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Vibrational analysis of trans-polyacetylene : (CH)ₓ and (CD)ₓ

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1. Introduction.

Polyacetylene, (CH)ₓ, has attracted great interest recently because of its conductivity properties when doped with appropriate dopants such as I₂ or AsF₅ [1, 2]. Although the pristine polymer has not yet been polymerized in a crystalline form, Raman and IR spectroscopies are very important techniques for elucidating its structure and both experimental and theoretical papers have already been published [3-12]. In this paper, we are concerned only with the trans isomer which is the more thermodynamically stable form of (CH)ₓ. Raman spectra were recorded using different exciting wavelengths from λ = 406.7 nm to λ = 676.4 nm. The two main modes observed in trans-(CH)ₓ (1060 and 1450 cm⁻¹) are strongly enhanced by resonance effects and shifted in frequency when the exciting laser line is changed. In addition, they show a double band structure for excitations in the blue range.

This change in the Raman band profile with different laser excitations has been explained using different models. Qualitatively, it was suggested by different authors [6, 10, 11] that it was due to a dispersion in the conjugation length of the trans-(CH)ₓ isomer. More quantitatively, a good fit to experimental Raman spectra was given using one or two distributions of conjugation length [10, 13, 14], either taking or not taking into account the electron-phonon interaction.

More recently, Mele [15] suggested that the high-frequency component of the Raman bands could be a result of a hot luminescence process induced by long chains. By dynamical calculations, several types of structural defects have also been studied by Zannoni and Zerbi [16]. They show that the activation of the perturbed density of states may affect the interpretation of the Raman spectra.

In this paper we present calculations of in-plane optical vibrational modes in trans-(CH)ₓ and in its deuterated derivative (CD)ₓ. The calculations were performed for an infinite chain from which results for shorter molecules were derived. The purpose is to explain the main features of the experimental spectra using the minimum number of free parameters (force constants).

2. Calculation method.

Wilson’s well-known GF matrix method [17] has been a very efficient technique for calculating the normal vibrations of polyatomic molecules because the force constants are expressed in terms of internal coordinates which have a direct meaning in chemistry. Similar calculations have also been made on long linear polymers [18]. For a perfect infinite chain, i.e. for a polymer having translational symmetry in one direction, from the point of view of a dynamical theory, the system can be considered as being more like a crystal
than a molecule. So, Fourier's dynamical matrix $D$ [19] seems more appropriate for the treatment of vibrations of long polymers than the $GF$ matrix for the following reasons:

a) the $D$ matrix is expressed in terms of Cartesian coordinates; we have no redundant Cartesian coordinates; the eigenvectors of the matrix $D$ directly provide the Cartesian components of each normal mode;

b) the $D$ matrix is Hermitian; the $GF$ matrix is not symmetric;

c) the dispersion curves $v(q)$ can be easily obtained in the reciprocal lattice.

Details of the methods calculation are given in appendix I.

3. Force constants and in-plane normal mode frequencies of $(CH)_x$ and $(CD)_x$.

The geometrical arrangement of the four atoms of the trans-$(CH)_x$ unit cell is shown in figure 1. In this figure, as given in reference [5], $l(C=C) = 1.34 \text{ Å}$, $l(C-C) = 1.48 \text{ Å}$, $l(C-H) = 1.08 \text{ Å}$ and $\alpha(C-C-C) = \alpha(C-C-H) = 120^\circ$. The factor group of trans-polyacetylene is isomorphous to the point group $C_{2n}$. At the centre of the Brillouin zone ($q = 0$) and in the plane of the molecule, four modes are Raman active ($A_g$ symmetry) and four modes are IR active ($B_u$ symmetry), two of them being translational motions of the polymer as a whole ($v = 0$).

Among the various experimental and theoretical results published, some uncertainties exist. For example, in the experimental Raman spectrum, a weak band appears at 1010 cm$^{-1}$ (or 740 cm$^{-1}$ in (CD)$_x$). As previously mentioned by Inagaki et al. [5], this vibrational mode corresponds to an ungerade mode at $q = 0$. It may also be assigned to an out-of-plane vibration mode. In any case, calculations of the normal mode frequencies at $q = 0$ in (CH)$_x$ (or in (CD)$_x$) with various values of force constants never led to the assignment of the 1010 cm$^{-1}$ mode to an in-plane Raman mode. Therefore, we have fitted our force constants according to the attribution given by Schügerl and Kuzmany [11]. In table I, we have reported the most significant data.

### Table I. — Vibration frequencies (in cm$^{-1}$) of trans-$(CH)_x$ and trans-$(CD)_x$ observed and calculated by different authors.

<table>
<thead>
<tr>
<th>References</th>
<th>Experimental</th>
<th>Theoretical</th>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman ($A_g$ modes)</td>
<td>1 060</td>
<td>1 072</td>
<td>1 064</td>
<td>1 060</td>
</tr>
<tr>
<td>IR ($B_u$ modes)</td>
<td>1 285</td>
<td>1 290</td>
<td>1 294</td>
<td>1 285</td>
</tr>
</tbody>
</table>

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Fig. 1. — Internal coordinates of a trans-polyacetylene chain.
the twenty four force constants given by Schügerl and Kuzmany [11].

It may be easily shown that, at \( q = 0 \), \( K(a^2) + 2 K(a, a) \) and \( K(b^2) + 2 K(b, b) \) are matrix elements of \( F_{op} \) (App. I). So, these terms are fitted to the experimental frequencies (eqs. (A.7) and (A.8)). Therefore, several choices of \( K(a^2) \) and \( K(a, a) \), as well as \( K(b^2) \) and \( K(b, b) \) can be made, since their sum remains constant. In order to limit the variation range of \( K(a^2) \) and \( K(b^2) \), two sets of parameters (force constants I and II) have been used in our calculations. In set I, the values of \( K(a^2) \) and \( K(b^2) \) are 5.42 and 3.4 mdy/rad.\(^{-1} \) respectively and in set II, they are 8.2 and 4.6 mdy/rad.\(^{-1} \). Those from set I are rather close to those proposed by Inagaki et al. [5] whereas those from set II resemble those given by Schügerl and Kuzmany [11] (deduced from ref. [20]). Nevertheless, a direct comparison is very difficult since the attribution of the experimental frequencies given in [5] is not exactly the same as ours and in reference [11], the parameters are different. For the two sets of parameters, the frequencies at \( q = 0 \) are the same since\( K(a^2) + 2 K(a, a) \) and \( K(b^2) + 2 K(b, b) \) are unchanged. However, they differ greatly at \( q \neq 0 \). \( K(q^2 \alpha \beta) \) has no effect on the frequencies at \( q = 0 \) but contributes when \( q \neq 0 \).

### 3.2 Attempt to explain the main features of Raman spectra.

#### 3.2.1 Normal modes and frequencies at \( q = 0 \).

From the force constants (I or II), the normal modes (eigenvectors and frequencies) are calculated at \( q = 0 \) in (CH)\(_x\) and (CD)\(_x\) (Fig. 2 and table I). Except for the 808 cm\(^{-1} \) frequency mode in (CD)\(_x\), good agreement is found between calculated and experimental frequencies (table I).

![Fig. 2. Calculated reduced displacements (eigenvectors) of the six in-plane modes of trans-(CH)\(_x\).](image)

#### 3.2.2 Frequency shift of the Raman lines with exciting wavelengths.

— The frequency shifts of the modes 1 and 3 (fig. 2) to higher frequencies when \( \lambda \) decreases is generally interpreted as an increase of force constants with decreasing chain length [5, 11]. Between \( \lambda = 676.4 \) nm and \( \lambda = 406.7 \) nm, the \( \Delta \nu \) frequency ranges within which the Raman lines (modes 1 and 3) are shifted are about 100 and 120 cm\(^{-1} \) for (CH)\(_x\) and 40 and 160 cm\(^{-1} \) for (CD)\(_x\) respectively. \( \Delta \nu \) is very small for mode 2 in both (CH)\(_x\) and (CD)\(_x\). In order to know which force constant affects the frequency of the Raman modes, calculations have been performed increasing separately each force constant by 30%. It turns out that only a variation of \( K(a^2) \) (or C=C stretch) can explain the \( \Delta \nu \) experimental value. In table III, we have reported the \( \Delta \nu \) calculated values obtained from an increase of 30% of \( K(a^2) \) in both sets of parameters I or II. On the one hand, it is observed that \( \Delta \nu(I) \) and \( \Delta \nu(II) \) are too small for mode 1 while for mode 3, \( \Delta \nu(\text{exp}) \) is between \( \Delta \nu(I) \) and \( \Delta \nu(II) \). So, it is not possible to get a calculated \( \Delta \nu \) value for modes 1 and 3 in good agreement with the experimental one. However, in the case of (CD)\(_x\), \( \Delta \nu(I) \) or \( \Delta \nu(II) \) are found to be much smaller for mode 1 and much larger for mode 3 than in (CH)\(_x\), qualitatively in agreement with the experimental data. Similar results were found in reference [11].

#### 3.2.3 Intensities of the Raman lines.

— In (CH)\(_x\) (or in (CD)\(_x\)), the observed absorption band in the visible range is probably due to a transition from the bonding \( \pi \) state to the antibonding \( \pi^* \) state of the electrons of the double carbon-carbon bonds (C=C). Therefore, in a first approximation, as we are in resonance conditions, only Raman lines corresponding to normal modes with large displacements along the C=C bond will be strongly enhanced by resonance effects [3, 5, 11]. The relative experimental intensities of the Raman lines of modes 1, 2, 3 in an infinite chain are given in table IV. The most important feature is the intensity of mode 2 in (CD)\(_x\) which is about twenty times stronger than in (CH)\(_x\) [7]. Schügerl et al. [11] assigned this result to a much stronger C=C bond stretch in (CD)\(_x\) than in (CH)\(_x\). Since the Raman intensities, to a good approximation, can be taken to be proportional to the square of the C=C bond stretch, the relative intensities of the Raman modes can be easily calculated from the eigenvector components. The results obtained from our calculations are given in table IV and compared with those deduced from reference [11]. They can...
Table III. — Frequency shifts $\Delta \nu$ (in cm$^{-1}$) of Raman lines calculated with a 30% increase of the force constant $K(a^2)$. $\Delta \nu(I)$ is calculated with parameters from set I [$K(a^2) = 5.42$ mdyn.$\text{Å}^{-1}$] and $\Delta \nu(II)$ from set II [$K(a^2) = 8.2$ mdyn.$\text{Å}^{-1}$]. These values are compared to the experimental $\Delta \nu$ frequency shifts between $\lambda_L = 676.4$ and 406.7 nm.

<table>
<thead>
<tr>
<th></th>
<th>(CH)$_x$</th>
<th>(CD)$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>modes</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Theoretical $\nu$</td>
<td>1 055</td>
<td>1 281</td>
</tr>
<tr>
<td>Experiment $\Delta \nu$</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>Theoretical $\Delta \nu(I)$</td>
<td>57</td>
<td>1</td>
</tr>
<tr>
<td>Theoretical $\Delta \nu(II)$</td>
<td>75</td>
<td>1</td>
</tr>
</tbody>
</table>

Table IV. — Relative intensities of the Raman lines, normalized to the intensity of mode 1: a) deduced from the calculations of reference [11]; b) from our work.

<table>
<thead>
<tr>
<th></th>
<th>(CH)$_x$</th>
<th>(CD)$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>modes</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>exper.</td>
<td>1</td>
<td>0.009</td>
</tr>
<tr>
<td>calcul. a</td>
<td>1</td>
<td>0.005</td>
</tr>
<tr>
<td>calcul. b</td>
<td>1</td>
<td>0.01</td>
</tr>
</tbody>
</table>

explain the strong increase in intensity of mode 2 on going from (CH)$_x$ to (CD)$_x$, but fail completely in their estimation of the intensities of the other modes. In fact, this could be expected because mode 3, which is assigned to the C═C stretch (see fig. 2), is found experimentally to be less intense in (CH)$_x$ than mode 1 assigned mainly to the C—C stretch. Therefore, the model is probably too crude and other factors should be taken into account in the calculations of the Raman lines intensities.


4.1 PHONON DISPERSION CURVES. — The experimental dispersion curves being unknown, we have calculated the phonon dispersion curves using two sets of parameters. The method of calculation is given in section 3, appendix I. The curves $v(\phi)$ (where $\phi = q.a$; $q$ : wavevector; $a$ : unit cell parameter) corresponding to $\phi = 0$ for the modes 1, 2, 3 and 5 (fig. 2) are very different according to which set of force constants (I or II) is used. In figures 3 and 4 we show these curves for (CH)$_x$ and (CD)$_x$ respectively. On the other hand, the curves corresponding to modes 4 and 6 and to the acoustic ones are not very dependent on the choice of parameters (force constants I or II) as shown in figure 5. It is observed that, using the set of force constants I, the curves $v(\phi)$ are rather flat. On the other hand, using the set of force constants II causes $v(\phi)$ to increase rapidly with $\phi$, especially for the curves 1 and 3 in (CH)$_x$ and 3 in (CD)$_x$.

4.2 UNPERTURBED DENSITY OF STATES. — We have calculated the full unperturbed density of states $\rho(\omega) = \sum \delta(\omega_q - \omega$) of an infinite chain of trans-
Fig. 4. — Dispersion curves calculated for trans-(CD)$_x$ :
(-----) force constants I; (---) force constants II.

Fig. 5. — Dispersion curves calculated for trans-(CH)$_x$ for the two acoustical modes and for the two highest frequency modes :
(-----) force constants I; (---) force constants II.

Fig. 6. — A and B : active Raman frequencies of trans-(CH)$_x$ molecules with respectively seven and twenty three C=C bonds; N is the number of modes at the corresponding frequency; C : total unperturbed phonon density of states $\rho(\omega)$ in an infinite chain of trans-(CH)$_x$. The width of the histogram bins is 4 cm$^{-1}$. The arrows indicate the modes at $q = 0$; the dashed curve represents the density of states projected on the C=C bonds. The dispersion of frequencies for $q \neq 0$ seemed to us too large with the parameters from set II (from 1 450 to 1 850 cm$^{-1}$), so we did the calculations using only the force constants from set I. In figure 6C, the solid curve represents the results obtained for (CH)$_x$ in the frequency range 1 050-1 500 cm$^{-1}$ (corresponding to the frequency range of the dispersion curves 1, 2, 3 and 5 (fig. 3)). We have also shown the density of states (with force constants I) projected onto the C=C bond (fig. 6C, dashed line). Similar calculations were performed for (CD)$_x$, and the results are shown in figure 7. In figure 6C (or 7C), the Raman active modes for the infinite chain are indicated by arrows (corresponding to $q = 0$). But the other modes can be activated when the translational symmetry of the chain is destroyed, either by impurities or when the chain is no longer infinite. As an example, the vibration frequencies of trans-(CH)$_x$ (and (CD)$_x$) « molecules » have been calculated, in an arbitrary fashion, for seven and twenty three double carbon bonds (C=C) (figs. 6A and 6B in (CH)$_x$, 7A and 7B in (CD)$_x$). Their point group $C_{2v}$ and their force constants have been supposed to be similar to those of an infinite chain. Consequently, the calculation of the normal mode frequencies is easily deduced from the $F^0$ matrix of table A. I, its line number being now equal to the number of C=C bonds. Since the force constants are those of an infinite chain, the frequencies of the finite molecules are distributed on the phonon dispersion curves of figure 3 for (CH)$_x$. The frequencies of the Raman active modes are given in figures 6A and 6B. It may be crudely supposed that two Raman lines cannot be separated when their frequency difference is equal to or less than 4 cm$^{-1}$. In such cases, the modes are jumbled in the histograms of figures 6A and 6B. The histogram in figure 6C gives a rather good picture of the Raman active modes in a trans-(CH)$_x$ of medium size. As a matter of fact, there is a good agreement between the experimental spectrum of (CH)$_x$ when $\lambda_L = 457.9$ nm and this histogram.

Fig. 7. — Similar to figure 6 but in trans-(CD)$_x$. 

CH$_x$. The dispersion of frequencies for $q \neq 0$ seemed to us too large with the parameters from set II (from 1 450 to 1 850 cm$^{-1}$), so we did the calculations using only the force constants from set I. In figure 6C, the solid curve represents the results obtained for (CH)$_x$ in the frequency range 1 050-1 500 cm$^{-1}$ (corresponding to the frequency range of the dispersion curves 1, 2, 3 and 5 (fig. 3)). We have also shown the density of states (with force constants I) projected onto the C=C bond (fig. 6C, dashed line). Similar calculations were performed for (CD)$_x$, and the results are shown in figure 7. In figure 6C (or 7C), the Raman active modes for the infinite chain are indicated by arrows (corresponding to $q = 0$). But the other modes can be activated when the translational symmetry of the chain is destroyed, either by impurities or when the chain is no longer infinite. As an example, the vibration frequencies of trans-(CH)$_x$ (and (CD)$_x$) « molecules » have been calculated, in an arbitrary fashion, for seven and twenty three double carbon bonds (C=C) (figs. 6A and 6B in (CH)$_x$, 7A and 7B in (CD)$_x$). Their point group $C_{2v}$ and their force constants have been supposed to be similar to those of an infinite chain. Consequently, the calculation of the normal mode frequencies is easily deduced from the $F^0$ matrix of table A. I, its line number being now equal to the number of C=C bonds. Since the force constants are those of an infinite chain, the frequencies of the finite molecules are distributed on the phonon dispersion curves of figure 3 for (CH)$_x$. The frequencies of the Raman active modes are given in figures 6A and 6B. It may be crudely supposed that two Raman lines cannot be separated when their frequency difference is equal to or less than 4 cm$^{-1}$. In such cases, the modes are jumbled in the histograms of figures 6A and 6B. The histogram in figure 6C gives a rather good picture of the Raman active modes in a trans-(CH)$_x$ of medium size. As a matter of fact, there is a good agreement between the experimental spectrum of (CH)$_x$ when $\lambda_L = 457.9$ nm and this histogram.
5. Discussion and conclusion.

Using two sets of parameters (force constants I or II), we have been able to calculate to good accuracy the frequencies of the vibration modes which are IR or Raman active for infinite chains of both \((\text{CH})_x\) and \((\text{CD})_x\). We have used a limited number (twelve) of parameters. From the results obtained at \(q = 0\), it is not possible to say which set is better, although set I seems more realistic with respect to a higher delocalization of the electrons on an infinite chain. The model does not lead to a good estimation of the intensities of the Raman lines.

A dispersion in the conjugation lengths of the trans-polyacetylene is responsible of the shifts and different profiles of the Raman bands observed experimentally by changing the excitation laser wavelength. From the calculations of the density of states of an infinite chain (with force constants I), it is shown that an accumulation of Raman active modes for finite molecules correspond to peaks of the density of states, in agreement with similar results obtained on linear polyenes and carotenoids [21]. The experimental spectra could therefore be explained from the phonon spectrum and calculations must not be limited to \(q = 0\) [16]. However, it is clear that the model is too crude and that it would be speculative to try to completely interpret the experimental results for the following reasons:

i) figure 7C (solid line) represents the histogram of the full density of states and the connection to the Raman intensity is not given,

ii) the force constants of the chains are assumed to be unperturbed. That is not true for very short chains. We do not take account of the long range interactions as well as the chain end effects.

A complete description of the Raman experimental results could probably be made by introducing different distributions in the conjugation lengths as was proposed recently by Kuzmany et al. [13] and Mulazzi et al. [14], and/or to consider a perturbation of the force constants in a reduced space of the infinite chain (defect space) and to treat the perturbed phonons by a Green's function technique.

Appendix I.

Calculation method.

1. Fourier's matrix, \(F\) and \(G\) matrices. — It is well known that the normal mode frequencies of a crystal are given by:

\[
D(q) - E\omega^2 = 0. \tag{A.1}
\]

\(E\) is the unit matrix, \(q\) the wave vector, \(\omega = 2\pi v\) the vibration pulsation and \(D(q)\) Fourier's dynamical matrix. The \(D(q)\) elements are:

\[
D_{\alpha\beta}(ss' q) = (M_s M_s)^{-1/2} \sum_{l'} \phi_{s\alpha}^0 (l') \exp iq.l' \phi_{s'\beta}^0 (l'). \tag{A.2}
\]

\(r(l')\) defines the equilibrium position of the \(l'\) unit cell; \(\alpha\) and \(\beta\) are the Cartesian axes \(x, y\) or \(z\) of the lattice; \(\phi_{s\alpha}^0 (l')\) is the force constant between the atom \(s'\) in the unit cell \(l'\) and the atom \(s\) in the unit cell \(l = 0\); \(M_s\) and \(M_{s'}\) are the mass of these atoms. The force constants are the elements of the \(F\) matrix given by Wilson [17]. According to the notation of Shimanouchi et al. [22], \(F^c\) and \(F^1\) are the matrices \(F\) expressed in terms of Cartesian and internal coordinates respectively. So, equation (A.2) may be written as follows:

\[
D(q) = G^{1/2}\left[ \sum_{l'} F^c_{l'} \exp iq.l' \right] G^{1/2}, \tag{A.3}
\]

\(F^c\) is the matrix of elements \(\phi_{s\alpha}^0 (l') G\) being the diagonal matrix of elements \(1/M_s\) [17].

2. Calculation at \(q = 0\).

- Direct method. — When \(q = 0\), equation (A.3) may be written:

\[
D(0) = G^{1/2}\left( \sum_{l'} F^c_{l'} \right) G^{1/2}. \tag{A.4}
\]

Let \(R\) and \(X\) be the vectors of the internal and Cartesian displacement coordinates respectively of all atoms of the crystal and let \(R_{l}\) and \(X_{l}\) be the same vectors restricted to the atoms of the \(l'\) unit cell. \(R\) and \(X\) are bound by the transformation matrix \(B\):

\[
R = BX. \tag{A.5}
\]

Table A.I. — Lines of the matrices \(B, F^1\) and \(F^c\). The order of these matrices is infinite.

\[
B \begin{array}{cccccc}
... & X_{-2} & X_1 & X_0 & X_1 & X_2 & ... & X_r \\
R_0 & ... & B_{-1} & R_0 & B_1 & ... & B_r \\
\end{array}
\]

\[
F^1 \begin{array}{cccccc}
... & R_{-1} & R_0 & R_1 & ... & R_r \\
R_0 & ... & F^1_{-1} & F^1_0 & F^1_1 & ... & F^1_r \\
\end{array}
\]

\[
F^c \begin{array}{cccccc}
... & X_{-2} & X_1 & X_0 & X_1 & X_2 & ... & X_r \\
X_1 & ... & F^c_{-2} & F^c_1 & F^c_0 & F^c_1 & F^c_2 & ... & F^c_{r+1} \\
X_0 & ... & F^c_{-2} & F^c_1 & F^c_0 & F^c_1 & F^c_2 & ... & F^c_r \\
X_1 & ... & F^c_{-2} & F^c_1 & F^c_0 & F^c_1 & F^c_2 & ... & F^c_{r+1} \\
\end{array}
\]
It can be easily shown that the $B$, $F'$ and $F''$ matrices of the infinite crystal can be represented as in table A.1 where $B_i$, $F'_i$, and $F''_i$ are the matrices $B$, $F'$ and $F''$ restricted to the unit cell $i$. Each matrix is composed of identical lines, but each line is translated with respect to the previous one (see matrix $F''_c$ in table A.1).

In our own calculation for trans-(CH)$_2$, the elements of each line of $B$, $F'$ and $F''$ which are different from zero are underlined in the table. The five underlined $F''_c$ matrices in $F''$ are deduced from the following relation:

$$F'' = (B)^T F' B$$  \hspace{1cm} (A.6)

where $T$ indicates the transpose conjugate.

Theoretically, the orders of $F'$ and $B$ are infinite, but here, the $X_0$ line of $F''$ (table A.1) can be calculated exactly from the matrices $B$ and $F'$ expressed on five unit cells only. This comes from the small number of matrix elements which are different from zero. The $F''_c$ elements of the $X_0$ line are inserted in equation (A.4) and the normal mode frequencies are calculated from equation (A.1).

- Matrices $B_{op}$, $F'_{op}$ and $F''_{op}$ — According to the translational symmetries of a crystal and the notations of Shimanouchi et al. [22], equation (A.6) may be written as follows:

$$F''_{op} = [B_{op}]^T F'_{op} B_{op}$$  \hspace{1cm} (A.7)

where $B_{op} = \sum_i B_i$; $F'_{op} = \sum_i F'_i$ and $F''_{op} = \sum_i F''_i$.

So, equation (A.4) becomes:

$$D(\theta) = G^{1/2} F''_{op} G^{1/2}.$$  \hspace{1cm} (A.8)

The calculations are easier with (A.7) than with (A.6), but the latter can be used for calculations at $q \neq 0$ and for finite molecules (see next section). Both methods, of course, lead to the same results.

3. Calculation at $q \neq 0$. — At $q \neq 0$, the normal mode frequencies are given by equations (A.1) and (A.3). But in (A.3) the matrices $F''_c$ must be known separately and therefore calculated from equation (A.6) only. Consequently, (A.7) cannot be used here. However, (A.7) has been extended to $q \neq 0$ by Piseri and Zerbi [23]. Both methods give the same normal mode frequencies.

References


