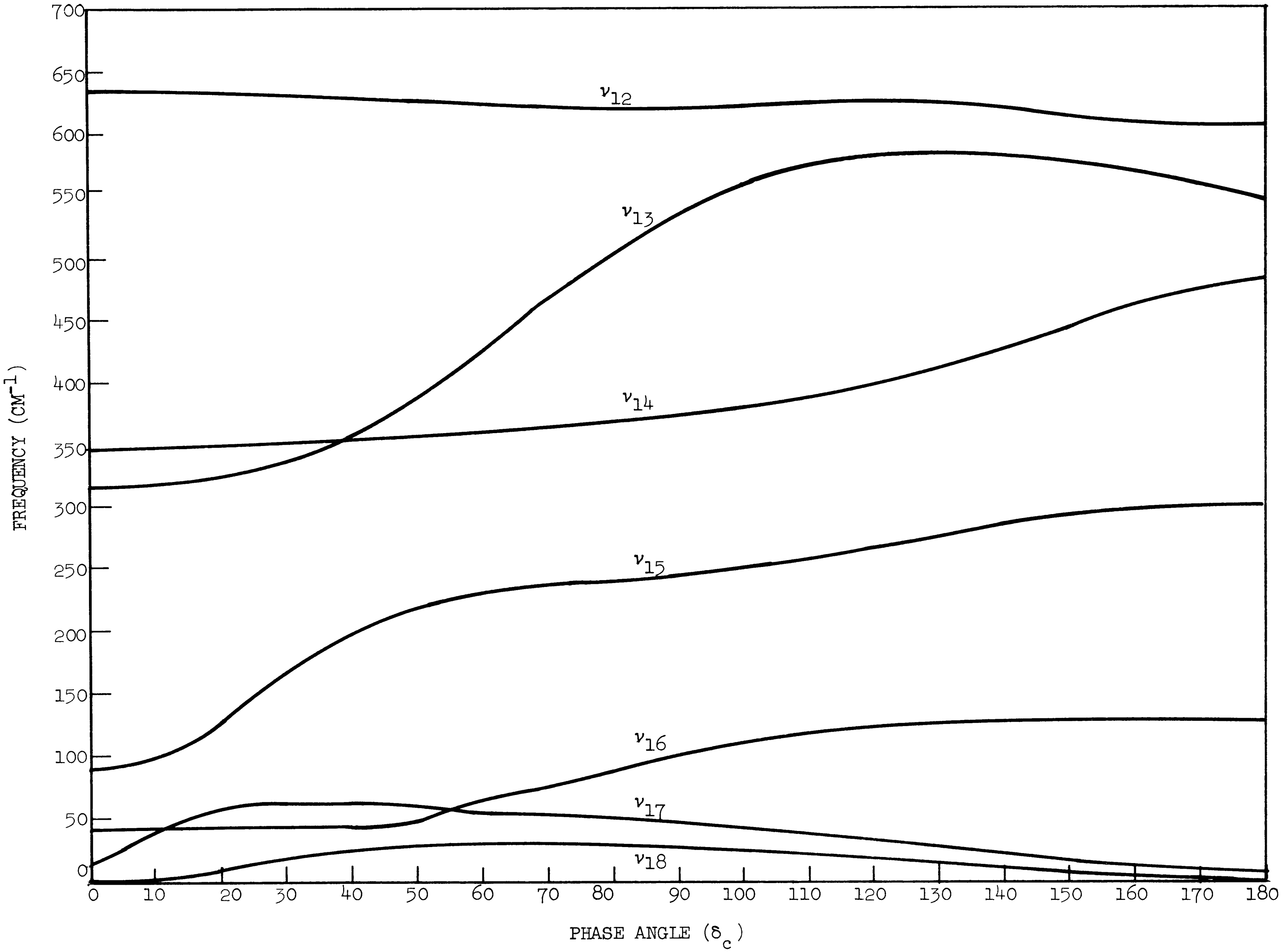


Fig. 6.4. Single-chain polyvinylchloride dispersion relations (F_τ = .06 mdyne - Å/rad^2).

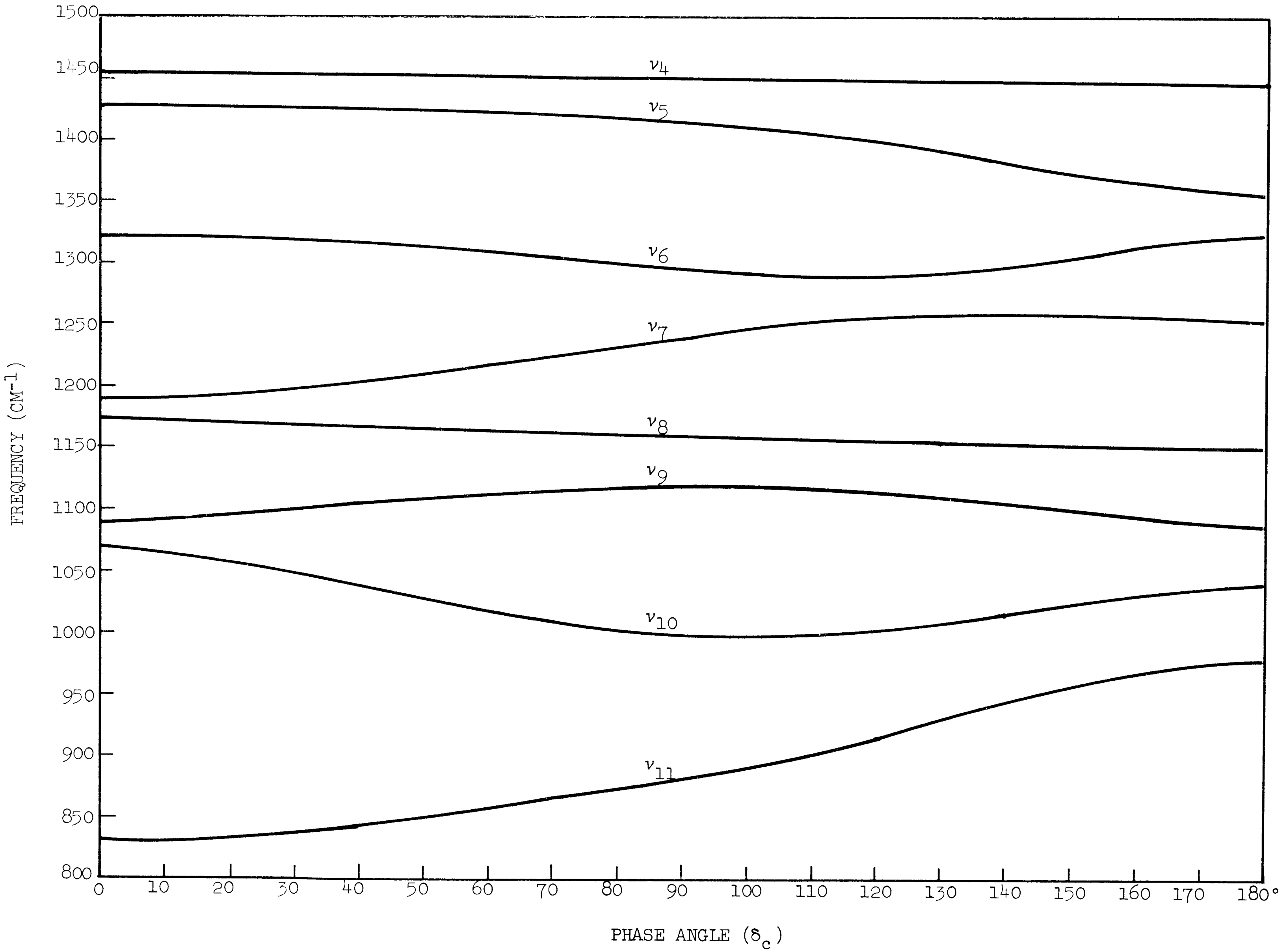


Fig. 6.4. (Concluded).

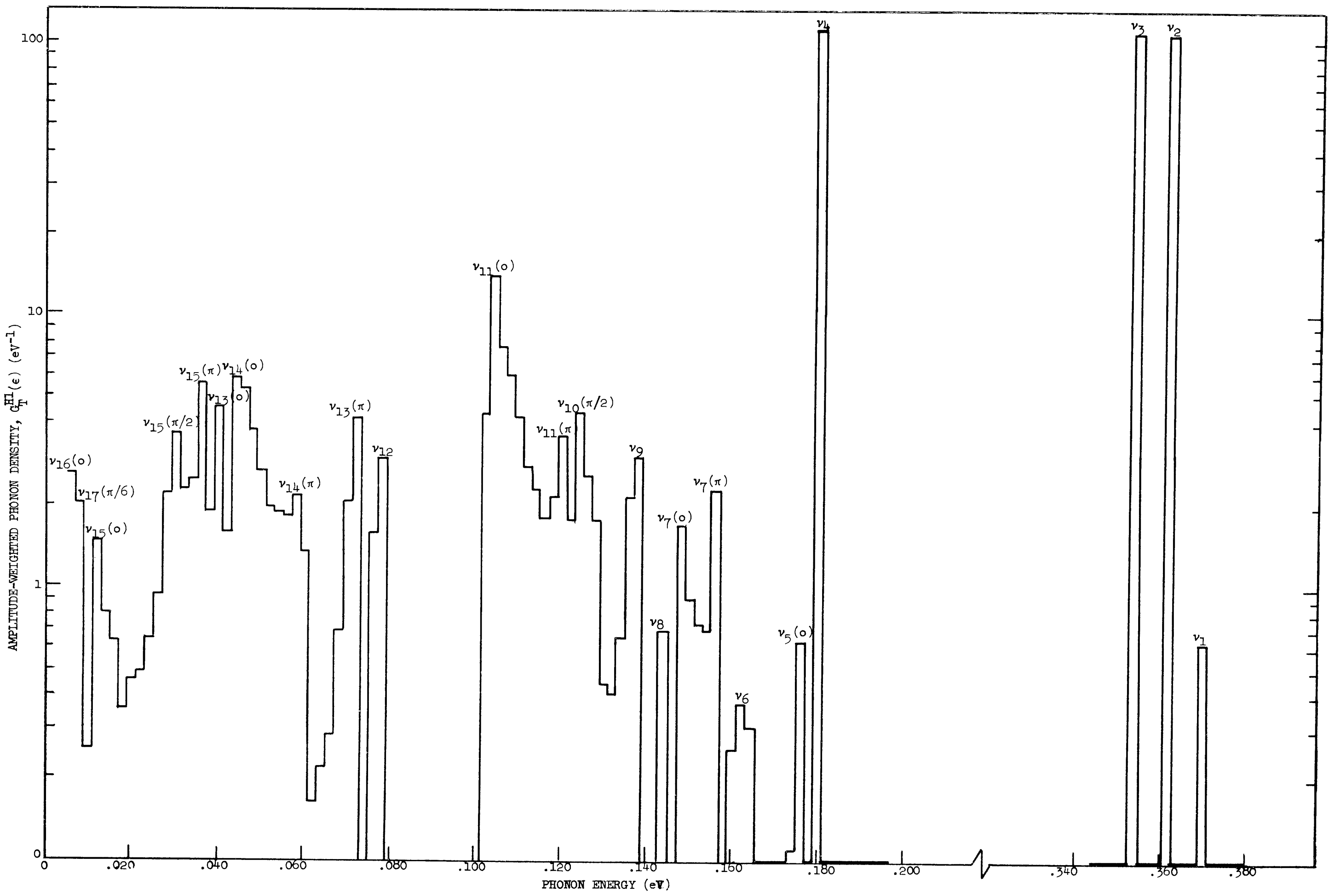


Fig. 6.5. Single-chain polyvinylchloride transverse (H^1 or H^2) hydrogen frequency function.

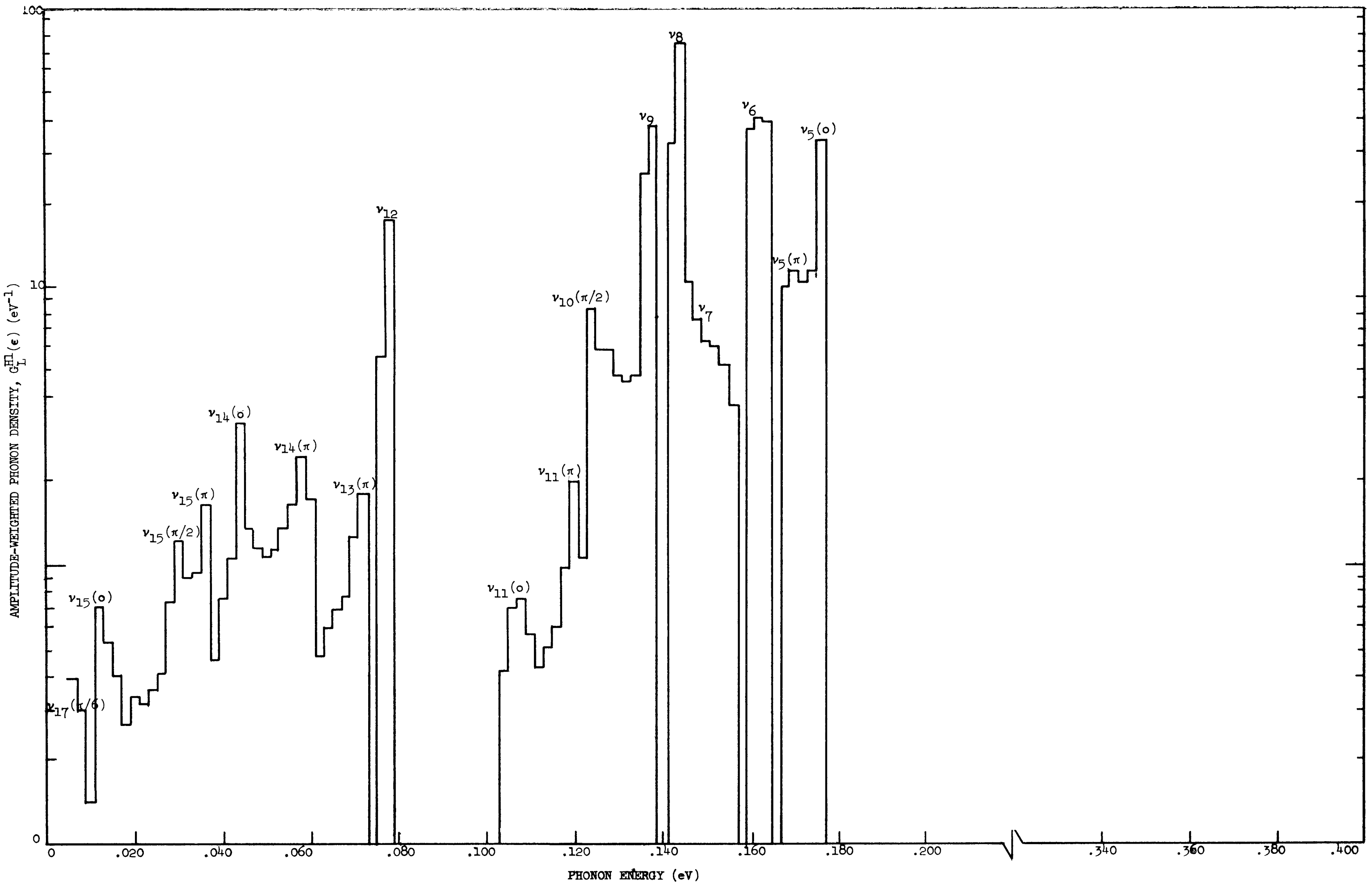


Fig. 6.6. Single-chain polyvinylchloride longitudinal (H^1 or H^2) hydrogen frequency function.

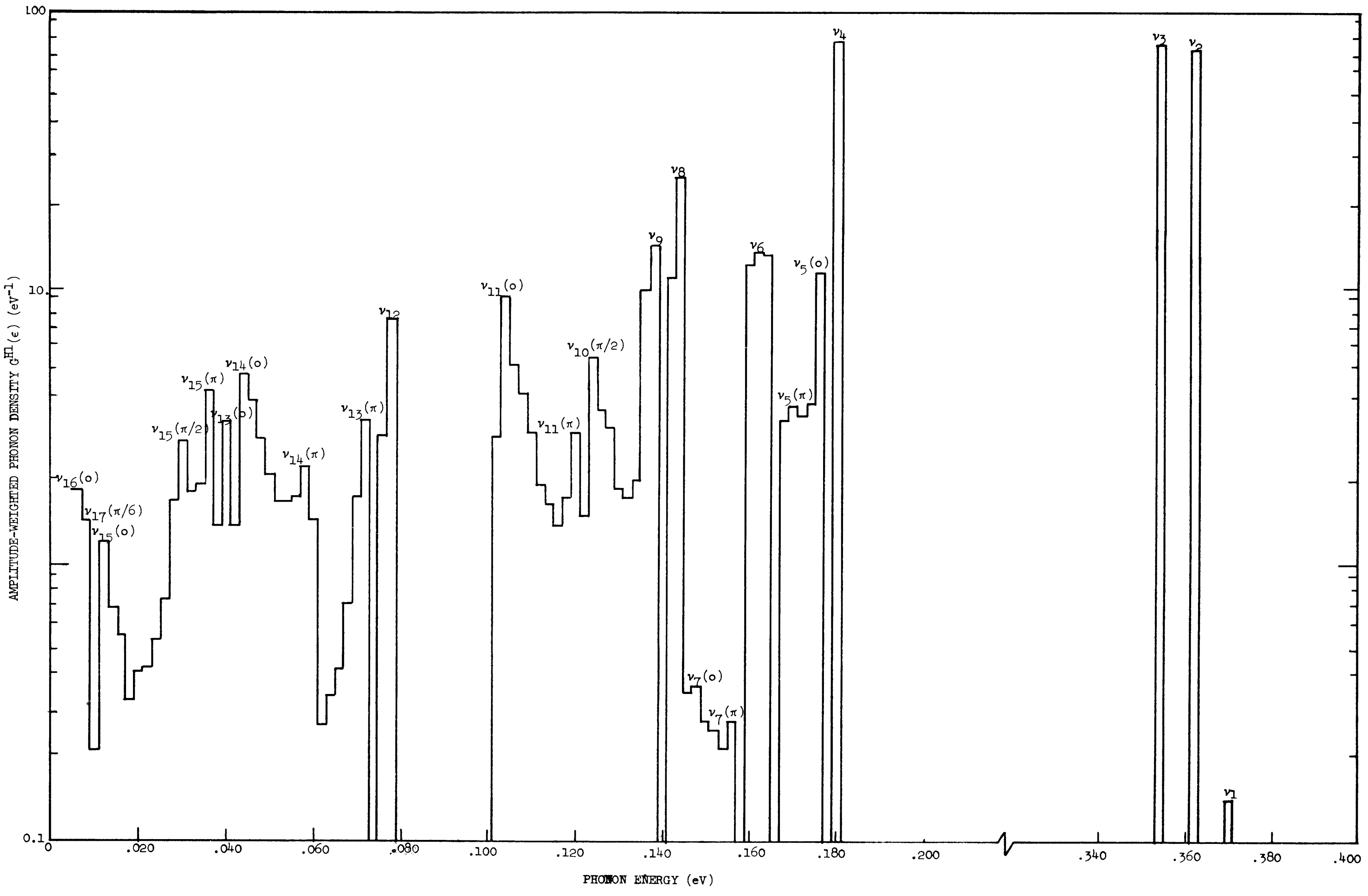


Fig. 6.7. Polyvinylchloride hydrogen (H^1 or H^2) frequency function for unoriented single-chains.

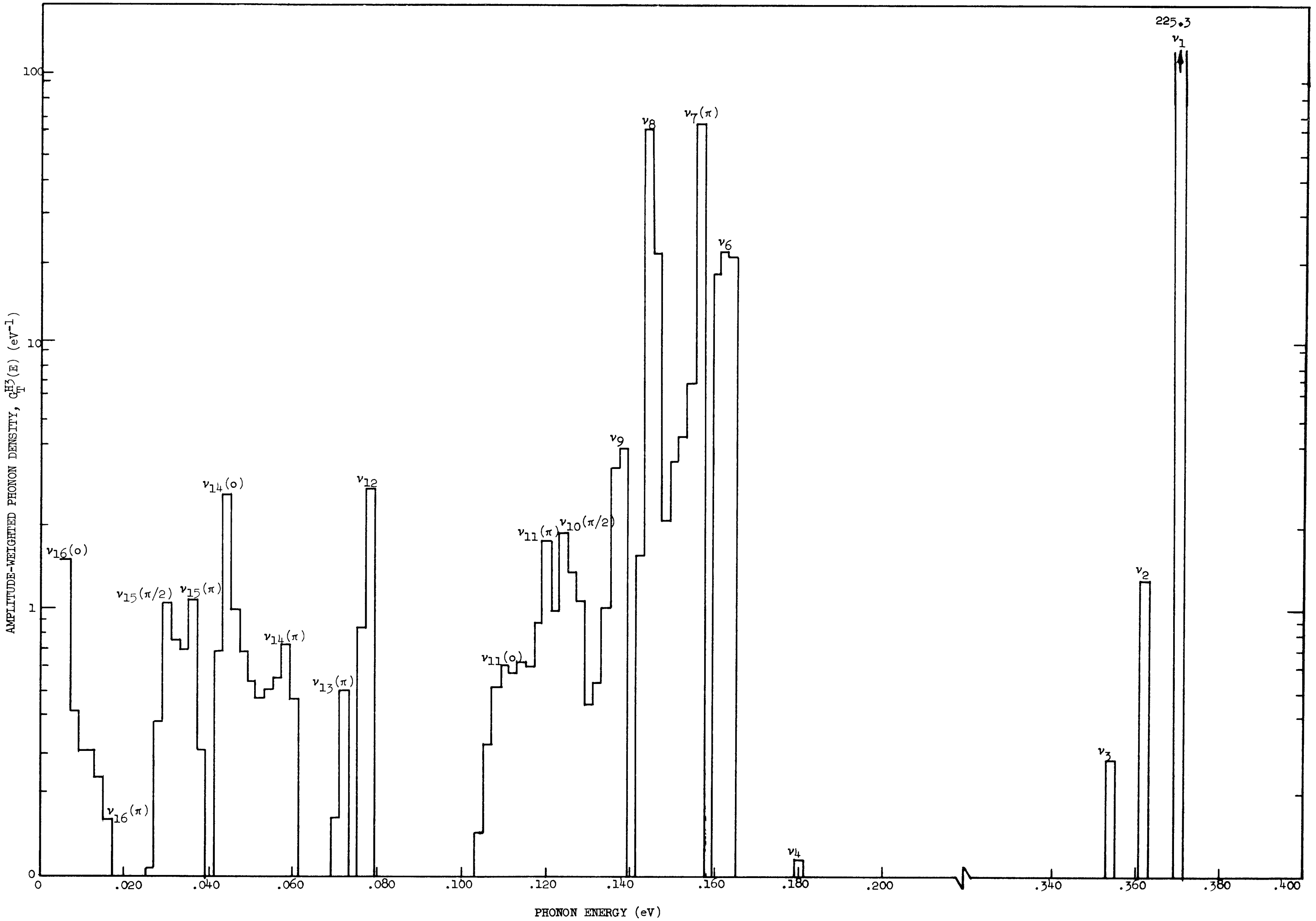


Fig. 6.8. Single-chain polyvinylchloride transverse (H^3) hydrogen frequency function.

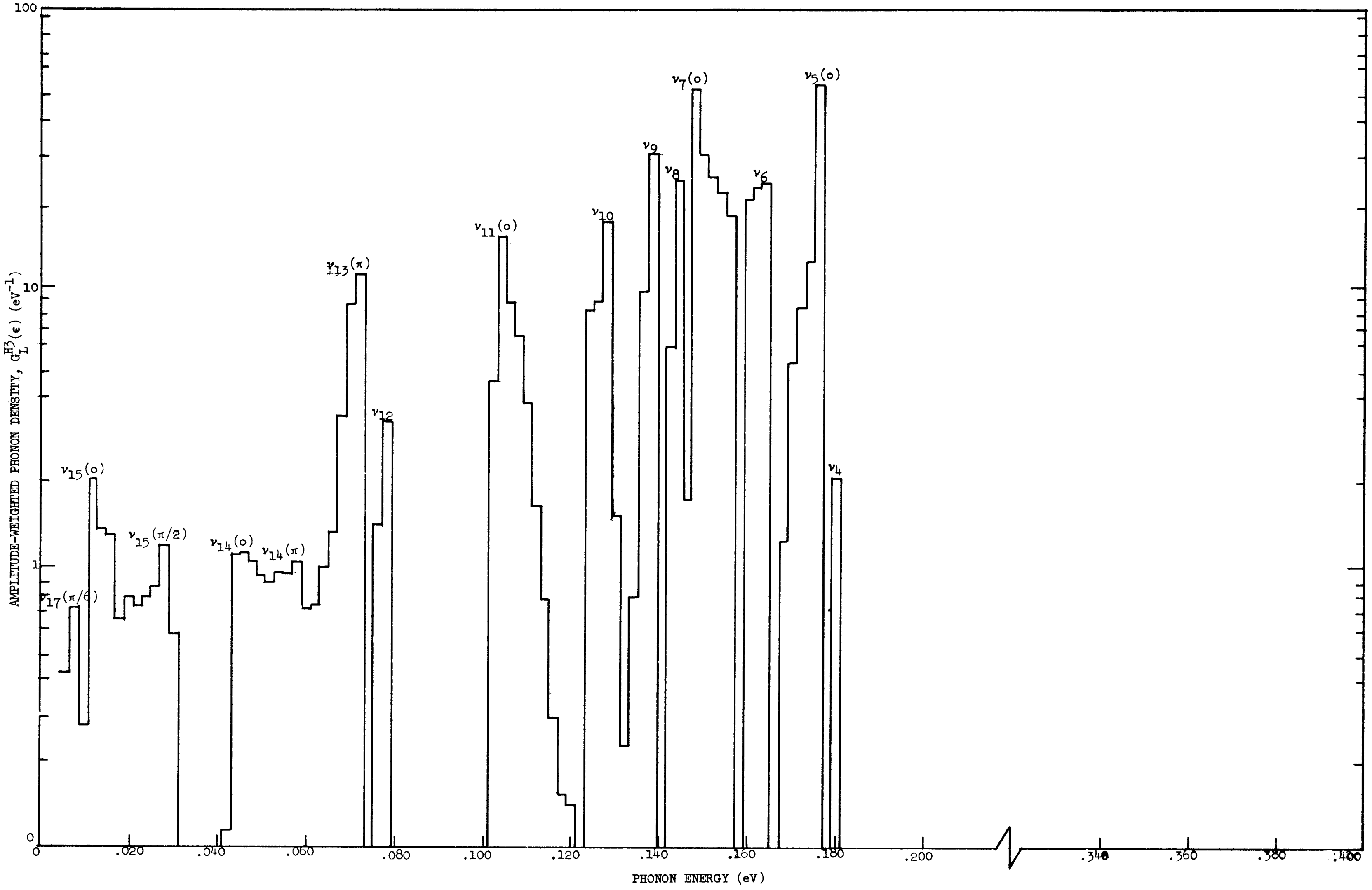


Fig. 6.9. Single-chain polyvinylchloride longitudinal (H^3) hydrogen frequency function.

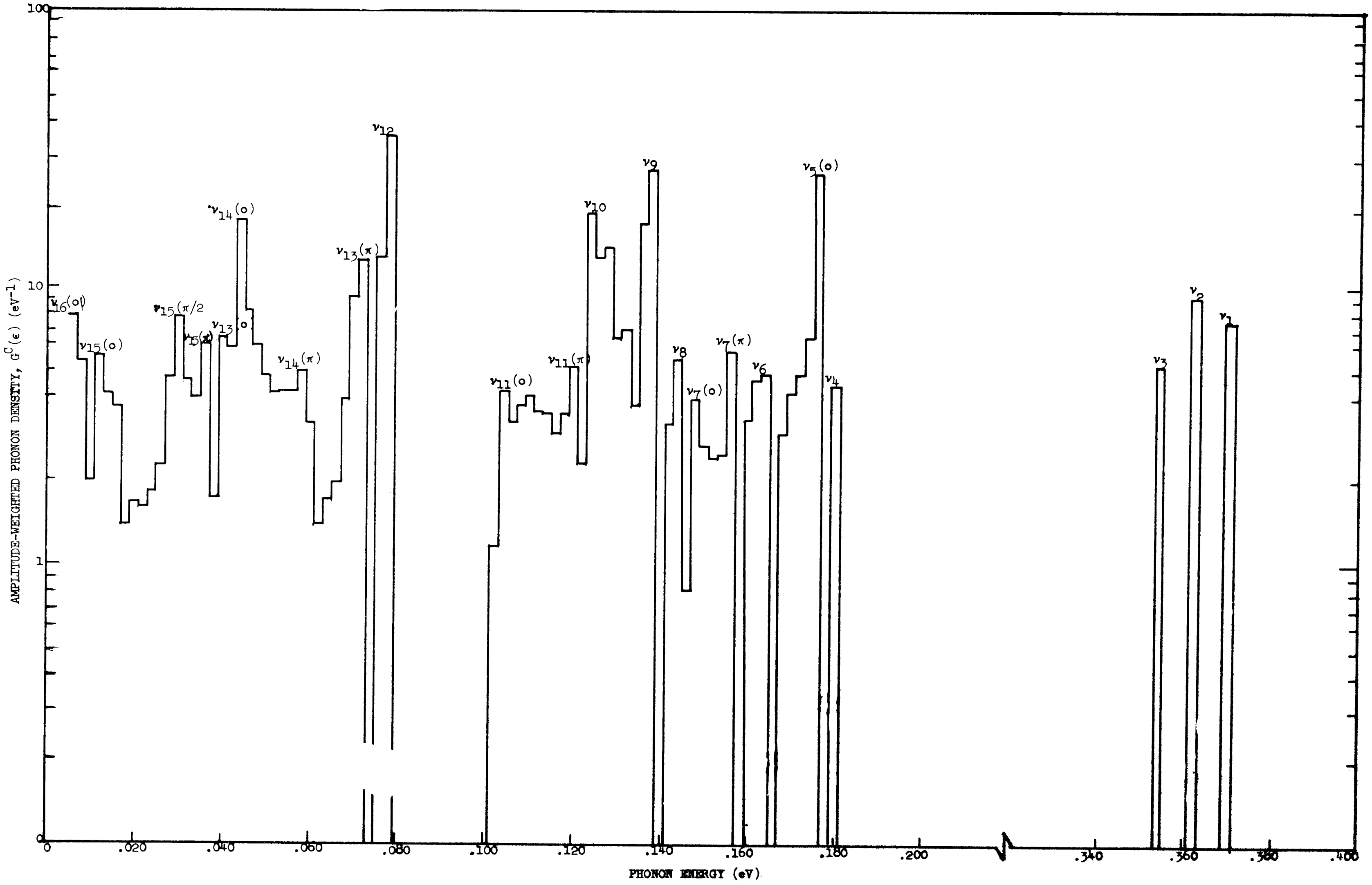


Fig. 6.10. Polyvinylchloride carbon frequency function for unoriented single-chains.

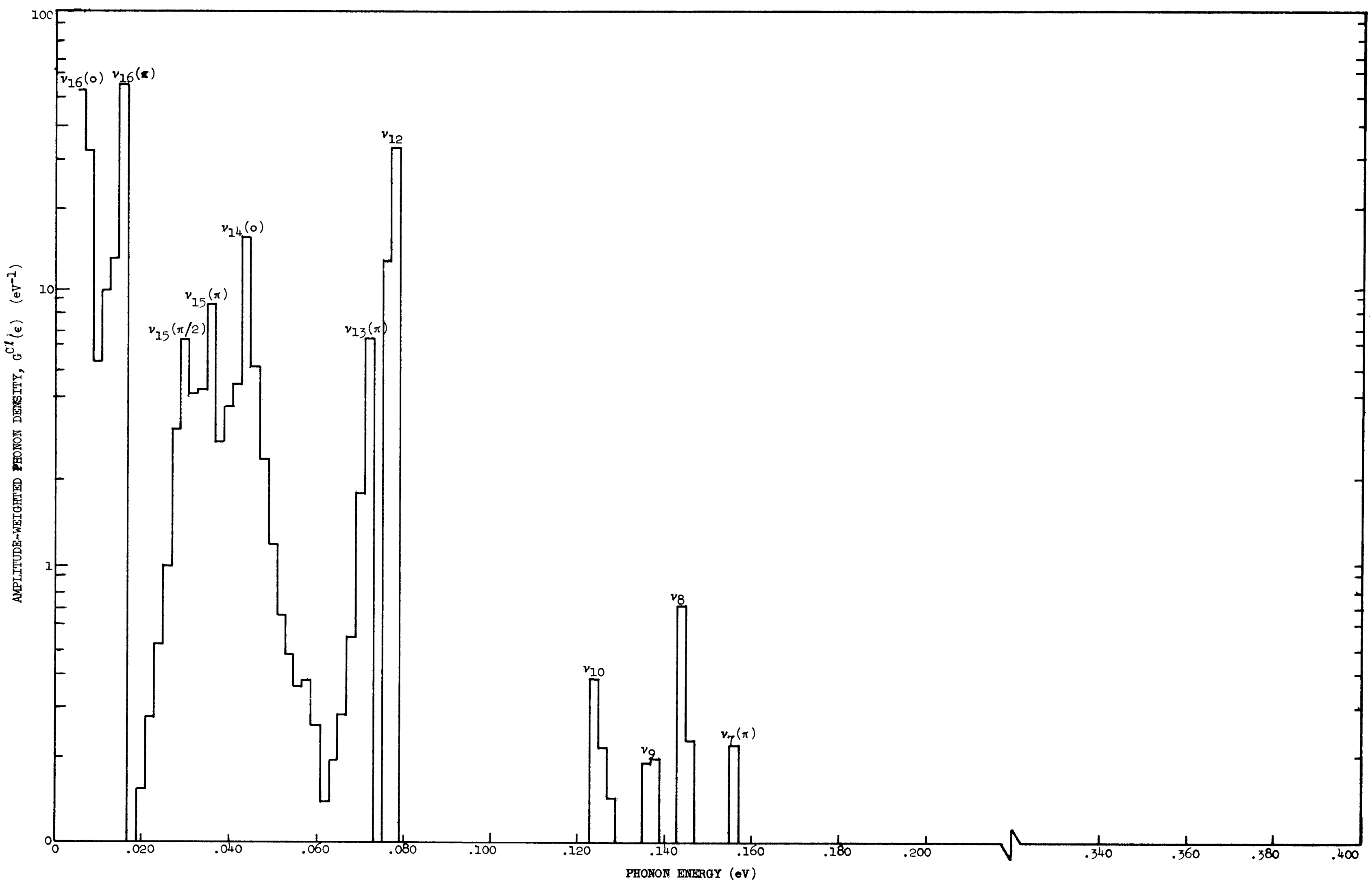


Fig. 6.11. Polyvinylchloride chlorine frequency function for unoriented single-chains.

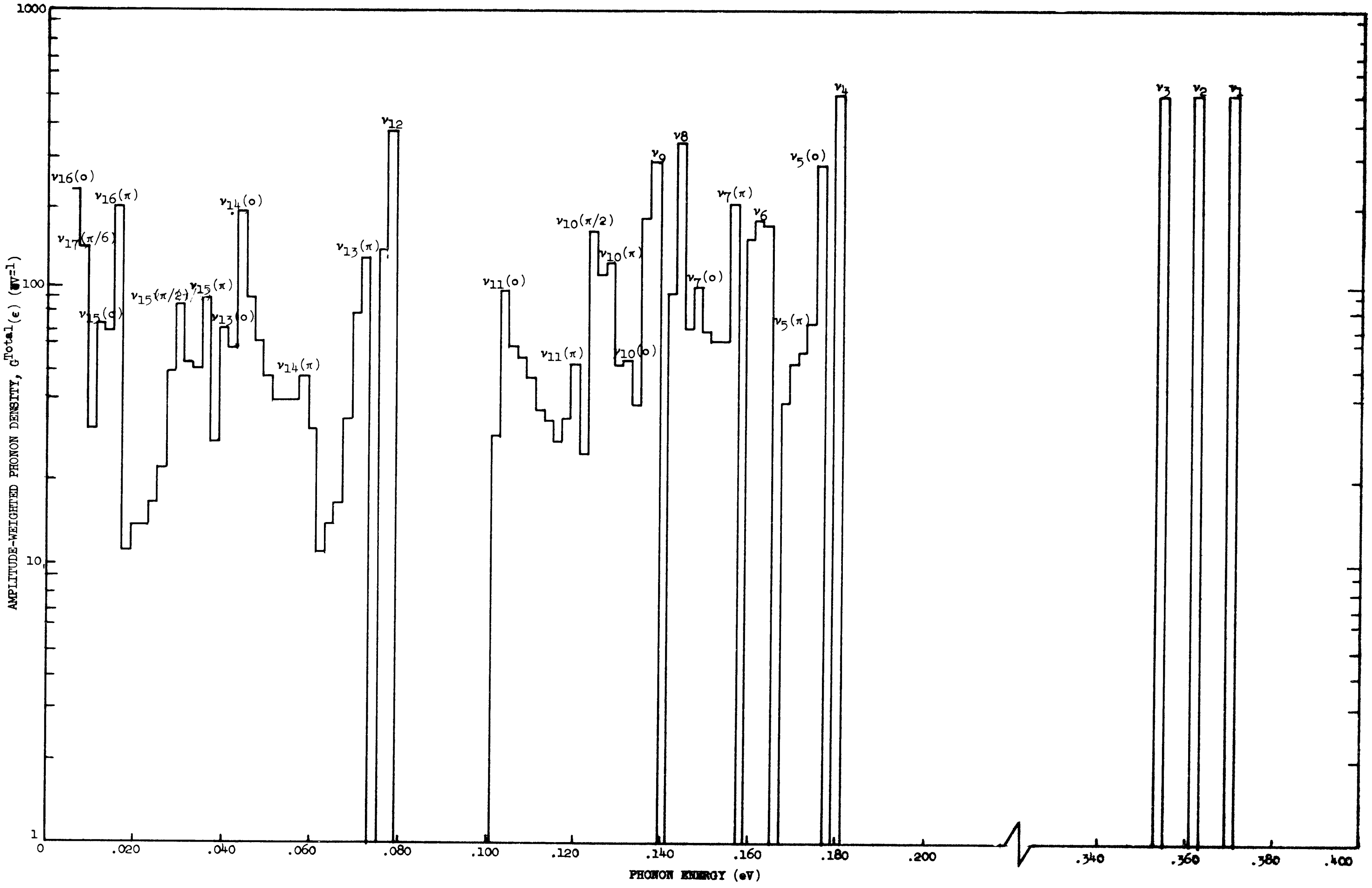


Fig. 6.12. Polyvinylchloride total frequency distribution, G(ϵ), for unoriented single-chains.

H. DIRECTIONAL DEBYE-WALLER COEFFICIENTS

The values of the hydrogen atom Debye-Waller coefficients for polyvinylchloride are obtained from Eqs. (2.45) and (2.25) using the frequency functions in Figs. 6.5 to 6.9. The results are shown in Table XV.

TABLE XV

POLYVINYLCHLORIDE DIRECTIONAL DEBYE-WALLER COEFFICIENTS

Transverse	Longitudinal
$2W_T^{(H^1 \text{ or } H^2)}/\kappa^2 = .035\text{Å}^2$	$2W_L^{(H^1 \text{ or } H^2)}/\kappa^2 = .021\text{Å}^2$
$2W_T^{H^3}/\kappa^2 = .022\text{Å}^2$	$2W_L^{H^3}/\kappa^2 = .022\text{Å}^2$

Approximately 50% of the values for the transverse coefficients and 10% of the values for the longitudinal coefficients are contributed by modes below .006 eV.

CHAPTER 7

POLYTETRAFLUOROETHYLENE

As mentioned in chapter I, the modest goal for this material is to simply obtain the dispersion curves. This is only one step beyond the results of Krimm and Liang[47] in that the same planar approximation is made for the true helical structure and the same diagonal force constants are utilized. However, it is felt that these approximate results might be useful to experimentalists attempting to measure the actual dispersion curve frequencies by coherent neutron scattering techniques. A more realistic calculation will be required when experimental data become available.

In this first approximation, since intermolecular forces are relatively weak, a single chain calculation is performed. The further assumption that the helical configuration may be replaced by a planar zig-zag structure is also made. Since the rotation angle about the chain axis between any two adjacent CF_2 chemical repeat units is $14\pi/13$ and it may be assumed also that the intermolecular forces are not long range forces, this is a reasonable first approach for obtaining the dispersion curves.

For the more complete details, one should consult Ref. 47. Only the essential points are reviewed here.

A. MOLECULAR STRUCTURE AND COORDINATES

The unit cell for polytetrafluoroethylene has been reported by Bunn and Howells[48] to be pseudo-hexagonal below 19°C and hexagonal above this temperature. There is one helical chain per unit cell, which contains 13 CF_2 groups below

19°C and 15 CF_2 groups above this temperature.

In the planar approximation, the problem becomes identical to that for single-chain polyethylene, except for the magnitudes of the molecular dimensions, atomic masses, and force constants.

In this case, the chain dimensions are those given in Table XVI.

TABLE XVI

PLANAR TEFLON REPEAT UNIT DIMENSIONS

$c = 2.51Å$

$r_{c-F} = 1.35Å$

$r_{c-c} = 1.54Å$

$\theta_{c-c-c} = 109° \; 28'$

$\theta_{F-c-F} = 109° \; 28'$

$\alpha_{F-c-c} = 109° \; 28'$

The internal intramolecular coordinates used here match those for single-chain polyethylene given in chapter 4, as do the repeat unit cartesian coordinate systems.

B. INTRAMOLECULAR FORCE CONSTANTS

The force constants which are used in this calculation are the diagonal terms in $\underline{\underline{F}}_{0,0}$. (See Eq. (4.3).) These are given in units of 10^5 dynes/cm or millidynes /Å.[47] However the B matrix elements used in this report[18] require bending and torsion force constants in units of millidyne -Å/rad.^{2} Therefore, the force constants used here are those given in Eq. (7.1), which follows.

$$\underline{\underline{F}}_{0,0} = \begin{array}{c|cccccccccc|}
 & \Delta r_{CC} & \Delta r_{C-F} & \Delta r_{C-F} & \Delta\theta_{CCC} & \Delta\theta_{FCF} & \Delta\alpha^{1}_{CCF} & \Delta\alpha^{2}_{CCF} & \Delta\alpha^{3}_{CCF} & \Delta\alpha^{4}_{CCF} & \Delta\tau \\
\Delta r_{CC} & 3.46 & & & & & & & & & \\
\Delta r_{C-F} & & 5.37 & & & & & & & & \\
\Delta r_{C-F} & & & 5.37 & & & & & \bigcirc & & \\
\Delta\theta_{CCC} & & & & .685 & & & & & & \\
\Delta\theta_{FCF} & & & & & 1.804 & & & & & \\
\Delta\alpha^{1}_{CCF} & & & & & & 1.295 & & & & \\
\Delta\alpha^{2}_{CCF} & & & & & & & 1.295 & & & \\
\Delta\alpha^{3}_{CCF} & & \bigcirc & & & & & & 1.295 & & \\
\Delta\alpha^{4}_{CCF} & & & & & & & & & 1.295 & \\
\Delta\tau & & & & & & & & & & 0.062
\end{array} \qquad (7.1)$$

where these values are obtained from the published values as shown below.

f_{CC} = 3.46 millidyne/Å

f_{CF} = 5.37 millidyne/Å

$\phi_{CCC} \times r^{2}_{CC} = 0.289 \times (1.54)^{2} = 0.685$ millidyne -Å

$\phi_{FCF} \times r^{2}_{CF} = 5.37 \times (1.35)^{2} = 1.804$ millidyne -Å

$\phi_{CCF} \times r_{CF} \times r_{CC} = 0.623 \times 1.35 \times 1.54 = 1.295$ millidyne -Å

$\tau \times r^{2}_{CC} = 0.026 \times (1.54)^{2} = 0.062$ millidyne -Å

It is interesting to observe that the torsion force constant which is used here is nearly identical to that which was finally used for the crystalline polyethylene torsion force constant (0.06) in order to match experimental results for the polyethylene torsion frequency.

The cartesian force constant matrices, which are not diagonal, are then obtained by using Eq. (3.48). Since only $\underline{\underline{F}}_{0,0}$ is nonzero:

$$\underline{\underline{A}}_{0,m} = (\tilde{\underline{\underline{B}}}^{s})_{0,0}\,\underline{\underline{F}}_{0,0}\,\underline{\underline{B}}^{s}_{0,m} \,. \tag{7.2}$$

C. DISPERSION CURVES

The frequency solutions to the dynamical matrix equation for polytetrafluoroethylene are displayed in Fig. 7.1.

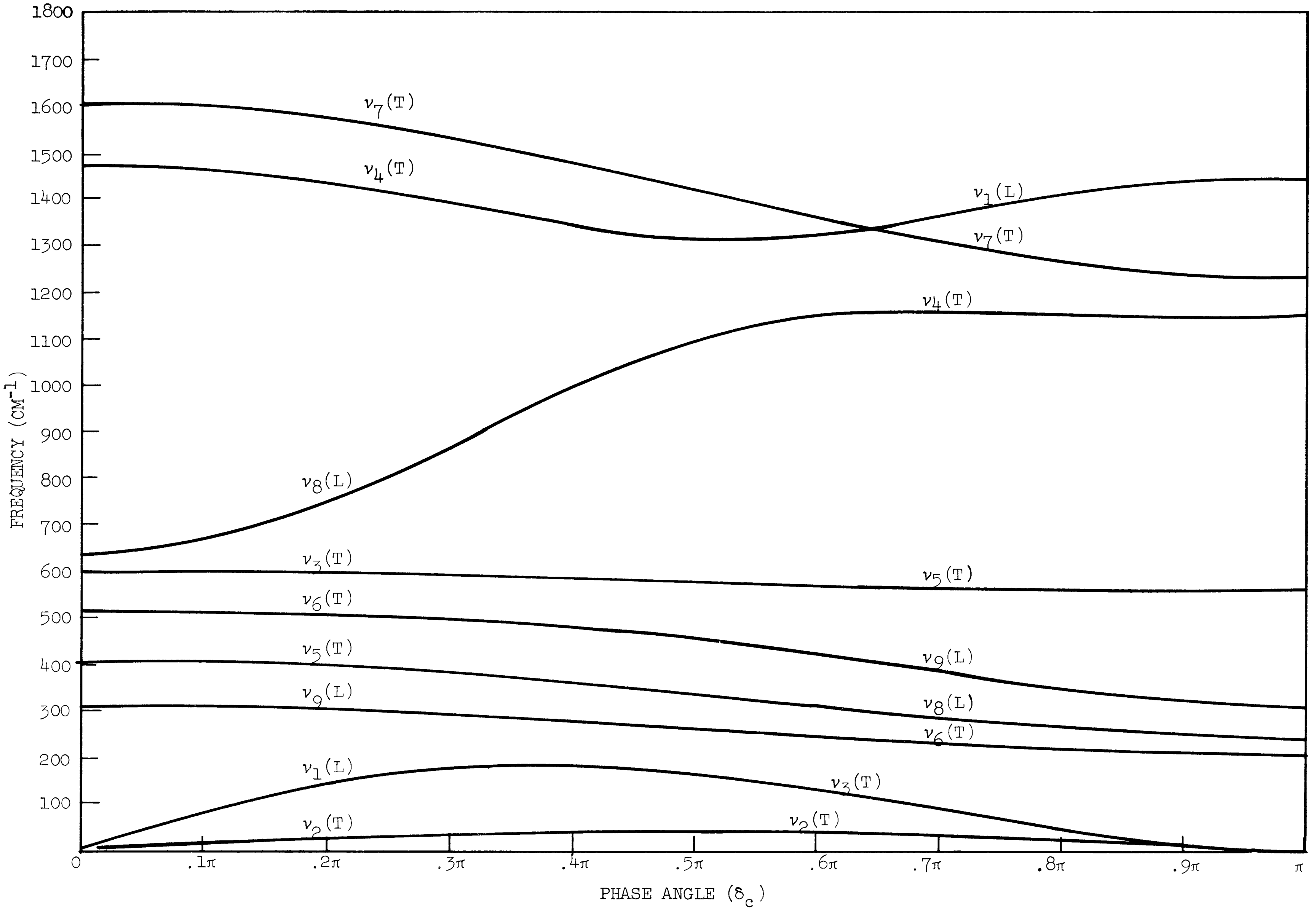


Fig. 7.1. Single-chain Teflon dispersion curves for planar approximation.

CHAPTER 8

CONCLUSIONS AND DISCUSSION

In this work, the directional frequency functions for normal and deuterated polyethylene, and polyvinylchloride have been calculated and used to obtain the directional Debye-Waller coefficients. For a third polymer, polytetrafluoroethylene (Teflon), the dispersion curves have been obtained using a planar approximation for the true helical molecular structure. In these analyses, the incoherent approximation has been used for the coherent scattering cross-sections of deuterated polyethylene and polyvinylchloride.

To obtain the dynamical matrix equations for the frequencies and cartesian polarization vectors, force constant matrices in internal coordinates were first transformed to a cartesian coordinate system and then to a system of cartesian symmetry coordinates.

The polyethylene calculations were first performed for an isolated molecule and then extended to a lattice of such molecules, where intermolecular forces and space group symmetry were considered.

A. POLYETHYLENE

The low frequency dispersion curves shown in Figs. 5.4 and 5.5 for crystalline normal and deuterated polyethylene both indicate a crossover between the ν_5 and ν_9 branches between $\delta_c = 0$ and $\delta_c = .1\pi$.

The finite number of frequency values in this δ_c region are connected in this way so that there are no discontinuities in the corresponding eigenvector solutions when plotted as functions of δ_c. This polarization vector continuity can be seen in Figs. 5.6 and 5.7, where the squares of the vector magnitudes are plotted for the transverse and longitudinal directions. The requirement that the flat dispersion curve branch near 150 cm^{-1} for $\delta_c < .1\pi$ be labelled ν_9 is particularly evident in Fig. 5.7 where the carbon motions are shown. This same requirement is seen in the ν_c^5 and ν_{ab}^9 curves near $\delta_c = .1\pi$, in Fig. 5.6.

Fig. 5.8, for the transverse one-phonon frequency function of crystalline polyethylene shows great similarity with the corresponding single-chain function in Fig. 4.8. Although the transverse single-chain calculation results in an overestimation of the G-function values below .010 eV, the main features of the spectrum are predicted as well in the single-chain anaylsis as in the analysis for the crystalline lattice. This is not surprising since the intermolecular forces primarily affect the lower vibrational frequencies where $\nu < 200\ cm^{-1}$. Therefore the transverse G-function obtained from the single-chain analysis is quite satisfactory, except for use in calculations of the Debye-Waller coefficient, where the low frequency contributions are heavily weighted by the cotgh $(\epsilon/2kT)$ term as shown in Eq. (2.27). At higher temperatures, this qualification is no longer necessary since the cotgh $(\epsilon/2kT)$ term in the Debye-Waller integrand gives increased weight to the higher frequency modes. The same comments apply in comparing the single-chain longitudinal G-function in Fig. 4.7 with the crystalline longitudinal function in Fig. 5.9. At liquid nitrogen temperature approximately 10% of the longitudinal and transverse Debye-Waller coefficients is contributed by modes below .006 eV. At this temperature, modes below .080 eV provide approximately 40% of the contribution to $2W_L$ and approximately 60% of the contribution to $2W_T$.

The two-phonon G-function values shown in Fig. 5.12 and 5.13 for crystalline polyethylene are not greatly changed by increasing the temperature from 2°K to 102°K. However, greater increases in temperature produce a relatively greater increase in the calculated two-phonon contribution. This same temperature relationship is also seen in the Debye-Waller coefficients in Fig. 5.14, where there is little difference between the 0°K and 100°K coefficients but there is a greater change with temperature above 100°K. Since polyethylene becomes increasingly amorphous above the glass transition temperature near 400°K, the results in Fig. 5.14, 5.15, and 5.16 for temperatures above 400°K, are expected to be only approximately correct. For example, the transverse coefficient in Fig. 5.14 is probably less than the true value in the high temperature region where "free" rotations of molecular segments occur. From Fig. 5.16, the ratio between the elastic peak magnitudes for the longitudinal and transverse orientations is 1.16 at 100°K and 1.64 at room temperature, for a neutron energy of $E_i = .030$ eV, and a scattering angle of $\Theta_s = \pi/2$.

The crystalline polyethylene, Debye-Waller factor weighted, one- and two-phonon frequency spectra are shown in Figs. 5.17 and 5.18 for the various temperatures from 2°K to 302°K. Due to the decrease of the Debye-Waller factors with temperature as seen in Fig. 5.15, the one-phonon peak at .022 eV is depressed with increasing temperature. This Debye-Waller temperature effect of course also applies to the two-phonon contribution near .044 eV, but this two-phonon term is itself temperature dependent, increasing with temperature as seen in Eq. (2.59) where $\beta = 1/kt$. Therefore, the amplitudes of the one- and two-phonon peaks become more nearly alike at the higher temperatures. This relationship can also be observed by comparing the room temperature neutron scattering measurements of Donovan[4,11] to the nitrogen temperature measurements of Myers[5,12] for polycrystalline polyethylene.

The calculated normal polyethylene directional frequency functions are compared to the experimental frequency functions in Figs. 8.1, 8.2, and 8.3 which follow. These functions show qualitative agreement only.

Several features in the above G-functions do show reasonable similarity however. From the data, note: (a) the peak near .024 eV, and (b) the shoulder at about .017 eV, (c) the broad maximum near .040 eV, and (d) the very broad peak near .065 eV in Fig. 8.2. These events correlate well with known features in the calculations. Relative to the above data these are, respectively: (a) the (ν_9) maximum frequency cutoff [the (ν_5) intercept, $\nu_5^a(0)$, occurs very near this cutoff and would not be experimentally resolved], (b) one of the intercepts at 0 or π phase angle for the crystalline mode ν_5^b, most probably $\nu_5^b(0)$ from the relative response of longitudinal and transverse magnitudes, (c) the broad two-phonon maximum near .044 eV, which correlates approximately with the experimental choice of .040 eV, and (d) the frequency limits for both crystalline branches of ν_5, which occur indistinguishably close together at .068 eV in the longitudinal data. With regard to (d), no attempt has been made to adjust the internal coordinate intramolecular force constants[28] to effect a better match with the experimental choice of .065 eV. In addition to these events, the results give some evidence to confirm the calculated discontinuities near .013 eV, associated with $\nu_5^b(\pi)$, and near .009 eV, associated with $\nu_5^a(\pi)$.

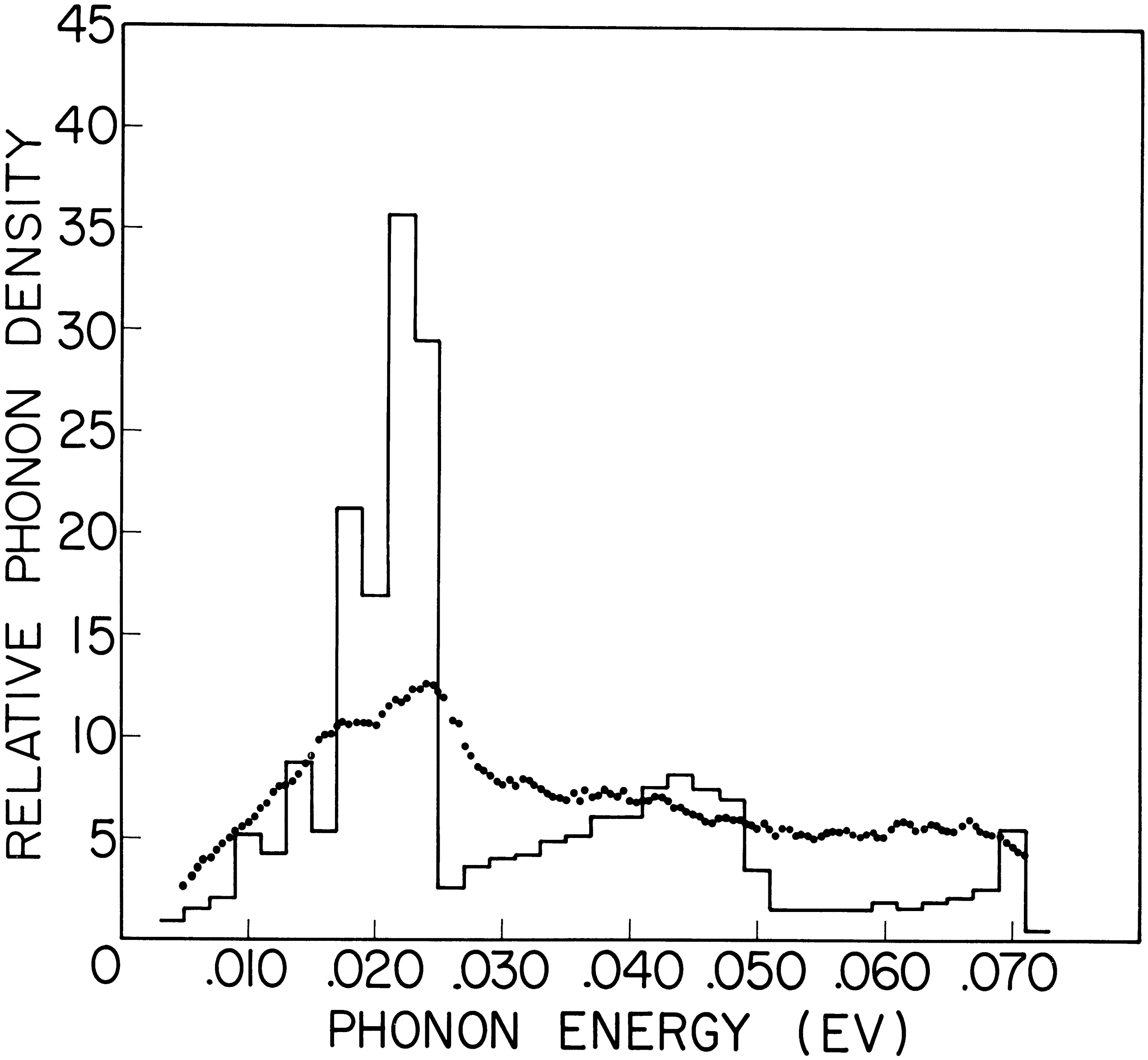


Fig. 8.1. Frequency function, $G(\epsilon)$, for unoriented normal polyethylene (experimental points from Ref. 5 for $E_f = .030$ eV, T = 100°K, $\Theta_s = 90°$; $G(\epsilon) = 1/3\ G_L(\epsilon) + 2/3\ G_T(\epsilon)$).

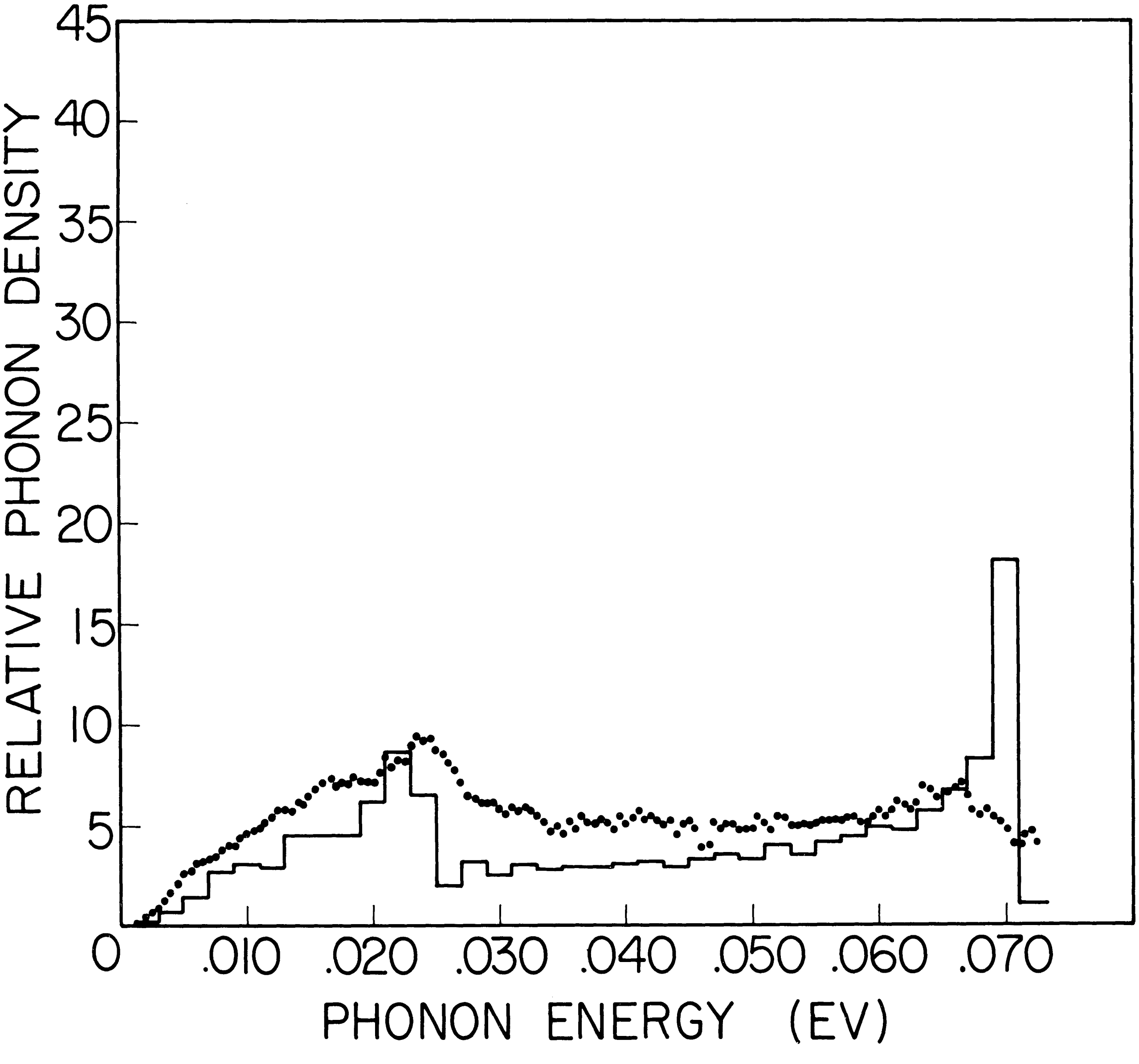


Fig. 8.2. Longitudinal frequency function $G_L(\epsilon)$, for oriented normal polyethylene (experimental points from Ref. 5; E_f = .030 eV, T = 100°K, θ_s = 90°).

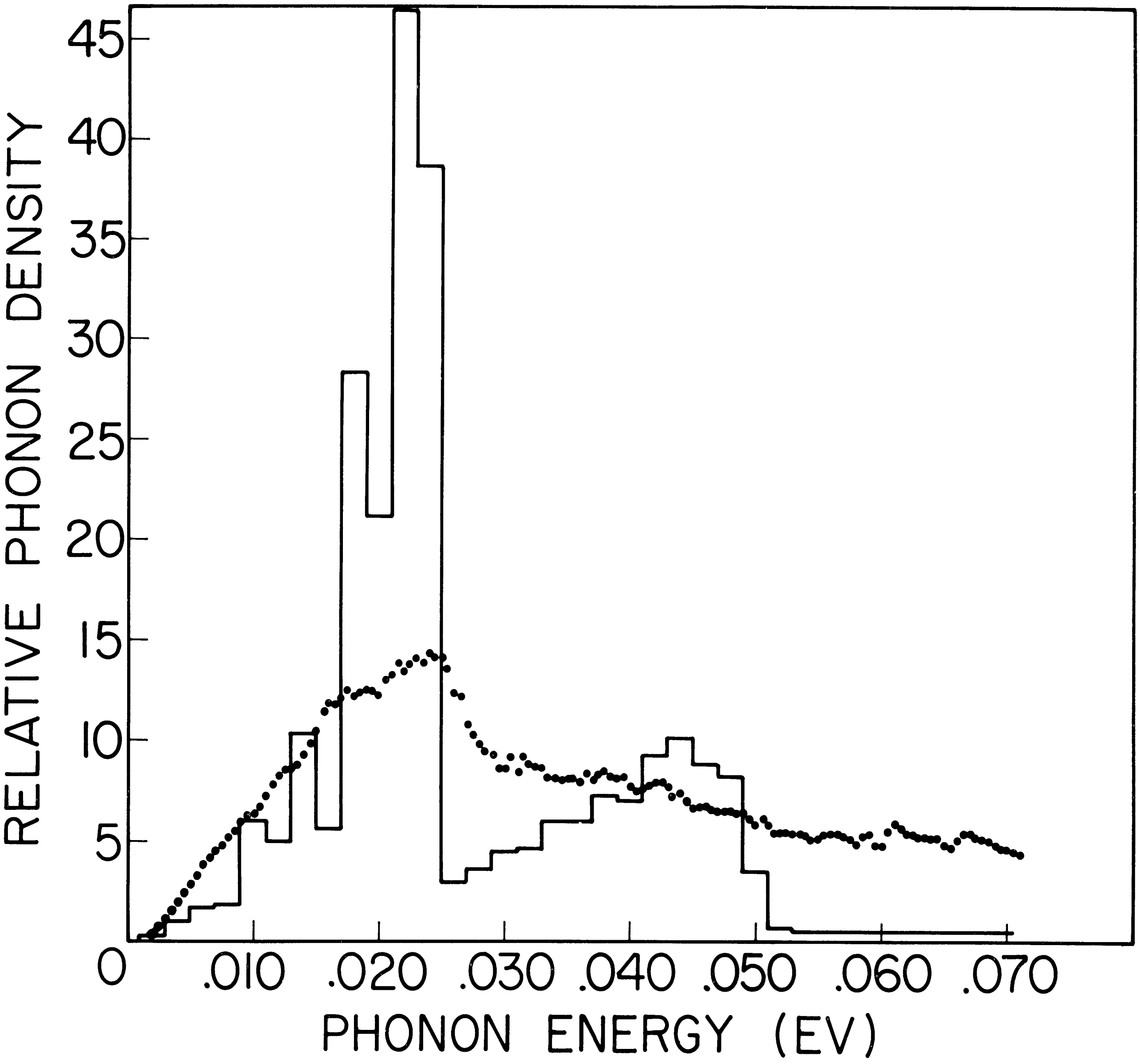


Fig. 8.3. Transverse frequency function, $G_T(\epsilon)$, for oriented normal polyethylene (experimental points from Ref. 5; E_f = .030 eV, T = 100°K, $\Theta_s = 90°$).

It may be said that the agreement between the calculated and experimental results in Figs. 8.1 to 8.3 is as good as should be expected at this stage of refinement. The theoretical analysis is of course based on an idealized model for polyethylene, i.e., a perfect, harmonic crystal. The forces, particularly the torsional forces, are not harmonic and the carbon chains do exhibit folding. Some work has been done on the latter effect,[49] but little has been done on anharmonic effects and these should be particularly significant for the torsional modes below .025 eV. Finally, the phonon wave vector has been restricted in the calculation to lie along the chain axis. This approximation should be evaluated.

B. POLYVINYLCHLORIDE

In Fig. 6.4, the dispersion curves for polyvinylchloride are shown. Except for the addition of the two lower frequency torsion branches ν_{17} and ν_{18} and the crossover shown for the ν_{13} and ν_{14} branches near $\delta_c = 40°$, these results match Opaskar's quite well.[45] An interesting point is that the introduction of the two torsion force constants of 0.06 mdyne -Å/rad^2, which were not included in Opaskar's analysis, causes the ν_{15} and ν_{16} branches to now have nonzero frequencies of 91 cm^{-1} and 41 cm^{-1}, respectively, at $\delta_c = 0$.

The $\nu_{17}(0)$ and $\nu_{17}(\pi)$ frequencies should be exactly zero but are not due to a slight discrepancy in obtaining the cartesian coordinate force constants, when double-precision matrix multiplication methods are not utilized in the interest of saving computer time. This discrepancy, which is not important, results in a small nonzero force on an atom and a small nonzero frequency for a pure translation or rotation of the entire molecule. The comparison of the calculated polyvinylchloride frequency functions with measured values must await the results of experiments which are now in progress.

C. POLYTETRAFLUOROETHYLENE

Each branch of the Teflon dispersion curves in Fig. 7.1 is labeled according to the direction of motion of the modes relative to the chain axis. For example, the branches for $0 \leq \delta_c \leq \pi/2$ include three longitudinally polarized and 6 transversely polarized branches. The branch labels referred to, for identification purposes only, are those of the $C(14\pi/13)$ helical chain modes described by Liang and Krimm.[47] A more realistic calculation, in which the actual helical structure and a more complete force field are included, is certainly desirable before an attempt is made to calculate the G-functions.

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APPENDIX

Page

I. POLYETHYLENE

Intramolecular Internal Coordinate to Cartesian Coordinate Transformation Submatrices, $\underline{\underline{B}}^{s}_{n,m}$, for Chain-Oriented Coordinate Systems. 153

The row and column labels are given in Eq. (4.1), page 39 of the text.

Internal Coordinate Intramolecular Force Constant Submatrices, $\underline{\underline{F}}_{n,m}$. 154

The row and column labels are given in Eq. (4.3), page 41 of the text.

Intramolecular Internal Coordinate to Cartesian Coordinate Transformation Submatrices, $\underline{\underline{B}}^{s}_{n,m}$, for Crystal-Oriented Coordinate Systems. 155

Deuterated Crystalline Polyethylene Frequency and Polarization Vector Solutions. 156-166

The phase angle varies from $\delta_c = 0$ to π in increments of $\pi/10$.

The eigenvector components, for crystal-oriented cartesian coordinate systems, are displayed beneath each frequency solution. The j indices label dispersion curve branches.

The format for the eigenvector components matches that used in Eq. (5.20), page 85 of the text, for the matrix columns.

Frequencies are given in units of cm^{-1}.

B2 SUBMATRIX $\underline{\underline{B}}^{s}_{0,\bar{1}}$

```
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.512474    .000000   -.379961   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
  .266172   -.563082    .189920   -.000000   -.000000    .000000   -.000000   -.000000    .000000
  .266172    .563082    .189920   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
  .000000   -.225331   -.000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
```

B3 SUBMATRIX $\underline{\underline{B}}^{s}_{0,0}$

```
  .559179    .000000   -.829047    .000000    .000000    .000000    .000000    .000000    .000000
 -.573572    .819155    .000000    .573572   -.819155   -.000000    .000000    .000000    .000000
 -.573572   -.819155    .000000    .000000    .000000    .000000    .573572    .819155   -.000000
 1.024948    .000000   -.000000    .000000    .000000    .000000    .000000    .000000    .000000
 1.474659   -.000000    .000000   -.737329   -.526598   -.000000   -.737329    .526598   -.000000
 -.088674   -.826297   -.989270    .354846    .263215    .799350    .000000    .000000    .000000
 -.088674    .826297   -.989270    .000000    .000000    .000000    .354846   -.263215    .799350
 -.088674   -.826297    .989270    .354846    .263215   -.799350    .000000    .000000    .000000
 -.088674    .826297    .989270    .000000    .000000    .000000    .354846   -.263215   -.799350
  .000000    .098867    .000000   -.231504   -.162099   -.156146    .231504   -.162099    .156146
```

B4 SUBMATRIX $\underline{\underline{B}}^{s}_{0,1}$

```
  .559179    .000000    .829047   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.512474    .000000    .379961   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.000000    .000000   -.000000   -.000000    .000000   -.000000   -.000000    .000000
  .266172   -.563082   -.189920   -.000000   -.000000    .000000   -.000000   -.000000    .000000
  .266172    .563082   -.189920   -.000000   -.000000    .000000   -.000000   -.000000    .000000
 -.000000   -.098867    .000000    .231504    .162099   -.156146   -.231504    .162099    .156146
```

B5 SUBMATRIX $\underline{\underline{B}}^{s}_{0,2}$

```
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000    .000000
  .000000    .225331    .000000    .000000    .000000    .000000    .000000    .000000    .000000
```

F1 SUBMATRIX $\underline{\underline{F}}_{0,\bar{2}}$

```
.000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000  -.002000  -.003000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000  -.003000  -.002000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
.000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
```

F2 SUBMATRIX $\underline{\underline{F}}_{0,\bar{1}}$

```
 .064000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
 .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
 .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
 .351000   .000000   .000000   .093000   .000000   .000000   .000000  -.058000  -.058000   .000000
 .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
 .261000   .000000   .000000  -.058000   .000000   .002000  -.002000   .106000  -.024000   .000000
 .261000   .000000   .000000  -.058000   .000000  -.002000   .002000  -.024000   .106000   .000000
-.004000   .000000   .000000   .000000   .000000  -.001000   .001000   .002000  -.002000   .000000
-.004000   .000000   .000000   .000000   .000000   .001000  -.001000  -.002000   .002000   .000000
 .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
```

F3 SUBMATRIX $\underline{\underline{F}}_{0,0}$

```
4.427000   .000000   .000000   .351000   .000000  -.004000  -.004000   .261000   .261000   .000000
 .000000  4.546000   .016000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
 .000000   .016000  4.546000   .000000   .000000   .000000   .000000   .000000   .000000   .000000
 .351000   .000000   .000000   .901000   .000000  -.124000  -.124000  -.124000  -.124000   .000000
 .000000   .000000   .000000   .000000   .550000   .000000   .000000   .000000   .000000   .000000
-.004000   .000000   .000000  -.124000   .000000   .666000  -.016000   .023000   .000000   .000000
-.004000   .000000   .000000  -.124000   .000000  -.016000   .666000   .000000   .023000   .000000
 .261000   .000000   .000000  -.124000   .000000   .023000   .000000   .666000  -.016000   .000000
 .261000   .000000   .000000  -.124000   .000000   .000000   .023000  -.016000   .666000   .000000
 .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .000000   .107000
```

B2 SUBMATRIX $\underline{\underline{B}}^{s}_{0,\bar{1}}$

-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.362411	-.402488	-.364556	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
.602325	-.162247	.191043	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.224334	.582066	.191043	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
.174424	-.157056	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000

B3 SUBMATRIX $\underline{\underline{B}}^{s}_{0,0}$

.374715	.416153	-.828496	.000000	.000000	.000000	.000000	.000000	.000000
-.995400	.095802	.000000	.995400	-.095802	-.000000	.000000	.000000	.000000
.199343	-.979930	.000000	.000000	.000000	.000000	-.199343	.979930	-.000000
-.724821	-.804976	-.000000	.000000	.000000	.000000	.000000	.000000	.000000
1.005416	1.116643	.000000	-.089600	-.930276	-.000000	-.915816	-.186368	-.000000
.559719	-.606396	1.012269	.042606	.444148	.821226	.000000	.000000	.000000
-.661614	.493274	1.012274	.000000	.000000	.000000	.437281	.088792	.821231
.559719	-.606396	1.012269	.042606	.444148	-.821226	.000000	.000000	.000000
-.661614	.493274	1.012274	.000000	.000000	.000000	.437281	.088792	-.821231
-.082275	.074070	-.000006	-.027815	-.289004	-.157747	.284514	.057878	.157753

B4 SUBMATRIX $\underline{\underline{B}}^{s}_{0,1}$

.374715	.416153	.828496	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.362411	-.402488	.364556	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.000000	-.000000	.000000	-.000000	-.000000	.000000	-.000000	-.000000	.000000
.602325	-.162247	-.191043	-.000000	-.000000	.000000	-.000000	-.000000	.000000
-.224334	.582066	-.191043	-.000000	-.000000	.000000	-.000000	-.000000	.000000
.082275	-.074070	-.000006	.027815	.289004	.157747	-.284514	-.057878	.157753

B5 SUBMATRIX $\underline{\underline{B}}^{s}_{0,2}$

.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.174424	.157056	.000000	.000000	.000000	.000000	.000000	.000000	.000000

EIGENVECTOR Δa^c Δb^c Δc^c Δa^{D1} Δb^{D1} Δc^{D1} Δa^{D2} Δb^{D2} Δc^{D2}

```
DELC =        .000000,              FREQ =    997.603951,             J =           1
.547434    -.464094    -.000000    .365324     .399312    -.000000    -.245331    -.363089    -.000000
DELC =        .000000,              FREQ =   1094.754761,             J =           2
.588432     .675242     .000000    .299143    -.083029     .000000    -.100996     .302018     .000000
DELC =        .000000,              FREQ =        .000000,            J =           3
.000000     .000000     .865342    .000000     .000000     .354389     .000000     .000000     .354389
DELC =        .000000,              FREQ =   2132.675598,             J =           4
-.308561   -.314755    -.000000    .651512    -.063182    -.000000    -.117899     .602793    -.000000
DELC =        .000000,              FREQ =    142.945490,             J =           5
-.358459    .323641    -.000000   -.099435     .616034    -.000000    -.613158     .037617    -.000000
DELC =        .000000,              FREQ =    792.973564,             J =           6
.000000     .000000    -.000009    .000000     .000000     .707118     .000000     .000000    -.707095
DELC =        .000000,              FREQ =   1032.205185,             J =           7
-.004361    .082719    -.000000    .055773     .664110    -.000000     .716069     .190343    -.000000
DELC =        .000000,              FREQ =   2207.879791,             J =           8
.361028    -.343524     .000000   -.582740     .095516     .000000    -.164300     .613145     .000000
DELC =        .000000,              FREQ =    913.943954,             J =           9
.000000     .000000    -.501182    .000000     .000000     .611876     .000000     .000000     .611903
DELC =        .000000,              FREQ =    999.334702,             J =          10
.549626    -.470874     .000000    .360247     .356553     .000000    -.283746    -.372516     .000000
DELC =        .000000,              FREQ =   1093.102142,             J =          11
.585201     .670058     .000000    .295865    -.122371     .000000    -.141563     .293274     .000000
DELC =        .000000,              FREQ =     53.880099,             J =          12
.000000     .000000     .868342    .000000     .000000     .348935     .000000     .000000     .352459
DELC =        .000000,              FREQ =   2128.322968,             J =          13
-.310313   -.316462     .000000    .650785    -.063834     .000000    -.119452     .601409     .000000
DELC =        .000000,              FREQ =   1047.939346,             J =          14
.056489     .097444    -.000000    .095387     .686737    -.000000     .686889     .186523    -.000000
DELC =        .000000,              FREQ =    789.504189,             J =          15
.000000     .000000     .008235    .000000     .000000     .700409     .000000     .000000    -.713694
DELC =        .000000,              FREQ =    108.936782,             J =          16
.355900    -.320132     .000000    .098846    -.610780     .000000     .622041    -.033058     .000000
DELC =        .000000,              FREQ =   2211.227386,             J =          17
.359584    -.342302     .000000   -.583349     .095710     .000000    -.162566     .614528     .000000
DELC =        .000000,              FREQ =    918.757133,             J =          18
.000000     .000000    -.495898    .000000     .000000     .622633     .000000     .000000     .605321
```

```
 DELC =        .314159,          FREQ =   1000.781464,              J =          1
 .525744   -.452732   -.015250   .352104    .387050    .203955   -.227042   -.351813   -.166408
 DELC =        .314159,          FREQ =   1090.275833,              J =          2
 .570988    .649540   -.085295   .285366   -.126474    .154250   -.147575    .279170    .154461
 DELC =        .314159,          FREQ =    205.822094,              J =          3
-.042409   -.019729    .844931  -.013765    .026602    .377692   -.015632   -.007097    .374247
 DELC =        .314159,          FREQ =   2130.786255,              J =          4
-.305310   -.312310    .001223   .652260   -.061983   -.009350   -.117374    .604986   -.009421
 DELC =        .314159,          FREQ =    145.614998,              J =          5
-.361811    .328828   -.029504  -.101649    .611115    .024500   -.609231    .040767   -.053631
 DELC =        .314159,          FREQ =    780.580505,              J =          6
-.128414    .110905   -.002685  -.080187   -.126229    .682805    .116182    .088490   -.679181
 DELC =        .314159,          FREQ =   1032.478943,              J =          7
 .016110    .111444   -.070908   .064884    .652934    .061350    .705759    .202100    .095159
 DELC =        .314159,          FREQ =   2206.584595,              J =          8
 .360018   -.341770    .000049  -.584403    .094815    .009813   -.163289    .613344   -.010658
 DELC =        .314159,          FREQ =    912.478851,              J =          9
-.159008   -.159845   -.522185  -.080351   -.070280    .566733   -.056858   -.075536    .578764
 DELC =        .314159,          FREQ =   1001.703423,              J =         10
 .528875   -.461193   -.008791   .347054    .335776    .192419   -.275835   -.364415   -.168563
 DELC =        .314159,          FREQ =   1089.793564,              J =         11
 .562225    .639829   -.085343   .277498   -.177636    .156004   -.195988    .266918    .157112
 DELC =        .314159,          FREQ =    213.128660,              J =         12
-.018400   -.041818    .848266  -.007553   -.013503    .369461    .023728   -.010411    .375427
 DELC =        .314159,          FREQ =   2126.495178,              J =         13
-.306995   -.313940    .001170   .651560   -.062600   -.008967   -.118703    .603737   -.008733
 DELC =        .314159,          FREQ =   1047.289902,              J =         14
 .090206    .128108   -.075875   .111310    .673686    .090795    .669598    .196665    .090380
 DELC =        .314159,          FREQ =    777.999229,              J =         15
-.124111    .109664    .006209  -.076497   -.124849    .678624    .110325    .085357   -.686370
 DELC =        .314159,          FREQ =    113.779606,              J =         16
 .361171   -.323045   -.024118   .101441   -.606735   -.050889    .617770   -.035581    .026477
 DELC =        .314159,          FREQ =   2209.895599,              J =         17
 .358609   -.340588    .000079  -.585011    .094953    .009767   -.161749    .614622   -.011240
 DELC =        .314159,          FREQ =    916.009216,              J =         18
-.164387   -.169753   -.516435  -.084795   -.070812    .574975   -.050138   -.079751    .570771
```

```
 DELC =        .628318,              FREQ =   1081.374283,                J =            1
 .511316     .563308    -.167773     .242268    -.247802     .280585    -.277712     .209407     .270718
 DELC =        .628318,              FREQ =   1007.215652,                J =            2
-.473447     .430948     .030922    -.319248    -.348819    -.357959     .196197     .330019     .300068
 DELC =        .628318,              FREQ =    378.183083,                J =            3
-.092457    -.088624     .771063    -.033820     .009130     .442911    -.001376    -.028226     .436878
 DELC =        .628318,              FREQ =   2125.582458,                J =            4
-.296319    -.305594     .000431     .654200    -.058630    -.016953    -.115913     .611039    -.017294
 DELC =        .628318,              FREQ =    152.289717,                J =            5
-.376375     .342106    -.008983    -.109842     .597770     .070778    -.597480     .049732    -.085820
 DELC =        .628318,              FREQ =    747.463982,                J =            6
-.222892     .192234    -.008977    -.138747    -.234977     .621667     .216290     .154853    -.617728
 DELC =        .628318,              FREQ =   1034.457535,                J =            7
 .051416     .146850    -.221093     .078875     .602126     .187135     .646393     .206751     .250085
 DELC =        .628318,              FREQ =   2202.859772,                J =            8
 .357030    -.336771     .000040    -.589172     .092786     .018628    -.160396     .613924    -.020103
 DELC =        .628318,              FREQ =    911.476860,                J =            9
-.310802    -.326733    -.572113    -.160010    -.172308     .412108    -.153721    -.164219     .440010
 DELC =        .628318,              FREQ =   1006.389977,                J =           10
 .480839    -.436514    -.006752     .315739     .283270     .332836    -.260481    -.344916    -.317288
 DELC =        .628318,              FREQ =   1083.659546,                J =           11
 .487902     .547941    -.154686     .223401    -.317846     .262114    -.332551     .194127     .264331
 DELC =        .628318,              FREQ =    382.383827,                J =           12
-.080403    -.101644     .774011    -.031521    -.008945     .433883     .014865    -.032033     .439926
 DELC =        .628318,              FREQ =   2121.493164,                J =           13
-.297793    -.307036     .000294     .653528    -.059155    -.016171    -.116593     .610196    -.015941
 DELC =        .628318,              FREQ =   1046.570511,                J =           14
 .144386     .163375    -.229411     .132903     .609737     .250190     .594290     .195930     .237116
 DELC =        .628318,              FREQ =    746.680359,                J =           15
-.220633     .191493     .001041    -.135470    -.233655     .622857     .207814     .151065    -.622692
 DELC =        .628318,              FREQ =    126.002691,                J =           16
 .375763    -.335070    -.011113     .108858    -.594460    -.086498     .605885    -.044171     .068145
 DELC =        .628318,              FREQ =   2206.055817,                J =           17
 .355747     .335682     .000107    -.589812     .092757     .018556    -.159425     .614871    -.021245
 DELC =        .628318,              FREQ =    912.300591,                J =           18
-.313560    -.341024    -.569367    -.162984    -.163681     .416687    -.137344    -.169572     .431975
```

```
 DELC =       .942478,            FREQ =   1011.664482,               J =             1
 .408980    -.412384    -.022229     .276123     .280700     .459804    -.186758    -.312764    -.425459
 DELC =       .942478,            FREQ =   1076.830292,               J =             2
 .417241     .437043    -.272727     .184546    -.346828     .363180    -.383623     .126960     .333154
 DELC =       .942478,            FREQ =    913.407898,               J =             3
 .418983     .452981     .558847     .223303     .303050    -.102339     .279878     .244523    -.129037
 DELC =       .942478,            FREQ =   2118.262634,               J =             4
-.283564    -.296274    -.003719     .656510    -.053753    -.021613    -.113817     .619658    -.022512
 DELC =       .942478,            FREQ =    158.728916,               J =             5
-.401034     .365333    -.005667    -.123883     .572470     .109958    -.575121     .065719    -.124210
 DELC =       .942478,            FREQ =    701.836998,               J =             6
-.274451     .245707    -.015694    -.171796    -.327058     .539698     .304147     .200099    -.551142
 DELC =       .942478,            FREQ =   1052.548828,               J =             7
-.017381     .019414    -.478171     .039809     .512742     .303919     .527930     .120940     .347102
 DELC =       .942478,            FREQ =   2197.154938,               J =             8
 .352261    -.329212    -.000030    -.596491     .089655     .025540    -.155995     .614783    -.027323
 DELC =       .942478,            FREQ =    477.377529,               J =             9
-.205299    -.208243     .619577    -.081125    -.023590     .517056    -.018815    -.073134     .500423
 DELC =       .942478,            FREQ =   1009.217667,               J =            10
 .435374    -.391677     .010468     .284699     .233184     .425645    -.231021    -.311707    -.435654
 DELC =       .942478,            FREQ =    914.384033,               J =            11
 .413509     .467411     .571855     .219270     .278276    -.110584     .259615     .250147    -.125696
 DELC =       .942478,            FREQ =   1080.435974,               J =            12
-.391109    -.437370     .219055    -.161356     .429707    -.305121     .438173    -.120165    -.312310
 DELC =       .942478,            FREQ =   2114.550995,               J =            13
-.284679    -.297521    -.003979     .655753    -.054155    -.020426    -.113492     .619482    -.020564
 DELC =       .942478,            FREQ =   1060.477615,               J =            14
 .071926     .062007    -.490383     .084379     .487952     .378640     .472106     .123676     .351768
 DELC =       .942478,            FREQ =    702.376694,               J =            15
-.280663     .243742    -.005685    -.172756    -.326449     .545860     .293893     .195962    -.550121
 DELC =       .942478,            FREQ =    139.740850,               J =            16
 .401273    -.355682    -.008450     .122015    -.571435    -.125478     .583724    -.059309     .104765
 DELC =       .942478,            FREQ =   2200.144836,               J =            17
 .351226    -.328200     .000081    -.597272     .089360     .025477    -.155925     .615145    -.028968
 DELC =       .942478,            FREQ =    479.121616,               J =            18
-.192680    -.225440     .619913    -.078947    -.037631     .505327    -.007018    -.080311     .508189
```

```
 DELC =      1.256637,          FREQ =   1010.824532,                  J =          1

 .361307    -.369793   -.003258    .242428    .238180    .497213   -.153634   -.278351   -.518552

 DELC =      1.256637,          FREQ =    906.547028,                  J =          2

 .410872     .450128    .433451    .224831    .352077    .225747    .324058    .254403    .213272

 DELC =      1.256637,          FREQ =   1114.472656,                  J =          3

-.008591    -.011714    .777132   -.026141   -.204912   -.390550   -.199266   -.048557   -.398232

 DELC =      1.256637,          FREQ =   2110.288300,                  J =          4

-.269487    -.286488   -.011290    .658154   -.048129   -.022977   -.111478    .629386   -.024657

 DELC =      1.256637,          FREQ =   1075.785873,                  J =          5

-.340767    -.337902    .074336   -.124094    .556837   -.233525    .592302   -.036660   -.178905

 DELC =      1.256637,          FREQ =    651.822311,                  J =          6

-.287793     .279020   -.016576   -.183995   -.408240    .452315    .389003    .231331   -.478652

 DELC =      1.256637,          FREQ =    159.950380,                  J =          7

 .437441    -.398341    .003826    .144538   -.532263   -.146914    .539270   -.089404    .159281

 DELC =      1.256637,          FREQ =   2190.127747,                  J =          8

 .346155    -.319968   -.000104   -.605668    .085784    .029847   -.150595    .615657   -.031627

 DELC =      1.256637,          FREQ =    481.544056,                  J =          9

-.343247    -.354034    .449702   -.140891   -.087274    .516878   -.060100   -.132023    .488812

 DELC =      1.256637,          FREQ =   1007.707710,                  J =         10

 .396541    -.334971    .010464    .257201    .198085    .512403   -.187889   -.268919   -.504850

 DELC =      1.256637,          FREQ =    910.801186,                  J =         11

 .404410     .464088    .446771    .217331    .326400    .218504    .319682    .262929    .220517

 DELC =      1.256637,          FREQ =   1116.404633,                  J =         12

-.008862    -.000999    .766078   -.026069   -.231911   -.394748   -.229094   -.047642   -.384709

 DELC =      1.256637,          FREQ =   2107.147919,                  J =         13

-.270108    -.287643   -.011694    .657088   -.048415   -.021422   -.109901    .630098   -.022262

 DELC =      1.256637,          FREQ =   1079.670853,                  J =         14

-.307863    -.352251    .111791   -.104308    .573447   -.207726    .574381   -.052884   -.230348

 DELC =      1.256637,          FREQ =    652.413956,                  J =         15

-.304264     .274989   -.010206   -.190583   -.408678    .457098    .376268    .226612   -.475910

 DELC =      1.256637,          FREQ =    149.265955,                  J =         16

 .438678    -.385828   -.007746    .141698   -.534487   -.162094    .548505   -.082030    .137919

 DELC =      1.256637,          FREQ =   2192.811707,                  J =         17

 .345507    -.318952    .000064   -.606770    .085137    .029829   -.151691    .615177   -.033668

 DELC =      1.256637,          FREQ =    479.538918,                  J =         18

-.327109    -.373340    .447896   -.136821   -.096508    .504143   -.050797   -.141191    .498293
```

```
DELC =     1.570796,            FREQ =    413.388908,              J =         1
.442235    .471298   -.339096    .182231   .147165   -.440132    .105756    .181015   -.418076
DELC =     1.570796,            FREQ =    604.712837,              J =         2
-.280513   .283069   -.009858   -.184980  -.484659    .373538    .469705    .247026   -.388328
DELC =     1.570796,            FREQ =   1195.137024,              J =         3
.073043    .079447    .867528    .024557  -.161321   -.299148   -.161359    .006764   -.305856
DELC =     1.570796,            FREQ =   2102.869934,              J =         4
-.256159  -.278050   -.020662    .658331  -.042473   -.021471   -.109266    .639113   -.023965
DELC =     1.570796,            FREQ =   1079.756912,              J =         5
-.293769  -.291255    .130063   -.096451   .583047   -.237192    .610684   -.012563   -.182631
DELC =     1.570796,            FREQ =   1004.022598,              J =         6
.318032   -.318796    .000626    .210689   .201106    .554090   -.120443   -.238513   -.577910
DELC =     1.570796,            FREQ =    151.342007,              J =         7
.485321   -.438143    .001622    .171585  -.474546   -.177270    .488038   -.119944    .184021
DELC =     1.570796,            FREQ =   2182.539734,              J =         8
.339390   -.309941   -.000094   -.615973   .081617    .031144   -.144753    .616177   -.032696
DELC =     1.570796,            FREQ =    891.810211,              J =         9
.341497    .373675    .339065    .189772   .321522    .425596    .289208    .215857    .421929
DELC =     1.570796,            FREQ =    408.336830,              J =         10
.426471    .484986   -.338002    .177454   .153274   -.434443    .096379    .187541   -.424830
DELC =     1.570796,            FREQ =    603.906479,              J =         11
-.299797   .282574   -.009919   -.194503  -.485063    .368013    .456770    .243984   -.391736
DELC =     1.570796,            FREQ =   1195.352020,              J =         12
.068167    .080085    .865506    .024866  -.164941   -.304135   -.168222    .006983   -.301942
DELC =     1.570796,            FREQ =   2100.463379,              J =         13
-.256183  -.279284   -.021178    .656669  -.042680   -.019660   -.106334    .640888   -.021357
DELC =     1.570796,            FREQ =   1080.946915,              J =         14
-.265111  -.308061    .137733   -.080260   .601039   -.191591    .600488   -.027112   -.223889
DELC =     1.570796,            FREQ =   1001.051987,              J =         15
.347045   -.286442    .002291    .222733   .156488    .577749   -.155544   -.230526   -.558817
DELC =     1.570796,            FREQ =    149.893726,              J =         16
.486830   -.425108   -.007574    .167754  -.480629   -.190287    .497341   -.112656    .163790
DELC =     1.570796,            FREQ =   2184.824951,              J =         17
.339249   -.308794    .000145   -.617623   .080549    .031195   -.147182    .614614   -.034969
DELC =     1.570796,            FREQ =    896.601334,              J =         18
.339336    .384064    .342161    .182196   .298270    .418638    .297784    .224041    .428933
```

```
DELC =      1.884955,             FREQ =    130.332090,              J =          1
 .542991   -.474792   -.002911    .203572   -.401149   -.193592    .425912   -.152252    .187890
DELC =      1.884955,             FREQ =    306.859070,              J =          2
 .492762    .554151   -.274847    .201469    .191011   -.342286    .141604    .216153   -.336975
DELC =      1.884955,             FREQ =   1263.681915,              J =          3
 .093464    .102375    .903358    .043709   -.126408   -.251477   -.129090    .029792   -.256994
DELC =      1.884955,             FREQ =   2096.657013,              J =          4
-.244754   -.271815   -.028624    .656867   -.037354   -.017995   -.107470    .648232   -.021078
DELC =      1.884955,             FREQ =   1084.929001,              J =          5
-.263449   -.266278    .134131   -.076905    .610378   -.204801    .629229    .001357   -.159213
DELC =      1.884955,             FREQ =    992.075516,              J =          6
 .269717   -.265863   -.000963    .175656    .160266    .601818   -.095022   -.197792   -.624253
DELC =      1.884955,             FREQ =    566.519226,              J =          7
-.262025    .259356   -.002867   -.179691   -.554477    .296195    .538661    .247871   -.291560
DELC =      1.884955,             FREQ =   2175.155182,              J =          8
 .332740   -.300012    .000045   -.626607    .077596    .029367   -.139018    .616032   -.030575
DELC =      1.884955,             FREQ =    877.436981,              J =          9
 .268662    .290285    .299291    .151293    .271120    .537657    .236417    .170130    .532608
DELC =      1.884955,             FREQ =    138.881344,              J =         10
 .537779   -.472568   -.005923    .196698   -.412275   -.199333    .430568   -.150059    .176457
DELC =      1.884955,             FREQ =    300.275230,              J =         11
 .489936    .553408   -.274924    .200969    .192374   -.348234    .136606    .216187   -.337725
DELC =      1.884955,             FREQ =   1263.315582,              J =         12
 .089843    .102388    .903689    .045035   -.125611   -.253504   -.130788    .030386   -.254344
DELC =      1.884955,             FREQ =   2176.979706,              J =         13
-.333184    .298591   -.000362    .629036   -.076078   -.029483    .142825   -.613196    .032858
DELC =      1.884955,             FREQ =   1083.168060,              J =         14
-.241434   -.281899    .135592   -.067321    .621771   -.160985    .622812   -.010117   -.197007
DFLC =      1.884955,             FREQ =    989.985344,              J =         15
 .289691   -.239734   -.003650    .183742    .116293    .621852   -.126857   -.192190   -.609572
DELC =      1.884955,             FREQ =    563.150703,              J =         16
-.275121    .265670   -.008217   -.188638   -.554360    .279843    .529669    .247927   -.300717
DELC =      1.884955,             FREQ =   2095.064087,              J =         17
-.244110   -.273304   -.029167    .654326   -.037532   -.016113   -.103239    .651192   -.018543
DELC =      1.884955,             FREQ =    880.247253,              J =         18
 .272360    .297596    .297338    .145558    .250216    .531674    .251497    .176786    .536534
```

```
 DELC =      2.199114,          FREQ =    97.789557,           J =          1
 .621135   -.476519   -.016644   .243431   -.314527   -.193992   .370673   -.170703   .156483
 DELC =      2.199114,          FREQ =   190.154552,           J =          2
 .488491    .632785   -.223942   .198826    .235766   -.242368   .154705    .249599   -.265923
 DELC =      2.199114,          FREQ =  1307.104034,           J =          3
 .091910    .100777    .920057   .048183   -.102168   -.231688  -.105883    .037069   -.236361
 DELC =      2.199114,          FREQ =  2168.662537,           J =          4
-.326910    .291048   -.000254   .636614   -.074103   -.024772   .133905   -.615183    .025610
 DELC =      2.199114,          FREQ =  1091.041275,           J =          5
-.248050   -.256544    .124434  -.066000    .629724   -.165027   .641595    .007055   -.131666
 DELC =      2.199114,          FREQ =   977.074600,           J =          6
 .213689   -.209006   -.004141   .136676    .118592    .639032  -.072614   -.154449   -.663628
 DELC =      2.199114,          FREQ =   540.046822,           J =          7
-.237130    .223810    .001627  -.170429   -.609166    .217587   .589791    .240128   -.201712
 DELC =      2.199114,          FREQ =  2091.778595,           J =          8
-.235611   -.267643   -.031482   .654313   -.033183   -.013539  -.106259    .656417   -.016732
 DELC =      2.199114,          FREQ =   865.292030,           J =          9
 .203260    .215464    .294232   .115767    .216233    .605152   .182932    .127620    .591243
 DELC =      2.199114,          FREQ =   183.439222,           J =          10
 .569304    .557767   -.225202   .230466    .199081   -.277153   .192429    .220705   -.242427
 DELC =      2.199114,          FREQ =   116.630153,           J =          11
-.547635    .557157   -.010853  -.209549    .352891    .165162  -.345735    .202924   -.181995
 DELC =      2.199114,          FREQ =  1306.554947,           J =          12
 .089070    .100607    .921093   .049770   -.099952   -.231758  -.105387    .037699   -.234147
 DELC =      2.199114,          FREQ =  2170.019440,           J =          13
-.327949    .289238   -.000623   .639989   -.072153   -.024921   .138988   -.610978    .027650
 DELC =      2.199114,          FREQ =  1086.445755,           J =          14
-.232036   -.269245    .123363  -.062814    .634812   -.129678   .639017   -.000495   -.162346
 DELC =      2.199114,          FREQ =   976.446892,           J =          15
 .225642   -.189478   -.008072   .141456    .080954    .650825  -.097642   -.150653   -.656316
 DELC =      2.199114,          FREQ =   533.863037,           J =          16
-.237325    .235135   -.007027  -.175872   -.608739    .194635   .587417    .242448   -.212419
 DELC =      2.199114,          FREQ =  2090.968231,           J =          17
-.234278   -.269507   -.031949   .650701   -.033375   -.011819  -.100925    .660602   -.014559
 DELC =      2.199114,          FREQ =   865.126381,           J =          18
 .211045    .219940    .290516   .112308    .198548    .602629   .199731    .132368    .591673
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```
 DELC =      2.513273,           FREQ =     51.836852,             J =          1
 .781362   -.279541   -.062599    .315033   -.165261   -.190026    .360609   -.105839    .059189
 DELC =      2.513273,           FREQ =     98.540828,             J =          2
 .283138    .787327   -.154736    .115720    .316009   -.110440    .082565    .314600   -.211577
 DELC =      2.513273,           FREQ =   1326.728043,             J =          3
 .074578    .081761    .930579    .040858   -.077143   -.228888   -.080543    .032623   -.232840
 DELC =      2.513273,           FREQ =   2163.621521,             J =          4
-.322420    .283894   -.000373    .644891   -.071424   -.017870    .129874   -.613953    .018378
 DELC =      2.513273,           FREQ =   1097.521652,             J =          5
-.243441   -.256253    .100431   -.061600    .643474   -.118885    .650687    .007910   -.097675
 DELC =      2.513273,           FREQ =    854.882103,             J =          6
 .140665    .146192    .308666    .080708    .154953    .649010    .127970    .087112    .622787
 DELC =      2.513273,           FREQ =    524.275421,             J =          7
-.214891    .190279    .003646   -.161433   -.645553    .141867    .621581    .230010   -.124133
 DELC =      2.513273,           FREQ =   2088.171814,             J =          8
-.228765   -.264950   -.026959    .651638   -.030196   -.008866   -.105632    .663195   -.011529
 DELC =      2.513273,           FREQ =    962.194542,             J =          9
-.149090    .145768    .007713   -.093851   -.077804   -.665906    .049986    .106951    .695869
 DELC =      2.513273,           FREQ =    107.587630,             J =         10
 .834074    .059736   -.122912    .335077   -.011940   -.230144    .344015    .025089   -.035827
 DELC =      2.513273,           FREQ =     68.362881,             J =         11
-.057584    .828588   -.114759   -.019643    .370543   -.026739   -.077186    .327903   -.212308
 DELC =      2.513273,           FREQ =   1326.155029,             J =         12
 .072412    .081474    .931830    .042249   -.074640   -.227459   -.079163    .033094   -.230988
 DELC =      2.513273,           FREQ =   2164.573151,             J =         13
-.323977    .281668   -.000718    .649212   -.069115   -.018005    .135987   -.608469    .019916
 DELC =      2.513273,           FREQ =   1090.584213,             J =         14
-.231699   -.266211    .098361   -.063388    .643838   -.094643    .651255    .003714   -.118837
 DELC =      2.513273,           FREQ =    851.733841,             J =         15
 .149392    .148389    .304654    .079201    .141827    .651551    .142472    .090015    .619307
 DELC =      2.513273,           FREQ =    515.946922,             J =         16
-.198278    .204909   -.005908   -.161179   -.643511    .118727    .626201    .233631   -.133304
 DELC =      2.513273,           FREQ =   2088.004669,             J =         17
-.226810   -.267208   -.027283    .646952   -.030423   -.007546   -.099478    .668496   -.009952
 DELC =      2.513273,           FREQ =    963.253090,             J =         18
-.155048    .132748    .012133   -.096222   -.050335   -.668302    .066942    .104560    .695957
```

```
 DELC =        2.827432,            FREQ =       .000000,             J =          1
 .816984    -.261302    -.037362    .333611    -.113149    -.103272    .340784    -.105379    .029324
 DELC =        2.827432,            FREQ =     76.218102,             J =          2
 .257784     .821732    -.083305    .104741     .319032    -.051642    .104072     .335546   -.111905
 DELC =        2.827432,            FREQ =   1331.327957,             J =          3
 .042520     .046601     .938208    .023517    -.043335    -.233832   -.045339     .018967   -.237194
 DELC =        2.827432,            FREQ =   2160.436218,             J =          4
-.319600     .279278    -.000276    .650367    -.069748    -.009350    .127295    -.612890    .009584
 DELC =        2.827432,            FREQ =   1102.953796,             J =          5
-.244733    -.260225     .057999   -.061074     .652784    -.063557    .657445     .006602   -.053388
 DELC =        2.827432,            FREQ =    951.135406,             J =          6
 .076848    -.075351    -.010687    .047846     .038392     .682393   -.025717    -.054978   -.717771
 DELC =        2.827432,            FREQ =    516.400757,             J =          7
-.201375     .166953     .002987   -.155769    -.665922     .070033    .637387     .221976   -.058392
 DELC =        2.827432,            FREQ =   2085.886597,             J =          8
-.224418    -.263349    -.015508    .649712    -.028445    -.004346   -.105411     .667790   -.005866
 DELC =        2.827432,            FREQ =    846.797813,             J =          9
 .073601     .07[illegible]2     .328179    .042357     .082529     .676225    .067129     .045018    .639355
 DELC =        2.827432,            FREQ =    101.816755,             J =          10
 .857676     .109425    -.071247    .348999     .055558    -.122861    .324437     .039538   -.023157
 DELC =        2.827432,            FREQ =       .000000,             J =          11
-.115675     .849648    -.058588   -.046196     .352246    -.004265   -.055940     .345901   -.110803
 DELC =        2.827432,            FREQ =   1330.801895,             J =          12
 .041267     .046350     .939431    .024338    -.041598    -.231198   -.044192     .019204   -.235629
 DELC =        2.827432,            FREQ =   2161.112091,             J =          13
-.321512     .276730    -.000490    .655399    -.067201    -.009430    .134076    -.606475    .010413
 DELC =        2.827432,            FREQ =   1094.456726,             J =          14
-.235317    -.268332     .056339   -.065917     .650233    -.051290    .659960     .004578   -.064053
 DELC =        2.827432,            FREQ =    841.382629,             J =          15
 .079471     .076228     .324475    .041992     .075427     .683494    .075696     .046379    .632528
 DELC =        2.827432,            FREQ =    506.881020,             J =          16
-.169431     .184773    -.003714   -.149758    -.660837     .055020    .647670     .226751   -.063917
 DELC =        2.827432,            FREQ =   2086.139801,             J =          17
-.222021    -.265904    -.015668    .644218    -.028706    -.003628   -.098759     .673886   -.005041
 DELC =        2.827432,            FREQ =    953.572533,             J =          18
-.079039     .068822     .015584   -.048710    -.023819    -.677133    .034280     .053818    .723361
```

```
 DELC =       3.141590,            FREQ =       .000000,               J =           1
 .787953   -.364522   -.000000    .323280   -.137407   -.000001    .316799   -.150005    .000000
 DELC =       3.141590,            FREQ =     84.951834,               J =           2
 .358371    .791752   -.000001    .145955    .304075   -.000000    .156990    .326019   -.000001
 DELC =       3.141590,            FREQ =   1331.270828,               J =           3
 .000000    .000000    .941330    .000000   -.000000   -.237075   -.000000    .000000   -.240193
 DELC =       3.141590,            FREQ =   2159.348022,               J =           4
-.318639    .277684   -.000000    .652282   -.069179   -.000000    .126407   -.612474    .000000
 DELC =       3.141590,            FREQ =   1105.162888,               J =           5
-.246171   -.262589    .000000   -.061415    .656335   -.000000    .660202    .005735   -.000000
 DELC =       3.141590,            FREQ =    947.031326,               J =           6
 .000001   -.000001   -.011872    .000000    .000000    .688010   -.000000   -.000000   -.725604
 DELC =       3.141590,            FREQ =    514.065903,               J =           7
-.197180    .158516    .000000   -.153988   -.672547    .000001    .641906    .218899   -.000000
 DELC =       3.141590,            FREQ =   2085.093597,               J =           8
-.222911   -.262799   -.000000    .649023   -.027875   -.000000   -.105371    .669429   -.000000
 DELC =       3.141590,            FREQ =    843.547813,               J =           9
 .000001    .000001    .337278    .000000    .000001    .685885    .000001    .000000    .644830
 DELC =       3.141590,            FREQ =    110.360845,               J =          10
 .844576    .222291   -.000001    .345295    .117478   -.000001    .311651    .084393   -.000000
 DELC =       3.141590,            FREQ =       .000000,               J =          11
-.231782    .836580   -.000000   -.094576    .334117    .000000   -.083120    .344852   -.000001
 DELC =       3.141590,            FREQ =   1330.777542,               J =          12
 .000000    .000000    .942489    .000000   -.000000   -.233926   -.000000    .000000   -.238734
 DELC =       3.141590,            FREQ =   2159.926178,               J =          13
-.320677    .275015   -.000000    .657579   -.066549   -.000000    .133419   -.605717    .000000
 DELC =       3.141590,            FREQ =   1096.112518,               J =          14
-.237446   -.270034    .000000   -.067276    .652780   -.000000    .663350    .004463   -.000000
 DELC =       3.141590,            FREQ =    837.262680,               J =          15
 .000001    .000001    .333805    .000000    .000001    .695134    .000001    .000000    .636682
 DELC =       3.141590,            FREQ =    504.180912,               J =          16
-.158739    .178037   -.000000   -.145427   -.665749    .000000    .654537    .224311   -.000000
 DELC =       3.141590,            FREQ =   2085.492920,               J =          17
-.220355   -.265465   -.000000    .643227   -.028149   -.000000   -.098553    .675815   -.000000
 DELC =       3.141590,            FREQ =    950.006073,               J =          18
-.000001    .000001    .017016   -.000000   -.000000   -.679756    .000000    .000000    .733241
```

Page

II. POLYVINYLCHLORIDE

Internal Coordinate to Cartesian Coordinate Transformation Submatrices, $\underline{\underline{B}}^{s}_{n,m}$, for Chain-Oriented Cartesian Coordinate Systems. 168-169

The row and column labels are given in Eq. (6.1), page 111 of the text.

Internal Coordinate Intramolecular Force Constant Submatrices, $\underline{\underline{F}}_{n,m}$. 170

The format is given in Eq. (6.3), page 115 of the text.

Frequencies in cm^{-1} and Squares of Polarization Vector Components for $\delta_c = 0$ to 180° in 20° Increments. 171-180

The cartesian eigenvector components are displayed beneath each frequency solution where the dispersion curve branches are labelled by the j indices.

The format for the cartesian components matches that for the columns in Eq. (6.1), page 111 of the text.

B2 SUBMATRIX $\underline{\underline{B}}^{5}_{0,\bar{T}}$

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.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 -.5302 .0000 -.3749 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .2651 -.5623 .1874 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .2651 .5623 .1874 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 -.0000 .2296 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
.0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000 .0000 -.0000 .0000
```

B3 SUBMATRIX $\underline{\underline{B}}^{5}_{0,0}$

```
 -.5774  .0000 -.8165  .0000  .0000  .0000  .0000  .0000  .0000  .5774 -.0000  .8165  .0000  .0000  .0000  .0000  .0000  .0000
  .5774  .8165  .0000 -.5774 -.8165 -.0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000
  .5774 -.8165  .0000  .0000  .0000  .0000 -.5774  .8165 -.0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000
 1.0604  .0000 -.0000  .0000  .0000  .0000  .0000  .0000  .0000 -.5302 -.0000  .3749  .0000  .0000  .0000  .0000  .0000  .0000
-1.2011 -.2271  .0000  .4541 -.3211 -.0000  .7470  .5283 -.0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000
 -.0380 -.7228 -.6690 -.2271  .1605  .4816  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000
  .1084  .8264 -.9797  .0000  .0000  .0000 -.3736 -.2640  .7923  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000
 -.0380 -.7228  .6690 -.2271  .1605 -.4816  .0000  .0000  .0000  .2651  .5623 -.1874  .0000  .0000  .0000  .0000  .0000  .0000
  .1084  .8264  .9797  .0000  .0000  .0000 -.3736 -.2640 -.7923  .2651 -.5623 -.1874  .0000  .0000  .0000  .0000  .0000  .0000
 -.0897 -.0305  .2634 -.1390  .0983  .0983  .2287  .1617 -.1617  .0000 -.0939 -.0000  .2287  .1617 -.1617 -.2287  .1617  .1617
  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .5774  .0000 -.8165  .0000  .0000  .0000  .0000  .0000  .0000
  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000 -.5774  .8165  .0000  .5774 -.8165 -.0000  .0000  .0000  .0000
  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000 -.5774 -.8165  .0000  .0000  .0000  .0000  .5774  .8165 -.0000
  .5302 -.0000 -.3749  .0000  .0000  .0000  .0000  .0000  .0000-1.0604  .0000 -.0000  .0000  .0000  .0000  .0000  .0000  .0000
  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000 1.4940 -.0000  .0000 -.7470 -.5283 -.0000 -.7470  .5283 -.0000
 -.2651  .5623  .1874  .0000  .0000  .0000  .0000  .0000  .0000 -.1084 -.8264 -.9797  .3736  .2640  .7923  .0000  .0000  .0000
 -.2651 -.5623  .1874  .0000  .0000  .0000  .0000  .0000  .0000 -.1084  .8264 -.9797  .0000  .0000  .0000  .3736 -.2640  .7923
  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000 -.1084 -.8264  .9797  .3736  .2640 -.7923  .0000  .0000  .0000
  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000 -.1084  .8264  .9797  .0000  .0000  .0000  .3736 -.2640 -.7923
 -.0000  .2296 -.0000  .0000  .0000  .0000  .0000  .0000  .0000 -.0000  .0939 -.0000 -.2287 -.1617 -.1617  .2287 -.1617  .1617
```

P4 SUBMATRIX $\underline{\underline{B}}^{5}_{,1}$

```
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000  .2296  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
-.5774  .0000  .8165  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.5302  .0000  .3749  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
.0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
-.2651 -.5623 -.1874  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
-.2651  .5623 -.1874  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000  .0000 -.0000  .0000
-.0897 -.0305 -.0634 -.1390  .0983 -.0983  .2287  .1617  .1617  .0000 -.2296 -.0000  .0000 -.0000  .0000  .0000 -.0000  .0000
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F2 SUBMATRIX
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$\underline{\underline{F}}_{\theta,T}$

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.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .3000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .7300 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .4170 .0000 .0000-.0110 .0000 .0000 .0000-.0520-.0520 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0750 .0000 .0000 .0240 .0000 .0000 .0000 .0700 .0370 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .3280 .0000 .0000-.0520 .0000 .0000 .0000-.0050 .1270 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0790 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
.0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
```

```
F3 SUBMATRIX
```

$\underline{\underline{F}}_{\theta,\theta}$

```
4.6230 .7300 .0000 .4170 .0000 .0000 .0790 .0750 .3280 .0000 .1010 .0000 .0000 .4170 .0000 .3280 .3280 .0790 .0790 .0000
 .73003.3380 .0000-.2200 .3330 .5500 .0000 .5500 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
 .0000 .00004.8460 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
 .4170-.2200 .00001.1300 .0000 .0000-.0310 .0000-.0310 .0000 .0000 .0000 .0000-.0110 .0000-.0520-.0520 .0000 .0000 .0000
 .0000 .3330 .0000 .0000 .8600 .0000 .0890 .0000 .0890 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
 .0000 .5500 .0000 .0000 .0000 .9820 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
 .0790 .0000 .0000-.0310 .0890 .0000 .6330 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
 .0750 .5500 .0000 .0000 .0000 .0000 .0000 .9820 .0000 .0000 .0000 .0000 .0000 .0240 .0000 .0370 .0700 .0000 .0000 .0000
 .3280 .0000 .0000-.0310 .0890 .0000 .0000 .0000 .6330 .0000 .0000 .0000 .0000-.0520 .0000 .1270-.0050 .0000 .0000 .0000
 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0600 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000
 .1010 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .00004.3870 .0000 .0000 .4170 .0000 .0790 .0790 .3280 .3280 .0000
 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .00004.5540 .0060 .0000 .0000 .0000 .0000 .0000 .0000 .0000
 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .00604.5540 .0000 .0000 .0000 .0000 .0000 .0000 .0000
 .4170 .0000 .0000-.0110 .0000 .0000 .0000 .0240-.0520 .0000 .4170 .0000 .00001.1300 .0000-.0310-.0310-.0310-.0310 .0000
 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .5500 .0000 .0000 .0000 .0000 .0000
 .3280 .0000 .0000-.0520 .0000 .0000 .0000 .0370 .1270 .0000 .0790 .0000 .0000-.0310 .0000 .6560-.0210 .0130 .0000 .0000
 .3280 .0000 .0000-.0520 .0000 .0000 .0000 .0700-.0050 .0000 .0790 .0000 .0000-.0310 .0000-.0210 .6560 .0000 .0130 .0000
 .0790 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .3280 .0000 .0000-.0310 .0000 .0130 .0000 .6560-.0210 .0000
 .0790 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .3280 .0000 .0000-.0310 .0000 .0000 .0130-.0210 .6560 .0000
 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0000 .0600
```

```
         DELC =        .000000,          FREQ =       .000000,              J =            1
.0985  .0000  .0977  .2770  .0004  .2803  .0085  .0000  .0083  .0985  .0000  .0978  .0081  .0000  .0080  .0084  .0000  .0084
         DELC =        .000000,          FREQ =    10.782683,               J =            2
.0920  .0000  .0929  .2942  .0005  .2892  .0074  .0000  .0077  .0920  .0000  .0929  .0075  .0000  .0076  .0079  .0000  .0080
         DELC =        .000000,          FREQ =    40.783369,               J =            3
.0460  .0485  .0002  .0830  .7349  .0007  .0161  .0120  .0000  .0467  .0000  .0002  .0039  .0000  .0023  .0039  .0000  .0015
         DELC =        .000000,          FREQ =    90.647484,               J =            4
.0000  .0000  .1416  .0001  .0000  .2624  .0000  .0000  .0436  .0000  .2397  .1479  .0166  .0538  .0122  .0158  .0538  .0121
         DELC =        .000000,          FREQ =   318.744640,               J =            5
.0000  .0001  .0783  .0000  .0000  .1649  .0000  .0000  .0005  .0000  .3140  .1393  .0435  .0983  .0087  .0449  .0979  .0095
         DELC =        .000000,          FREQ =   346.505070,               J =            6
.1010  .3041  .0000  .2496  .0512  .0000  .0261  .0130  .0000  .1847  .0001  .0000  .0149  .0000  .0210  .0135  .0001  .0206
         DELC =        .000000,          FREQ =   635.249420,               J =            7
.1478  .4288  .0000  .0938  .1986  .0000  .0011  .0196  .0000  .0095  .0000  .0000  .0041  .0006  .0450  .0045  .0007  .0459
         DELC =        .000000,          FREQ =   829.755760,               J =            8
.0000  .0000  .0003  .0000  .0000  .0011  .0000  .0000  .1579  .0000  .2148  .0241  .2572  .0442  .0000  .2559  .0446  .0000
         DELC =        .000000,          FREQ =  1067.801300,               J =            9
.3349  .0088  .0799  .0004  .0033  .0001  .0131  .0078  .0054  .3606  .0029  .0202  .0031  .0075  .1308  .0120  .0073  .0079
         DELC =        .000000,          FREQ =  1088.146973,               J =           10
.0853  .0015  .2542  .0001  .0007  .0003  .0043  .0014  .0149  .0923  .0065  .0521  .0062  .0021  .1662  .0000  .0018  .3102
         DELC =        .000000,          FREQ =  1171.993027,               J =           11
.0382  .0277  .0000  .0004  .0102  .0000  .3525  .2767  .0004  .0000  .0001  .0001  .0004  .0001  .1593  .0001  .0001  .1338
         DELC =        .000000,          FREQ =  1189.499481,               J =           12
.0008  .0000  .0016  .0000  .0000  .0005  .0002  .0004  .5502  .0005  .1010  .1364  .0373  .0003  .0641  .0353  .0006  .0705
         DELC =        .000000,          FREQ =  1321.556519,               J =           13
.0012  .1204  .0000  .0011  .0001  .0000  .2681  .0613  .0000  .0186  .0000  .0000  .0039  .0001  .2635  .0037  .0001  .2580
         DELC =        .000000,          FREQ =  1426.702667,               J =           14
.0003  .0000  .2588  .0000  .0000  .0003  .0000  .0000  .2108  .0003  .0090  .2890  .0031  .0000  .1108  .0046  .0000  .1129
         DELC =        .000000,          FREQ =  1454.781876,               J =           15
.0227  .0011  .0000  .0001  .0001  .0000  .0000  .0009  .0000  .0317  .0000  .0000  .2873  .1842  .0004  .2867  .1842  .0006
         DELC =        .000000,          FREQ =  2855.486053,               J =           16
.0000  .0000  .0000  .0000  .0000  .0000  .0010  .0012  .0000  .0639  .0000  .0000  .1619  .3050  .0000  .1619  .3050  .0000
         DELC =        .000000,          FREQ =  2927.124908,               J =           17
.0000  .0000  .0000  .0000  .0000  .0000  .0000  .0000  .0003  .0000  .1119  .0000  .1408  .3031  .0000  .1408  .3031  .0000
         DELC =        .000000,          FREQ =  2984.324524,               J =           18
.0313  .0590  .0000  .0000  .0000  .0000  .3014  .6058  .0000  .0007  .0000  .0000  .0001  .0006  .0001  .0001  .0006  .0001
```

```
      DELC =      .349066,         FREQ =      8.051599,            J =          1
.1832 .0000 .0008 .5617 .0003 .0241 .0150 .0000 .0004 .1826 .0000 .0006 .0153 .0000 .0003 .0153 .0000 .0003
      DELC =      .349066,         FREQ =     40.190042,            J =          2
.C465 .C486 .0004 .0808 .7294 .0067 .0161 .0120 .0002 .0472 .0001 .0001 .0042 .0000 .0017 .0038 .0000 .0020
      DELC =      .349066,         FREQ =     57.235491,            J =          3
.0C41 .0018 .0296 .0130 .0063 .8125 .0003 .0001 .0000 .0028 .0599 .0299 .0036 .0130 .0030 .0043 .0130 .0028
      DELC =      .349066,         FREQ =    126.970289,            J =          4
.0021 .C066 .2674 .0023 .0001 .0002 .0008 .0002 .0597 .0004 .2150 .2714 .0146 .0482 .0244 .0143 .0482 .0242
      DELC =      .349066,         FREQ =    325.212990,            J =          5
.0C87 .C066 .1118 .0029 .0008 .1537 .0019 .0001 .0001 .0141 .2639 .1707 .0374 .0825 .0114 .0388 .0822 .0122
      DELC =      .349066,         FREQ =    347.996250,            J =          6
.C933 .2883 .0002 .2422 .0488 .0004 .0238 .0126 .0015 .1737 .0148 .0023 .0210 .0090 .0199 .0196 .0091 .0195
      DELC =      .349066,         FREQ =    633.642563,            J =          7
.1446 .4215 .C001 .0949 .1994 .0000 .0010 .0191 .0004 .0091 .0036 .0011 .0074 .0011 .0435 .0078 .0012 .0442
      DELC =      .349066,         FREQ =    833.392937,            J =          8
.0C55 .0067 .0004 .C000 .0003 .0010 .0006 .0007 .1569 .0014 .2104 .0251 .2510 .0429 .0020 .2495 .0434 .0023
      DELC =      .349066,         FREQ =   1056.581940,            J =          9
.2825 .CC99 .0942 .0005 .0035 .0001 .0106 .0075 .0029 .3507 .0013 .0120 .0052 .0065 .1272 .0118 .0062 .0673
      DELC =      .349066,         FREQ =   1095.884628,            J =         10
.1319 .C024 .2361 .C001 .0007 .0004 .0061 .0024 .0253 .0938 .0137 .0671 .0070 .0026 .1627 .0030 .0024 .2423
      DELC =      .349066,         FREQ =   1170.366119,            J =         11
.C283 .C284 .C00C .0004 .0093 .0000 .3251 .2533 .0426 .0009 .0072 .0071 .0035 .0001 .1546 .0031 .0001 .1360
      DELC =      .349066,         FREQ =   1193.757462,            J =         12
.0145 .CCC1 .0006 .0000 .0007 .0004 .0257 .0215 .5008 .0079 .0891 .1218 .0328 .0007 .0752 .0312 .0010 .0760
      DELC =      .349066,         FREQ =   1320.108170,            J =         13
.0C13 .1185 .0002 .0011 .0001 .0000 .2704 .0626 .0003 .0186 .0006 .0006 .0041 .0001 .2615 .0040 .0001 .2561
      DELC =      .349066,         FREQ =   1426.406143,            J =         14
.0C04 .C003 .2578 .0000 .000C .0003 .0000 .0000 .2081 .0003 .0085 .2900 .0032 .0002 .1119 .0047 .0002 .1140
      DELC =      .349066,         FREQ =   1454.593292,            J =         15
.0219 .0011 .0003 .0001 .0001 .000C .0000 .0008 .0006 .0322 .0000 .0003 .2868 .1843 .0004 .2862 .1842 .0005
      DELC =      .349066,         FREQ =   2855.454742,            J =         16
.0C00 .00C0 .0000 .0000 .0000 .0000 .0010 .0011 .0000 .0638 .0000 .0000 .1619 .3050 .0000 .1619 .3050 .0000
      DELC =      .349066,         FREQ =   2927.107849,            J =         17
.0000 .0000 .0000 .0000 .0000 .000C .0001 .0002 .0003 .0000 .1118 .0000 .1408 .3030 .0000 .1408 .3030 .0000
      DELC =      .349066,         FREQ =   2984.306854,            J =         18
.0312 .C590 .0000 .0000 .0000 .00C0 .3013 .6057 .000C .0007 .0001 .0000 .0002 .0007 .0001 .0002 .0007 .0001
```

```
          DELC =          .698132,             FREQ =     23.529515,                 J =              1
.1192  .0040  .0020  .5896  .0598  .0764  .0066  .0010  .0008  .1176  .0002  .0014  .0098  .0000  .0010  .0098  .0000  .0010
          DELC =          .698132,             FREQ =     40.676315,                 J =              2
.0899  .0451  .0017  .C125  .6571  .0491  .0218  .0109  .0008  .0899  .0000  .0010  .0080  .0002  .0021  .0077  .0002  .0021
          DELC =          .698132,             FREQ =     62.253693,                 J =              3
.0111  .0135  .0010  .0653  .0205  .6761  .0005  .0008  .004C  .0091  .1272  .0024  .0073  .0259  .0010  .0075  .0259  .0010
          DELC =          .698132,             FREQ =    196.157688,                 J =              4
.0231  .0237  .1682  .0016  .0000  .0961  .0058  .0005  .0467  .0104  .2564  .1730  .0183  .0581  .0209  .0184  .0580  .0208
          DELC =          .698132,             FREQ =    351.826778,                 J =              5
.0937  .2594  .0271  .2265  .0451  .0053  .0226  .0115  .0089  .1857  .0082  .0056  .0231  .0098  .0149  .0257  .0096  .0173
          DELC =          .698132,             FREQ =    356.501324,                 J =              6
.0C17  .0045  .2062  .0045  .0002  .0949  .0002  .0004  .0066  .0052  .1609  .2810  .0345  .0607  .0240  .0319  .0606  .0219
          DELC =          .698132,             FREQ =    629.540115,                 J =              7
.1369  .4030  .0004  .0978  .2016  .0002  .0008  .0179  .0009  .0076  .0130  .0045  .0151  .0022  .0398  .0154  .0023  .0405
          DELC =          .698132,             FREQ =    843.337112,                 J =              8
.0217  .0222  .0014  .0000  .0007  .0008  .0027  .0026  .1531  .0071  .1982  .0290  .2342  .0396  .0067  .2321  .0401  .0078
          DELC =          .698132,             FREQ =   1037.065231,                 J =              9
.2551  .C161  .0952  .0006  .0044  .0000  .0089  .0090  .0020  .3703  .0043  .0038  .0100  .0059  .1125  .0163  .0054  .0803
          DELC =          .698132,             FREQ =   1106.164978,                 J =             10
.1441  .0037  .2392  .0000  .0006  .0006  .0055  .0036  .0466  .0552  .0255  .0907  .0101  .0021  .1580  .0062  .0020  .2063
          DELC =          .698132,             FREQ =   1167.317200,                 J =             11
.0164  .0306  .0009  .0004  .0085  .0000  .2957  .2274  .0778  .0045  .0115  .0089  .0058  .0002  .1580  .0055  .0002  .1476
          DELC =          .698132,             FREQ =   1203.849716,                 J =             12
.0342  .COC1  .0002  .0000  .0011  .0003  .0497  .0402  .4474  .0206  .0732  .1024  .0269  .0014  .0896  .0259  .0016  .0851
          DELC =          .698132,             FREQ =   1315.903290,                 J =             13
.0013  .1130  .0006  .0010  .0001  .0000  .2767  .0664  .0014  .0187  .0023  .0024  .0047  .0001  .2560  .0046  .0001  .2506
          DELC =          .698132,             FREQ =   1425.322021,                 J =             14
.0006  .0011  .2547  .0000  .0001  .0003  .0001  .0000  .2005  .0002  .0070  .2929  .0035  .0006  .1153  .0050  .0006  .1174
          DELC =          .698132,             FREQ =   1454.048950,                 J =             15
.0198  .C0C9  .0012  .0001  .0001  .0000  .0000  .0008  .0023  .0336  .0001  .0010  .2857  .1845  .0002  .2849  .1844  .0004
          DELC =          .698132,             FREQ =   2855.369812,                 J =             16
.0000  .0000  .0000  .0000  .000C  .0000  .0009  .0010  .0000  .0637  .0000  .0000  .1620  .3051  .0000  .1620  .3051  .0000
          DELC =          .698132,             FREQ =   2927.062317,                 J =             17
.0000  .0000  .0000  .0000  .0000  .0000  .0005  .0007  .0003  .0000  .1116  .0000  .1406  .3028  .0000  .1407  .3028  .0000
          DELC =          .698132,             FREQ =   2984.261627,                 J =             18
.0311  .0590  .0000  .0000  .0000  .0000  .3011  .6053  .0000  .0006  .0002  .0000  .0002  .0009  .0001  .0002  .0009  .0001
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         DELC =       1.047198,            FREQ =     30.018087,             J =            1
.0066 .0373 .0002 .4144 .4911 .0289 .0007 .0084 .0000 .0063 .0020 .0002 .0008 .0000 .0012 .0008 .0000 .0012
         DELC =       1.047198,            FREQ =     53.026761,             J =            2
.0654 .C0C0 .0037 .0008 .0853 .6546 .0129 .0009 .0000 .0668 .0598 .0011 .0097 .0137 .0008 .0098 .0137 .0008
         DELC =       1.047198,            FREQ =     62.692419,             J =            3
.1215 .C472 .0029 .2713 .1633 .080C .0109 .0043 .0097 .1138 .1045 .0039 .0124 .0174 .0037 .0122 .0174 .0036
         DELC =       1.047198,            FREQ =    228.475094,             J =            4
.0682 .0384 .0503 .0003 .0004 .1956 .0148 .0006 .0226 .0399 .2951 .0672 .0227 .0661 .0144 .0229 .0660 .0145
         DELC =       1.047198,            FREQ =    358.495075,             J =            5
.0725 .2270 .0049 .2063 .0355 .0000 .0167 .0110 .0090 .1490 .0553 .0058 .0476 .0419 .0139 .0476 .0418 .0142
         DELC =       1.047198,            FREQ =    424.086063,             J =            6
.0C59 .C002 .3317 .C031 .0043 .0388 .0008 .0001 .0379 .0415 .0346 .3621 .0160 .0185 .0352 .0160 .0183 .0350
         DELC =       1.047198,            FREQ =    624.666939,             J =            7
.1289 .3786 .0019 .1016 .2037 .0004 .0006 .0163 .0007 .0049 .0254 .0117 .0227 .0031 .0365 .0229 .0031 .0370
         DELC =       1.047198,            FREQ =    857.223938,             J =            8
.0497 .C369 .0048 .0000 .0009 .0006 .0066 .0047 .1428 .0216 .1795 .0393 .2102 .0350 .0110 .2072 .0357 .0134
         DELC =       1.047198,            FREQ =   1017.309120,             J =            9
.2298 .C281 .0977 .0006 .0055 .0000 .0071 .0118 .0052 .3800 .0138 .0014 .0183 .0056 .0937 .0255 .0050 .0709
         DELC =       1.047198,            FREQ =   1114.016968,             J =           10
.1451 .0070 .2389 .0000 .0006 .0006 .0029 .0069 .0731 .0214 .0372 .1103 .0146 .0013 .1471 .0100 .0013 .1814
         DELC =       1.047198,            FREQ =   1164.082306,             J =           11
.0C82 .0322 .0068 .0003 .0079 .0000 .2712 .2051 .0876 .0080 .0104 .0050 .0059 .0004 .1753 .0059 .0004 .1693
         DELC =       1.047198,            FREQ =   1216.838654,             J =           12
.0483 .C016 .0043 .C001 .0011 .0001 .0666 .0499 .4120 .0278 .0606 .0875 .0226 .0020 .0984 .0221 .0021 .0931
         DELC =       1.047198,            FREQ =   1309.363861,             J =           13
.0C12 .1036 .0008 .0010 .0002 .0000 .2855 .0723 .0048 .0190 .0046 .0055 .0054 .0001 .2479 .0054 .0001 .2426
         DELC =       1.047198,            FREQ =   1422.892883,             J =           14
.0C09 .0022 .2489 .0000 .0002 .0003 .0001 .0000 .1903 .0002 .0051 .2976 .0036 .0009 .1208 .0051 .0010 .1227
         DELC =       1.047198,            FREQ =   1453.198608,             J =           15
.0166 .0007 .0020 .0001 .0001 .0000 .0000 .0007 .0042 .0357 .0002 .0016 .2843 .1851 .0001 .2834 .1850 .0003
         DELC =       1.047198,            FREQ =   2855.239471,             J =           16
.0000 .0000 .0000 .0000 .000C .0000 .0008 .0009 .0000 .0636 .0000 .0000 .1622 .3052 .0000 .1622 .3052 .0000
         DELC =       1.047198,            FREQ =   2926.993408,             J =           17
.0001 .0000 .0000 .0000 .0000 .0000 .0010 .0015 .0002 .0000 .1114 .0000 .1405 .3024 .0000 .1405 .3024 .0000
         DELC =       1.047198,            FREQ =   2984.192322,             J =           18
.0309 .C590 .0000 .0000 .0000 .0000 .3008 .6047 .0000 .0005 .0005 .0000 .0004 .0013 .0001 .0004 .0013 .0001
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      DELC =       1.396263,            FREQ =     27.138902,              J =          1
.0003  .0518  .0000  .3110  .5936  .0211  .0022  .0106  .0001  .0003  .0053  .0000  .0006  .0000  .0012  .0005  .0000  .0012
      DELC =       1.396263,            FREQ =     48.971233,              J =          2
.0004  .0276  .0002  .1163  .0002  .5941  .0020  .0004  .0033  .0008  .1751  .0000  .0068  .0322  .0008  .0069  .0322  .0008
      DELC =       1.396263,            FREQ =     87.414615,              J =          3
.1474  .0369  .0098  .2799  .1462  .1415  .0141  .0037  .0089  .1397  .0283  .0053  .0114  .0031  .0047  .0113  .0031  .0046
      DELC =       1.396263,            FREQ =    239.553902,              J =          4
.1212  .0313  .0112  .0036  .0041  .2245  .0230  .0003  .0077  .0716  .2702  .0363  .0236  .0605  .0134  .0238  .0604  .0134
      DELC =       1.396263,            FREQ =    367.180813,              J =          5
.0714  .2013  .0057  .1764  .0248  .0005  .0149  .0103  .0112  .1470  .0654  .0112  .0619  .0555  .0124  .0620  .0555  .0126
      DELC =       1.396263,            FREQ =    501.205795,              J =          6
.0018  .0108  .3329  .0079  .0142  .0161  .0000  .0006  .0666  .0678  .0046  .3347  .0183  .0105  .0423  .0183  .0104  .0422
      DELC =       1.396263,            FREQ =    621.234978,              J =          7
.1262  .3459  .0093  .1030  .1998  .0009  .0006  .0143  .0000  .0009  .0383  .0287  .0255  .0029  .0373  .0257  .0029  .0378
      DELC =       1.396263,            FREQ =    872.724686,              J =          8
.0902  .0429  .0166  .0000  .0006  .0004  .0130  .0062  .1173  .0501  .1546  .0639  .1807  .0295  .0120  .1761  .0305  .0156
      DELC =       1.396263,            FREQ =   1002.517670,              J =          9
.1898  .0476  .1091  .0006  .0067  .0000  .0042  .0164  .0189  .3606  .0304  .0028  .0312  .0060  .0746  .0400  .0051  .0559
      DELC =       1.396263,            FREQ =   1118.454651,              J =         10
.1472  .0141  .2240  .0001  .0010  .0006  .0004  .0153  .1028  .0043  .0476  .1236  .0201  .0007  .1280  .0147  .0009  .1547
      DELC =       1.396263,            FREQ =   1160.974121,              J =         11
.0024  .0310  .0249  .0003  .0071  .0000  .2399  .1759  .0828  .0086  .0069  .0010  .0047  .0006  .2072  .0049  .0006  .2015
      DELC =       1.396263,            FREQ =   1231.122711,              J =         12
.0558  .0063  .0147  .0002  .0009  .0001  .0915  .0601  .3804  .0262  .0516  .0763  .0198  .0023  .0978  .0197  .0023  .0942
      DELC =       1.396263,            FREQ =   1301.292618,              J =         13
.0008  .0895  .0004  .0008  .0004  .0000  .2912  .0782  .0149  .0199  .0065  .0109  .0058  .0002  .2395  .0059  .0001  .2349
      DELC =       1.396263,            FREQ =   1418.310654,              J =         14
.0013  .0034  .2390  .0001  .0003  .0003  .0002  .0000  .1796  .0002  .0032  .3035  .0032  .0011  .1288  .0045  .0011  .1303
      DELC =       1.396263,            FREQ =   1452.127441,              J =         15
.0128  .0005  .0023  .0001  .0001  .0000  .0000  .0006  .0055  .0383  .0002  .0018  .2833  .1861  .0001  .2825  .1860  .0001
      DELC =       1.396263,            FREQ =   2855.078339,              J =         16
.0000  .0000  .0000  .0000  .0000  .0000  .0006  .0007  .0000  .0633  .0000  .0000  .1624  .3052  .0000  .1624  .3052  .0000
      DELC =       1.396263,            FREQ =   2926.908569,              J =         17
.0001  .0000  .0000  .0000  .0000  .0000  .0017  .0025  .0002  .0000  .1111  .0000  .1403  .3019  .0000  .1403  .3019  .0000
      DELC =       1.396263,            FREQ =   2984.107880,              J =         18
.0307  .0590  .0000  .0000  .0000  .0000  .3005  .6039  .0000  .0004  .0008  .0000  .0005  .0017  .0001  .0005  .0017  .0001
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           DELC =       1.745329,            FREQ =     22.355015,                  J =            1
.0000  .0672  .0000  .2442  .6283  .0280  .0022  .0119  .0002  .0000  .0138  .0000  .0007  .0003  .0011  .0007  .0003  .0011
           DELC =       1.745329,            FREQ =     39.812308,                  J =            2
.0000  .0450  .0000  .2282  .0010  .4207  .0024  .0007  .0033  .0000  .2118  .0000  .0064  .0361  .0009  .0064  .0361  .0009
           DELC =       1.745329,            FREQ =    110.993520,                  J =            3
.0870  .0413  .0110  .2363  .1032  .3562  .0068  .0032  .0086  .0840  .0317  .0037  .0067  .0030  .0039  .0066  .0031  .0038
           DELC =       1.745329,            FREQ =    250.549265,                  J =            4
.1725  .0115  .0012  .0365  .0177  .1812  .0285  .0000  .0013  .0901  .2328  .0295  .0261  .0567  .0158  .0263  .0565  .0158
           DELC =       1.745329,            FREQ =    379.411369,                  J =            5
.0860  .1822  .0075  .1359  .0131  .0024  .0160  .0095  .0134  .1618  .0600  .0188  .0725  .0610  .0130  .0727  .0610  .0132
           DELC =       1.745329,            FREQ =    557.795677,                  J =            6
.0017  .0632  .2558  .0260  .0511  .0082  .0004  .0029  .0873  .1165  .0013  .2255  .0339  .0105  .0359  .0338  .0103  .0359
           DELC =       1.745329,            FREQ =    622.260521,                  J =            7
.1368  .2762  .0408  .0910  .1685  .0020  .0011  .0109  .0071  .0060  .0451  .0738  .0182  .0013  .0507  .0183  .0013  .0510
           DELC =       1.745329,            FREQ =    890.293915,                  J =            8
.1298  .0406  .0457  .0001  .0003  .0003  .0204  .0071  .0721  .0813  .1269  .1139  .1483  .0233  .0095  .1420  .0246  .0137
           DELC =       1.745329,            FREQ =    997.641861,                  J =            9
.1361  .0714  .1294  .0004  .0073  .0000  .0012  .0227  .0503  .3087  .0505  .0054  .0460  .0070  .0582  .0571  .0058  .0424
           DELC =       1.745329,            FREQ =   1118.482681,                  J =           10
.1514  .0266  .1910  .0001  .0017  .0005  .0014  .0303  .1302  .0025  .0557  .1309  .0259  .0006  .1029  .0199  .0008  .1275
           DELC =       1.745329,            FREQ =   1158.353683,                  J =           11
.0002  .0254  .0616  .0001  .0057  .0001  .1944  .1351  .0696  .0055  .0031  .0003  .0028  .0006  .2514  .0031  .0005  .2405
           DELC =       1.745329,            FREQ =   1245.339050,                  J =           12
.0572  .0179  .0311  .0004  .0009  .0000  .1498  .0820  .3328  .0172  .0474  .0644  .0192  .0021  .0786  .0192  .0022  .0777
           DELC =       1.745329,            FREQ =   1293.325867,                  J =           13
.0001  .0678  .0003  .0006  .0007  .0000  .2721  .0761  .0482  .0219  .0062  .0223  .0048  .0003  .2379  .0050  .0003  .2355
           DELC =       1.745329,            FREQ =   1410.693222,                  J =           14
.0019  .0046  .2227  .0001  .0004  .0003  .0002  .0000  .1695  .0002  .0016  .3101  .0024  .0009  .1402  .0033  .0009  .1408
           DELC =       1.745329,            FREQ =   1450.964279,                  J =           15
.0089  .0003  .0019  .0000  .0000  .0000  .0000  .0004  .0059  .0409  .0001  .0014  .2828  .1875  .0001  .2823  .1874  .0000
           DELC =       1.745329,            FREQ =   2854.905731,                  J =           16
.0000  .0000  .0000  .0000  .0000  .0000  .0004  .0005  .0001  .0631  .0000  .0000  .1626  .3053  .0000  .1626  .3053  .0000
           DELC =       1.745329,            FREQ =   2926.818115,                  J =           17
.0001  .0001  .0000  .0000  .0000  .0000  .0025  .0036  .0001  .0000  .1108  .0000  .1400  .3013  .0000  .1401  .3014  .0000
           DELC =       1.745329,            FREQ =   2984.017792,                  J =           18
.0305  .0589  .0000  .0000  .0000  .0000  .3001  .6031  .0000  .0003  .0012  .0000  .0007  .0022  .0001  .0006  .0022  .0001
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          DELC =      2.094395,           FREQ =    16.550159,            J =          1
.0000 .09C8 .0000 .1672 .6488 .0376 .0016 .0134 .0004 .0000 .0342 .0000 .0007 .0015 .0009 .0007 .0015 .0009
          DELC =      2.094395,           FREQ =    29.672337,            J =          2
.0000 .0536 .0000 .3565 .0046 .2545 .0036 .0006 .0023 .0000 .2341 .0000 .0061 .0383 .0006 .0062 .0383 .0006
          DELC =      2.094395,           FREQ =   123.844499,            J =          3
.0360 .0380 .0093 .1579 .0635 .5940 .0020 .0024 .0063 .0397 .0331 .0017 .0030 .0031 .0020 .0030 .0031 .0020
          DELC =      2.094395,           FREQ =   267.475544,            J =          4
.1928 .0001 .0000 .1104 .0397 .0989 .0283 .0007 .0000 .0753 .2063 .0264 .0314 .0605 .0186 .0318 .0603 .0185
          DELC =      2.094395,           FREQ =   398.086720,            J =          5
.1215 .1641 .0102 .0840 .0030 .0057 .0203 .0084 .0161 .1859 .0424 .0317 .0775 .0578 .0180 .0776 .0578 .0181
          DELC =      2.094395,           FREQ =   580.385475,            J =          6
.0051 .1549 .1445 .0574 .1128 .0047 .0010 .0066 .0806 .1571 .0164 .0977 .0528 .0111 .0167 .0527 .0109 .0170
          DELC =      2.094395,           FREQ =   626.470596,            J =          7
.1643 .17C3 .0786 .0649 .1109 .0036 .0034 .0063 .0338 .0621 .0382 .1073 .0091 .0005 .0687 .0090 .0005 .0687
          DELC =      2.094395,           FREQ =   914.296265,            J =          8
.1403 .0414 .0819 .0001 .0003 .0003 .0266 .0091 .0273 .0813 .1079 .1810 .1232 .0180 .0118 .1148 .0195 .0150
          DELC =      2.094395,           FREQ =  1003.691696,            J =          9
.0885 .C865 .1627 .0002 .007C .0000 .0001 .0285 .0939 .2523 .0620 .0076 .0527 .0076 .0447 .0670 .0060 .0326
          DELC =      2.094395,           FREQ =  1113.650833,            J =         10
.1585 .C430 .1483 .0001 .0028 .0003 .0049 .0463 .1417 .0092 .0611 .1361 .0316 .0008 .0807 .0247 .0012 .1087
          DELC =      2.094395,           FREQ =  1156.228058,            J =         11
.0C18 .C170 .1109 .0001 .0040 .0002 .1354 .0880 .0589 .0015 .0009 .0030 .0014 .0005 .2985 .0016 .0004 .2761
          DELC =      2.094395,           FREQ =  1256.101410,            J =         12
.0497 .0443 .0413 .0008 .0014 .00C0 .3068 .1389 .2113 .0045 .0494 .0381 .0215 .0016 .0340 .0216 .0015 .0335
          DELC =      2.094395,           FREQ =  1289.868866,            J =         13
.0025 .0312 .0147 .0002 .0007 .0000 .1627 .0433 .1628 .0247 .0015 .0514 .0014 .0007 .2476 .0016 .0007 .2523
          DELC =      2.094395,           FREQ =  1399.386490,            J =         14
.0031 .0055 .1962 .0001 .0005 .0002 .0002 .0000 .1588 .0001 .0005 .3172 .0015 .0006 .1570 .0019 .0006 .1558
          DELC =      2.094395,           FREQ =  1449.867569,            J =         15
.0053 .0002 .0013 .0000 .0000 .0000 .0000 .0003 .0058 .0433 .0001 .0008 .2826 .1889 .0001 .2825 .1888 .0000
          DELC =      2.094395,           FREQ =  2854.741730,            J =         16
.0000 .0000 .0000 .0000 .0000 .0000 .0003 .0003 .0001 .0629 .0000 .0000 .1628 .3054 .0000 .1628 .3054 .0000
          DELC =      2.094395,           FREQ =  2926.733582,            J =         17
.0002 .0001 .0000 .0000 .000C .0000 .0031 .0046 .0001 .0000 .1105 .0000 .1398 .3008 .0000 .1399 .3009 .0000
          DELC =      2.094395,           FREQ =  2983.934021,            J =         18
.0303 .0589 .0000 .0000 .0000 .0000 .2997 .6024 .0000 .0002 .0015 .0001 .0008 .0026 .0001 .0008 .0026 .0001
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        DELC =      2.443461,           FREQ =     10.218006,                J =          1
.0000 .1231 .0000 .0922 .6457 .0365 .0009 .0147 .0004 .0000 .0747 .0000 .0006 .0048 .0006 .0006 .0048 .0006
        DELC =      2.443461,           FREQ =     19.830628,                J =          2
.0000 .0513 .0000 .4813 .0279 .1118 .0049 .0005 .0011 .0000 .2328 .0000 .0060 .0378 .0003 .0061 .0378 .0003
        DELC =      2.443461,           FREQ =    127.425830,                J =          3
.0109 .0231 .0070 .0769 .0300 .7976 .0004 .0013 .0037 .0182 .0222 .0005 .0013 .0020 .0007 .0013 .0020 .0007
        DELC =      2.443461,           FREQ =    284.725910,                J =          4
.1734 .0070 .0002 .1867 .0557 .0371 .0234 .0022 .0000 .0371 .1968 .0215 .0397 .0709 .0188 .0403 .0706 .0187
        DELC =      2.443461,           FREQ =    425.959740,                J =          5
.1742 .1456 .0129 .0352 .0003 .0073 .0268 .0072 .0179 .1890 .0218 .0525 .0762 .0490 .0295 .0760 .0490 .0295
        DELC =      2.443461,           FREQ =    581.223373,                J =          6
.0007 .1537 .1092 .0537 .1086 .0055 .0022 .0064 .0853 .2442 .0204 .0532 .0576 .0103 .0102 .0581 .0102 .0106
        DELC =      2.443461,           FREQ =    620.814392,                J =          7
.2010 .1580 .0507 .0724 .1158 .0032 .0052 .0057 .0343 .0983 .0428 .0653 .0124 .0004 .0612 .0115 .0005 .0612
        DELC =      2.443461,           FREQ =    943.983627,                J =          8
.1218 .0566 .0821 .0001 .0008 .0002 .0326 .0156 .0062 .0492 .1061 .2260 .1154 .0153 .0252 .1044 .0172 .0253
        DELC =      2.443461,           FREQ =   1016.966103,                J =          9
.0577 .0790 .2244 .0001 .0056 .0001 .0011 .0290 .1425 .2205 .0550 .0105 .0432 .0069 .0323 .0627 .0047 .0246
        DELC =      2.443461,           FREQ =   1104.667999,                J =         10
.1754 .0618 .1058 .0001 .0040 .0002 .0060 .0571 .1239 .0164 .0659 .1480 .0377 .0012 .0644 .0290 .0018 .1013
        DELC =      2.443461,           FREQ =   1154.083282,                J =         11
.0034 .0089 .1592 .0000 .0021 .0002 .0727 .0446 .0581 .0001 .0003 .0043 .0009 .0003 .3413 .0008 .0002 .3026
        DELC =      2.443461,           FREQ =   1257.572433,                J =         12
.0323 .0631 .0225 .0010 .0024 .0000 .4876 .2018 .0597 .0000 .0488 .0095 .0218 .0008 .0137 .0221 .0008 .0119
        DELC =      2.443461,           FREQ =   1298.073700,                J =         13
.0105 .0035 .0711 .0000 .0004 .0000 .0329 .0065 .3204 .0190 .0003 .0798 .0001 .0011 .2183 .0001 .0012 .2348
        DELC =      2.443461,           FREQ =   1384.423798,                J =         14
.0058 .0063 .1541 .0002 .0007 .0002 .0001 .0000 .1408 .0000 .0000 .3282 .0009 .0004 .1833 .0009 .0004 .1778
        DELC =      2.443461,           FREQ =   1448.985443,                J =         15
.0024 .0001 .0008 .0000 .0000 .0000 .0000 .0001 .0055 .0452 .0000 .0003 .2825 .1900 .0002 .2826 .1900 .0000
        DELC =      2.443461,           FREQ =   2854.607513,                J =         16
.0000 .0000 .0000 .0000 .0000 .0000 .0001 .0001 .0001 .0627 .0000 .0000 .1630 .3055 .0000 .1630 .3054 .0000
        DELC =      2.443461,           FREQ =   2926.664429,                J =         17
.0002 .0001 .0000 .0000 .0000 .0000 .0037 .0054 .0000 .0000 .1103 .0000 .1397 .3004 .0000 .1397 .3005 .0000
        DELC =      2.443461,           FREQ =   2983.865295,                J =         18
.0302 .0589 .0000 .0000 .0000 .0000 .2994 .6018 .0000 .0001 .0018 .0001 .0009 .0030 .0000 .0009 .0029 .0000
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        DELC =      2.792527,          FREQ =      4.107531,             J =            1
.0000 .1539 .0000 .0584 .6010 .0163 .0006 .0151 .0002 .0000 .1318 .0000 .0006 .0106 .0002 .0006 .0106 .0002
        DELC =      2.792527,          FREQ =     11.156023,             J =            2
.0000 .0429 .0000 .5528 .0876 .0246 .0057 .0010 .0002 .0000 .2050 .0000 .0059 .0341 .0001 .0059 .0341 .0001
        DELC =      2.792527,          FREQ =    127.048115,             J =            3
.0021 .0069 .0056 .0203 .0079 .9343 .0000 .0004 .0022 .0104 .0070 .0001 .0007 .0006 .0001 .0007 .0006 .0001
        DELC =      2.792527,          FREQ =    295.765736,             J =            4
.1469 .0197 .0001 .2310 .0613 .0079 .0188 .0035 .0000 .0088 .1942 .0171 .0476 .0802 .0172 .0484 .0800 .0172
        DELC =      2.792527,          FREQ =    459.661556,             J =            5
.2302 .1414 .0103 .0083 .0079 .0044 .0342 .0067 .0132 .1187 .0083 .0845 .0741 .0435 .0486 .0736 .0436 .0485
        DELC =      2.792527,          FREQ =    568.193016,             J =            6
.0067 .0593 .1199 .0157 .0374 .0107 .0033 .0025 .1146 .4588 .0056 .0317 .0490 .0067 .0104 .0506 .0066 .0106
        DELC =      2.792527,          FREQ =    610.391602,             J =            7
.2009 .2323 .0099 .1121 .1815 .0010 .0036 .0086 .0084 .0331 .0641 .0210 .0237 .0008 .0382 .0218 .0008 .0384
        DELC =      2.792527,          FREQ =    968.697830,             J =            8
.0964 .0858 .0372 .0000 .0021 .0001 .0404 .0276 .0026 .0157 .1186 .2323 .1234 .0151 .0405 .1092 .0174 .0359
        DELC =      2.792527,          FREQ =   1032.357697,             J =            9
.0302 .0430 .3235 .0000 .0029 .0002 .0017 .0183 .2060 .2167 .0299 .0106 .0190 .0049 .0251 .0469 .0020 .0190
        DELC =      2.792527,          FREQ =   1093.624649,             J =           10
.2110 .0862 .0547 .0001 .0056 .0001 .0048 .0665 .0688 .0164 .0752 .1736 .0473 .0018 .0503 .0340 .0027 .1010
        DELC =      2.792527,          FREQ =   1151.926331,             J =           11
.0026 .0027 .1958 .0000 .0006 .0003 .0210 .0125 .0648 .0011 .0002 .0025 .0008 .0001 .3748 .0003 .0001 .3199
        DELC =      2.792527,          FREQ =   1254.285782,             J =           12
.0230 .0604 .0056 .0010 .0033 .0000 .5590 .2295 .0097 .0001 .0472 .0024 .0207 .0006 .0082 .0210 .0005 .0079
        DELC =      2.792527,          FREQ =   1313.819702,             J =           13
.0078 .0000 .1523 .0000 .0002 .0001 .0035 .0004 .4119 .0111 .0007 .0631 .0004 .0012 .1572 .0003 .0012 .1885
        DELC =      2.792527,          FREQ =   1367.454880,             J =           14
.0114 .0067 .0846 .0002 .0008 .0001 .0000 .0000 .0921 .0001 .0003 .3609 .0007 .0002 .2289 .0003 .0002 .2127
        DELC =      2.792527,          FREQ =   1448.420090,             J =           15
.0006 .0000 .0006 .0000 .0000 .0000 .0000 .0000 .0053 .0464 .0000 .0001 .2824 .1907 .0002 .2827 .1907 .0001
        DELC =      2.792527,          FREQ =   2854.519226,             J =           16
.0000 .0000 .0001 .0000 .0000 .0000 .0000 .0000 .0001 .0626 .0000 .0000 .1631 .3055 .0000 .1631 .3055 .0000
        DELC =      2.792527,          FREQ =   2926.619537,             J =           17
.0002 .0001 .0000 .0000 .0000 .0000 .0041 .0059 .0000 .0000 .1101 .0000 .1395 .3002 .0000 .1396 .3003 .0000
        DELC =      2.792527,          FREQ =   2983.821381,             J =           18
.0300 .0589 .0000 .0000 .0000 .0000 .2992 .6014 .0000 .0000 .0019 .0001 .0010 .0032 .0000 .0010 .0032 .0000
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          DELC =       3.141593,              FREQ =        .000000,                J =            1
.0000  .1909  .0000  .0000  .5702  .0000  .0000  .0160  .0000  .0000  .1908  .0000  .0000  .0160  .0000  .0000  .0160  .0000
          DELC =       3.141593,              FREQ =       5.860341,                J =            2
.0000  .0144  .0000  .6257  .1241  .0000  .0065  .0005  .0000  .0000  .1570  .0000  .0065  .0295  .0000  .0065  .0295  .0000
          DELC =       3.141593,              FREQ =     126.501095,                J =            3
.0000  .0000  .0051  .0000  .0000  .9836  .0000  .0000  .0017  .0084  .0000  .0000  .0006  .0000  .0000  .0006  .0000  .0000
          DELC =       3.141593,              FREQ =     299.328583,                J =            4
.1366  .0251  .0000  .2438  .0621  .0000  .0172  .0039  .0000  .0000  .1935  .0155  .0508  .0836  .0165  .0516  .0833  .0164
          DELC =       3.141593,              FREQ =     479.663044,                J =            5
.2744  .1587  .0000  .0016  .0189  .0000  .0410  .0074  .0000  .0000  .0038  .1171  .0766  .0455  .0670  .0755  .0456  .0669
          DELC =       3.141593,              FREQ =     554.690308,                J =            6
.0001  .0001  .1301  .0001  .0001  .0156  .0000  .0000  .1347  .6352  .0000  .0000  .0395  .0008  .0006  .0417  .0007  .0006
          DELC =       3.141593,              FREQ =     606.906776,                J =            7
.1843  .2653  .0001  .1276  .2092  .0000  .0025  .0099  .0001  .0001  .0724  .0103  .0303  .0015  .0281  .0282  .0015  .0285
          DELC =       3.141593,              FREQ =     976.068832,                J =            8
.0848  .1029  .0063  .0000  .0029  .0000  .0447  .0350  .0027  .0029  .1270  .2266  .1299  .0154  .0459  .1141  .0179  .0390
          DELC =       3.141593,              FREQ =    1040.743942,                J =            9
.0026  .0109  .3968  .0000  .0066  .0003  .0017  .0058  .2606  .2255  .0095  .0014  .0007  .0038  .0259  .0358  .0002  .0160
          DELC =       3.141593,              FREQ =    1087.206940,                J =           10
.2459  .1076  .0066  .0000  .0071  .0000  .0040  .0755  .0144  .0081  .0860  .1983  .0571  .0022  .0417  .0383  .0035  .1037
          DELC =       3.141593,              FREQ =    1150.916382,                J =           11
.0015  .0002  .2101  .0000  .0000  .0003  .0000  .0001  .0693  .0019  .0001  .0008  .0007  .0000  .3884  .0002  .0000  .3262
          DELC =       3.141593,              FREQ =    1252.640076,                J =           12
.0206  .0578  .0000  .0010  .0037  .0000  .5790  .2385  .0000  .0000  .0468  .0014  .0203  .0005  .0043  .0207  .0005  .0050
          DELC =       3.141593,              FREQ =    1324.238925,                J =           13
.0004  .0000  .2381  .0000  .0000  .0002  .0000  .0000  .5097  .0083  .0000  .0009  .0003  .0013  .0944  .0003  .0014  .1446
          DELC =       3.141593,              FREQ =    1356.861038,                J =           14
.0186  .0072  .0020  .0003  .0010  .0000  .0000  .0000  .0015  .0000  .0009  .4274  .0008  .0001  .2870  .0001  .0000  .2530
          DELC =       3.141593,              FREQ =    1448.227066,                J =           15
.0000  .0000  .0005  .0000  .0000  .0000  .0000  .0000  .0052  .0469  .0000  .0001  .2824  .1910  .0002  .2828  .1909  .0001
          DELC =       3.141593,              FREQ =    2854.489990,                J =           16
.0000  .0000  .0001  .0000  .0000  .0000  .0000  .0000  .0001  .0626  .0000  .0000  .1631  .3055  .0000  .1631  .3055  .0000
          DELC =       3.141593,              FREQ =    2926.605377,                J =           17
.0002  .0001  .0000  .0000  .0000  .0000  .0042  .0061  .0000  .0000  .1100  .0000  .1395  .3001  .0000  .1396  .3002  .0000
          DELC =       3.141593,              FREQ =    2983.807373,                J =           18
.0300  .0589  .0000  .0000  .0000  .0000  .2992  .6012  .0000  .0000  .0020  .0001  .0010  .0033  .0000  .0010  .0032  .0000
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