

with the expected value; however  $b_0$  is significantly less than the normal diameter of  $I^-$ .

During the preliminary search for suitable crystals, it was observed more frequently than not that specimens displayed extra spots along the festoons of constant  $h$  and  $k$ , although the irregularity was not observed on the  $00l$  line. Such behavior suggests some kind of modified layer stacking arrangement with a longer than normal  $c_0$ ; at no time was a tendency toward a change in  $a_0$  or  $b_0$  observed. It was, in fact, only after a considerable search that a crystal which gave a simple orderly pattern was found. We have found numerous crystals with the 'perfected' structure elucidated in this manuscript, however, and believe it to be the correct one to ascribe to  $CrI_2$ . Specimens which showed irregular spots gave poor quality photographs and the irregularities were not reproducible in the various imperfect crystals examined; hence no attempt was made to determine the structure of anyone of them. In extreme cases, the festoons appeared as a nearly continuous line. These irregularities may be a consequence of the non-equilibrium conditions under which crystals were grown.

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## Lattice Vibrations of Molecular Chains

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The lattice vibrations of linear chains consisting of one and of two different types of ring-shaped molecules are derived assuming central and non-central harmonic restoring forces between next neighbours. Restricting the problem to two degrees of freedom at a time it is shown that the general normal modes of the chain consist of mixed vibrations containing both translational and rotational components. The contribution of the translational and rotational components changes continuously along each branch of the dispersion curve; their phase relationships however remain constant through the entire fundamental range. Dispersion curves and amplitude ratios are calculated for different sets of parameters. The extension of the results to centrosymmetrical molecules of other shapes is discussed.

### Introduction

Since Born & Kármán's pioneer paper (1912) on the lattice vibrations of monatomic chains the vibrational modes of atomic lattices have been the subject of many theoretical investigations (Brillouin, 1946; Blackman, 1955; de Launay, 1956). The study of the lattice vibrations of molecular structures has been

given much less attention, most of the investigations having been concerned with the internal vibrations of the molecules. These internal vibrations lie in the visible and ultraviolet range ( $1/\lambda \sim 300\text{--}3000\text{ cm.}^{-1}$ ) while the lattice vibrations lie in the far infrared ( $1/\lambda \sim 50\text{--}150\text{ cm.}^{-1}$ ). Apart from the far infrared emission and absorption spectra, lattice vibrations are observable also in the low-frequency Raman spectra and they are mainly responsible for the diffuse scattering of X-rays and the inelastic scattering of

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thermal neutrons by molecular crystals (Sándor & Wooster, 1961).

Among the few theoretical studies on the lattice vibrations of molecular crystals there were two attempts to derive the normal modes of simple molecular chains. Raskin, Sechkarev & Skripov (1949) studied the lattice vibrations of molecular chains having two diatomic molecules in the unit cell related to each other by (i) mirror plane, (ii) screw axis, (iii) centre of symmetry. In all three cases the molecular interaction was attributed to quasielastic interatomic forces and only first-neighbour interaction was considered. Since the aim of this investigation was to provide a theoretical basis for the Raman-spectra studies of the authors, only the fundamental frequencies of the chain (corresponding to infinite wavelength) were calculated and these could be directly related to the observable Raman frequencies. The normal modes associated with these fundamental frequencies were found to be generally of mixed character, containing both translational and rotational components. A practically important exception was the chain of centrosymmetric molecules, the fundamental vibrations of which were either pure rotational or pure translational. Skripov (1949) has shown that this latter result could be easily extended to three-dimensional molecular structures. Apart from calculating the fundamental frequencies the authors made no attempt to derive either the shape of the dispersion curves or the relationship between the translational and rotational components.

Another approach to the problem of lattice vibrations of molecular crystals is due to Asano & Tomishima (1957). These authors studied the vibrational modes of complex inorganic crystals, and in a short appendix extended their results to chains of spherical molecules. Two cases were considered: (i) chains consisting of identical spheres and (ii) chains consisting of two types of sphere alternately. The molecules were allowed two degrees of freedom: one for transverse linear and one for angular vibrations. Secular equations were derived for both types of

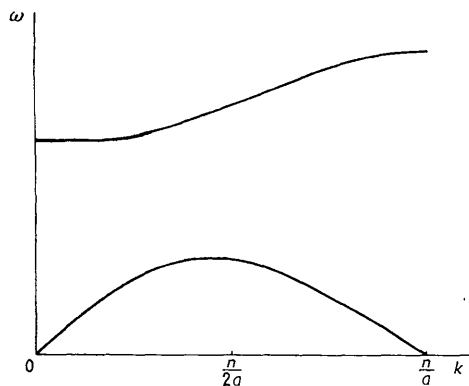


Fig. 1. Dispersion curves of a linear chain of identical spheres derived from the secular equation of Asano & Tomishima.

chains and typical dispersion curves plotted for both cases.

The results of this analysis have several shortcomings. The two dispersion curves of a chain of identical spheres are given by two intersecting curves, one resembling a sine, the other a cosine curve. The 'sine' curve is labelled transverse acoustic, the 'cosine' curve rotational acoustic. This result is at variance with the secular equation of the authors which yields two non-intersecting dispersion curves of the type shown in Fig. 1. Furthermore it can be shown that, apart from the terminal points, every other point of the dispersion curves is associated with mixed vibrations having both translational and rotational components. But even these corrected dispersion curves are unacceptable, because they attribute zero rotational frequency to the boundaries of the fundamental range ( $k = \pm 1/\lambda = \pm \pi/a$ ) which implies the untenable assumption that the configuration corresponding to opposite angular displacement of neighbouring molecules (see Fig. 5) is an equilibrium configuration. Thus one has to conclude that even the secular equation given by the authors is at fault.

### A. Lattice vibrations of a monomolecular chain

#### *The secular equation for transverse vibrations*

In what follows the lattice vibrations of molecular chains will be derived using a suitably modified version of the Born-Kármán method. First the monomolecular chain, i.e. a chain consisting of identical molecules, will be considered. The following simplifying assumptions are made.

(i) The chain is infinite, is linear and consists of close-packed plane molecules having masses  $M$ , moments of inertia  $I$  and spacings  $a$ . The molecules are plane rings containing six close-packed spherical atoms, thus resembling the carbon skeleton of a

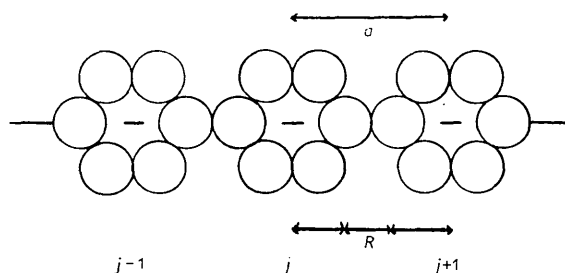


Fig. 2. Equilibrium position of three neighbours in a linear chain of identical ring-shaped molecules.

benzene molecule (see Fig. 2). The distance  $R$  of each atomic centre from the centre of the parent molecule is equal to the diameter of the atom and also to the distance between the nearest atomic centres of neighbouring molecules in equilibrium position. In equilibrium all molecules lie in the same plane and the

short lines drawn across the centres of the molecules in Figs. 2 to 6 all point in the chain direction.

(ii) The interaction between neighbouring molecules is represented by two harmonic restoring forces: a central force  $F^c$  with force constant  $c_1$ , acting between the centres of neighbouring molecules, and a non-central force  $F^{nc}$  with force constant  $c_2$  acting between the centres of the nearest atoms of neighbouring molecules (see Fig. 3). The central force  $F^c$  depends only on the linear displacements of neighbouring molecules, while the non-central force  $F^{nc}$  depends also on their angular displacements relative to the equilibrium position.

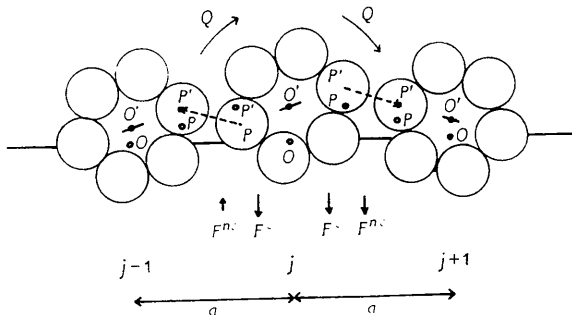


Fig. 3. Instantaneous positions of three neighbours in a vibrating linear chain of identical ring-shaped molecules. The instantaneous positions of the molecular and atomic centres are indicated with dashed letters.

(iii) Each molecule in the chain has six degrees of freedom, three for translational and three for rotational vibrations. At first we consider only two degrees of freedom: a transverse translational vibration in the equilibrium plane of the molecules and a rotational vibration around an axis perpendicular to this plane. Only vibrations of small amplitude will be admitted.

In deriving the equation of motion for the transverse translational vibration of the  $j$ th molecule only the transverse component of the total force acting on it need to be considered. Denoting the instantaneous transverse and angular displacements of the  $j$ th molecule by  $u_j$  and  $\delta_j$  respectively we get the instantaneous transverse component of the central force acting on the  $j$ th molecule due to the  $(j+1)$ th molecule.

$$F_{j,j+1}^c = c_1(u_{j+1} - u_j). \quad (1)$$

On the other hand the instantaneous transverse component of the non-central force acting on the  $j$ th molecule due to the  $(j+1)$ th molecule is given by

$$F_{j,j+1}^{nc} = c_2(u_{j+1} - u_j) - c_2R(\delta_{j+1} + \delta_j). \quad (2)$$

Equation (2) is an approximation for the case when the angular displacement  $\delta_j$  is so small that the transverse displacement of an atom having its centre in the chain axis in equilibrium can be taken equal to  $R\delta_j$ . Similarly the instantaneous transverse components of  $F^c$  and  $F^{nc}$  due to the  $(j-1)$ th molecule are respectively

$$F_{j,j-1}^c = c_1(u_{j-1} - u_j) \quad (3)$$

$$F_{j,j-1}^{nc} = c_2(u_{j-1} - u_j) + c_2R(\delta_{j-1} + \delta_j). \quad (4)$$

From (1)–(4) the equation of motion for the translational vibration of the  $j$ th molecule:

$$M\ddot{u}_j = (c_1 + c_2)(u_{j+1} + u_{j-1} - 2u_j) - c_2R(\delta_{j+1} - \delta_{j-1}), \quad (5)$$

where the right-hand side is the instantaneous transverse component of the total force acting on the  $j$ th molecule. The angular displacements in the equation indicate that non-central forces can generate translational vibrations even if the translational displacements are zero (see Fig. 4).

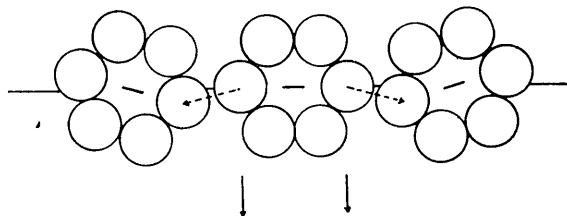


Fig. 4. Non-central forces arising from the angular displacements of the neighbours can generate transverse translational vibrations even if the translational displacements of the neighbours are zero.

To derive the equation of motion for the rotational vibration of the  $j$ th molecule we calculate the total instantaneous moment of the non-central forces acting on it. The instantaneous moment of the transverse component of  $F_{j,j+1}^{nc}$  can be approximated by

$$Q_{j,j+1}^n \sim R \cdot F_{j,j+1}^{nc} = c_2R(u_{j+1} - u_j) - c_2R^2(\delta_{j+1} + \delta_j). \quad (6)$$

Similarly the instantaneous moment of the transverse component of  $F_{j,j-1}^{nc}$  is

$$Q_{j,j-1}^n \sim -R \cdot F_{j,j-1}^{nc} = c_2R(u_j - u_{j-1}) - c_2R^2(\delta_{j-1} + \delta_j). \quad (7)$$

The sum of equations (6) and (7) does not give the total moment responsible for the rotational vibrations of the molecules. Indeed, for the arrangement shown in Fig. 5, where

$$u_{j-1} = u_j = u_{j+1} = 0 \quad \text{and} \quad \delta_{j-1} = \delta_{j+1} = -\delta_j$$

equations (6) and (7) both yield zero suggesting that the anti-phase rotational vibration (associated with  $k = \pi/a$ ) has zero frequency. However this is at variance with the experimental evidence of both the thermal diffuse scattering of X-rays by molecular crystals (Sándor & Wooster, 1961) and the Raman spectroscopy (see e.g. Kastler & Rousset, 1941).

The moment giving rise to anti-phase rotational vibration in Fig. 5 cannot be attributed to the horizontal components of the non-central forces, because the horizontal displacements of the atoms in Fig. 5 are second-order small quantities in  $\delta$ . To account for the anti-phase rotational vibration we introduce an additional moment of the type

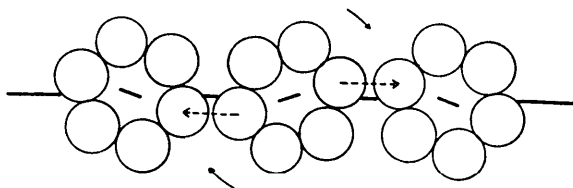


Fig. 5. The arrangement in which translational displacements are zero and neighbours have equal but opposite angular displacements gives rise to anti-phase rotational vibrations.

$$-c_3\delta_j$$

acting on the  $j$ th molecule in Fig. 5, where  $c_3$  is a new constant. The introduction of a new constant can however be avoided by assuming that the moment responsible for the anti-phase rotational vibration is of the same order of magnitude as the moment responsible for the in-phase rotational vibrations associated with  $k=0$  (see Fig. 6). This assumption is

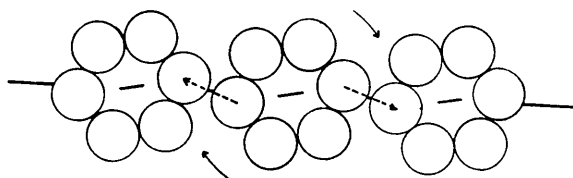


Fig. 6. Non-central forces can generate rotational vibrations about an axis perpendicular to the chain direction even if the angular displacements of the neighbours are the same and the translational displacements are zero. (In-phase rotational vibration associated with infinite wavelength.)

supported by the near equality of the fundamental frequencies of the in-phase and antiphase rotational Raman lines observed in molecular crystals (see e.g. Kastler & Rousset, 1941). The additional moment responsible for the anti-phase rotational vibration can then be conveniently given the form

$$Q_j^h \sim -2c_2R^2\delta_j. \quad (8)$$

From equations (6)–(8) the equation of motion for the rotational vibration of the  $j$ th molecule

$$I\ddot{\delta}_j = c_2R(u_{j+1} - u_{j-1}) - c_2R^2(\delta_{j+1} + \delta_{j-1} + 4\delta_j), \quad (9)$$

where the right-hand side is the total instantaneous moment acting on the  $j$ th molecule.

We try to solve equations (5) and (9) by two travelling plane waves

$$u_j = u \cdot \exp i(\omega t - kja) \quad (10)$$

and

$$\delta_j = \delta \cdot \exp i(\omega t - kja). \quad (11)$$

The first wave represents transverse translational, the second rotational vibrations,  $u$  and  $\delta$  are respective amplitudes,  $\omega = 2\pi\nu$  is the angular frequency,  $ja$  is the position vector of the  $j$ th molecule in equilibrium and  $k = 2\pi/\lambda$  is the wave vector. Since both the

wave vector and the position vector can have only two directions, their vector character can be indicated by a sign. Substituting the solutions (10) and (11) in equations (5) and (9) we get after rearrangement

$$\begin{aligned} [M\omega^2 - 4(c_1 + c_2) \sin^2 \frac{1}{2}ka]u + (2ic_2R \sin ka)\delta &= 0 \\ (-2ic_2R \sin ka)u + [I\omega^2 - 4c_2R^2(\cos^2 \frac{1}{2}ka + \frac{1}{2})]\delta &= 0. \end{aligned} \quad (12)$$

These two simultaneous homogeneous equations for the amplitudes  $u$  and  $\delta$  are compatible only if the determinant of their coefficients vanishes i.e. if

$$\begin{vmatrix} M\omega^2 - 4(c_1 + c_2) \sin^2 \frac{1}{2}ka & 2ic_2R \sin ka \\ -2ic_2R \sin ka & I\omega^2 - 4c_2R^2(\cos^2 \frac{1}{2}ka + \frac{1}{2}) \end{vmatrix} = 0 \quad (13)$$

This determinantal equation, known as the secular equation, is a quadratic equation in  $\omega^2$ . Since it is the characteristic equation of a Hermitian matrix it yields two real roots of  $\omega^2$  for every value of the wave vector  $k$ . This means that the dispersion curve  $\omega$  versus  $k$  of our monomolecular chain with two degrees of freedom has two branches, one corresponding to the positive sign of the square root ('plus' branch), the other to the negative sign ('minus' branch).

#### Dispersion curves for transverse vibrations

Before deriving the general solution of the secular equation, first we determine the two fundamental frequencies corresponding to infinite wavelength, i.e. to  $k=0$ . For this particular wave vector equation (13) yields the following solutions

$$\omega_-^2 = 0 \quad (14)$$

for the 'minus' branch and

$$\omega_+^2 = 6c_2R^2/I \quad (15)$$

for the 'plus' branch.

From the mathematical expression of (15) it is obvious that  $\omega$  represents pure rotational vibration. Since this frequency can be observed in the low-frequency Raman spectra, it is convenient to express all solutions of the secular equation in terms of this fundamental frequency which will be called  $\omega_f$ .

Furthermore, to simplify the calculation of the dispersion curve we introduce two new dimensionless parameters,  $\alpha$  and  $\beta$ , related to the five parameters of the problem by the following equations:

$$\alpha = c_1/c_2 \quad (16)$$

and

$$\beta = I/MR^2. \quad (17)$$

$\beta$  can be considered as a molecular form factor. For our ring shaped molecules  $\beta=1$ .

Substituting the fundamental frequency  $\omega_f$  and the two new parameters  $\alpha$  and  $\beta$  in (13), the secular equation takes the form

$$\begin{vmatrix} \omega^2 - \frac{2}{3}(\alpha + 1)\beta\omega_f^2 \sin^2 \frac{1}{2}ka & (i/3R)\omega_f^2 \sin ka \\ -(i\beta R/3)\omega_f^2 \sin ka & \omega^2 - \frac{2}{3}\omega_f^2 (\cos^2 \frac{1}{2}ka + \frac{1}{2}) \end{vmatrix} = 0 \quad (18)$$

yielding the two real roots

$$\omega^2 = (\omega_f^2/3) \left\{ (\alpha + 1)\beta \sin^2 \frac{1}{2}ka + (\cos^2 \frac{1}{2}ka + \frac{1}{2}) \right\} \pm \left\{ [(\alpha + 1)\beta \sin^2 \frac{1}{2}ka - (\cos^2 \frac{1}{2}ka + \frac{1}{2})]^2 + \beta \sin^2 ka \right\}^{\frac{1}{2}} \quad (19)$$

From equation (19) the following conclusions can be drawn:

(i) Both roots are even periodic functions of the wave vector with the period  $2\pi/a$ , known as the first Brillouin zone. The fundamental range of the wave vector can be conveniently taken as

$$-\pi/a \leq k \leq \pi/a \quad (20)$$

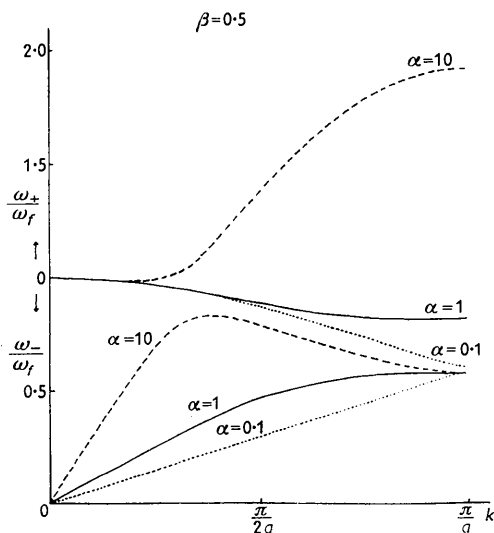


Fig. 7.

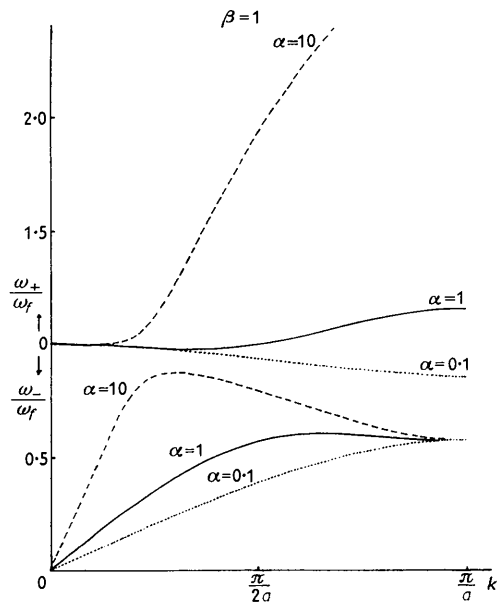


Fig. 8.

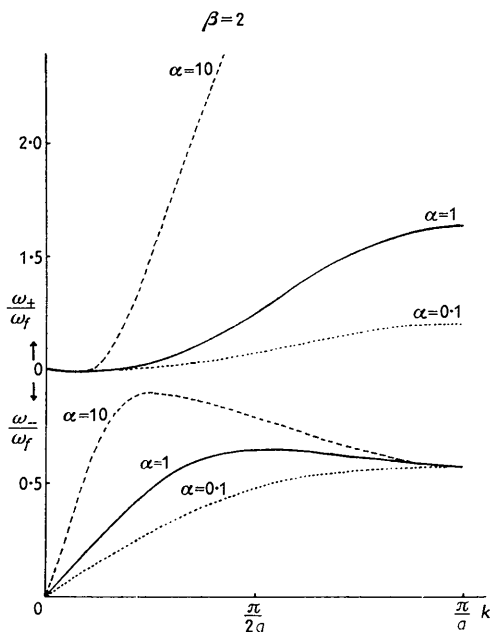


Fig. 9.

Figs. 7-9. Dispersion curves for transverse vibrations of a linear chain of identical ring-shaped molecules for different values of the parameters  $\alpha$  and  $\beta$ . Some of the very steeply rising branches have not been plotted in the entire  $(0 - \pi/a)$  range.

Since  $\omega(k)$  is an even function, it is enough to study the dispersion curve from say  $k=0$  to  $k=\pi/a$ .

(ii) Since the secular equation has been derived for an infinite chain,  $k$  can take any value, so that there are infinite solutions within the fundamental range. However, the results can be easily extended to finite chains by introducing the cyclic boundary conditions of Born (1923). For a chain consisting of  $N$  molecules these boundary conditions restrict the wave vector to the following values

$$k = (2/Na)j, \text{ where } j = \pm 1, \pm 2, \pm 3, \dots, \pm \frac{1}{2}N. \quad (21)$$

In macroscopic chains  $N$  is so great that the possible wave vectors constitute a quasi-continuum.

(iii) Since in general both roots depend on the masses as well on the moments of inertia of the molecules, the general normal modes of the chain represent mixed vibrations, i.e. superpositions of translational and rotational vibrations of the same frequency. However, for particular values of the wave vector the vibration may be purely translational or purely rotational. This is so for example with  $k=0$  (see equations (14)–(15)). The only other case is  $k=\pi/a$ , for which the secular equation yields the following two roots

$$\omega_+^2 = \frac{2}{3}(\alpha + 1)\beta\omega_f^2 = 4(c_1 + c_2)/M \quad (22)$$

and

$$\omega_-^2 = \omega_f^2/3 = 2c_2R^2/I, \quad (23)$$

$\omega_+$  corresponds to a purely translational vibration while  $\omega_-$  to a purely rotational vibration.

(iv) If the frequencies are expressed in terms of  $\omega_f$ , three out of the four limiting frequencies of the  $(0-\pi/a)$  range (see equations (14), (15) and (23)) are fixed, only the fourth (see equation (22)) depends on  $\alpha$  and  $\beta$ . Since this fourth frequency can take any positive value, the 'plus' branch of the dispersion curve is not necessarily an 'upper' branch in the entire fundamental range, but for appropriate values of the parameters it may intersect the 'minus' branch near the end of the fundamental range. From equations (22) and (23) the condition for this intersection is

$$2(\alpha + 1)\beta < 1. \quad (24)$$

For small absolute values of  $k$  the 'plus' branch is always an 'upper' branch, since the 'minus' branch starts from zero at  $k=0$  while the 'plus' branch starts from a positive  $\omega$  value.

Further details of the dispersion curves can be derived from Figs. 7–9 which show nine dispersion curves calculated for the following values of the parameters

$$\alpha = 0.1, 1.0, 10.0 \text{ and } \beta = 0.5, 1.0, 2.0. \quad (25)$$

The common feature of all these dispersion curves can be summarized as follows. The 'plus' branch has always two stationary values, one at  $k=0$  and one at  $k=\pi/a$ . The 'minus' branch has always one sta-

tionary value at  $k=\pi/a$ , and for larger values of  $\alpha$  it has an additional stationary value lying inside the range  $(0, \pi/a)$ . The markedly horizontal trend of the 'plus' branch near  $k=0$  accounts well for the sharpness of the low-frequency rotational Raman lines of molecular crystals, and the stationary values of both branches at  $k=\pi/a$  are in agreement with the observed intensity distribution of the extended thermal diffuse scattering of X-rays by molecular crystals (Sándor & Wooster, 1961).

*The character of the normal modes for transverse vibrations*

The character of the mixed normal modes can be best studied by comparing the amplitudes of the translational and rotational vibrations associated with the same frequency in various parts of the fundamental range. The ratio of these amplitudes can be determined from the two homogeneous equations (12) by substituting in them the roots of the secular equation (19). In order to get a dimensionless ratio, it is convenient to calculate the ratio  $u/R\delta$  instead of  $u/\delta$ . From the first equation of (19) we get

$$u/(R\delta) = -2ic_2 \sin ka / [M\omega^2 - 4(c_1 + c_2) \sin^2 \frac{1}{2}ka]. \quad (26)$$

By substituting  $\alpha$ ,  $\beta$  and  $\omega_f$  this can be transformed into

$$u/(R\delta) = i\beta \sin ka / [2(\alpha + 1)\beta \sin^2 \frac{1}{2}ka - (3\omega^2/\omega_f^2)]. \quad (27)$$

From equation (27) we may draw the following conclusions:

(i) For general values of  $k$  the amplitude ratio is different from zero which again demonstrates that the general normal modes of our monomolecular chain are mixed vibrations, the superpositions of translational and rotational vibrations having the same frequency.

(ii) The amplitude ratio is always imaginary. This means that there is a constant  $\pi/2$  phase difference between the translational and rotational vibrations associated with any particular normal mode.

Further details can be derived from Figs. 10–12 which show the variation of the amplitude ratios along the nine dispersion curves plotted in Figs. 7–9. The main characteristics of these amplitude-ratio curves can be summarized as follows. In the two branches of the dispersion curve the amplitude ratios are of opposite sign, indicating that in the 'minus' branch the translational vibration is ahead of the rotational vibration by  $\pi/2$ , while in the 'plus' branch it is the other way round.

All amplitude-ratio curves show a continuous change in the character of the normal mode along the fundamental range. At  $k=0$  the vibration in the 'plus' branch is purely rotational, that in the 'minus' branch purely translational. As  $k$  increases, the contribution of the rotational vibration in the 'minus' branch continuously decreases until at  $k=\pi/a$  the relations

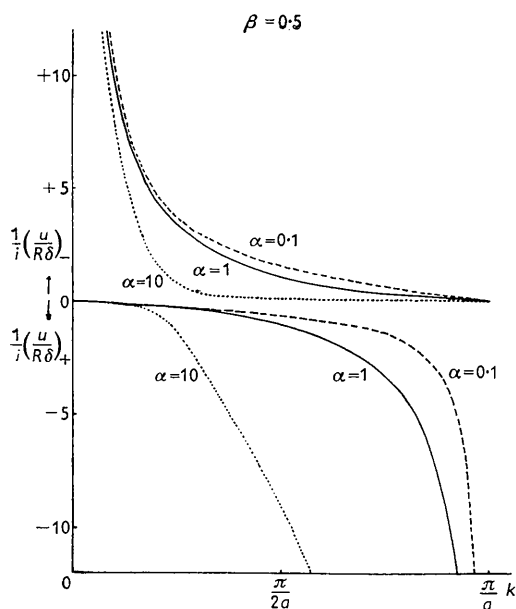


Fig. 10.

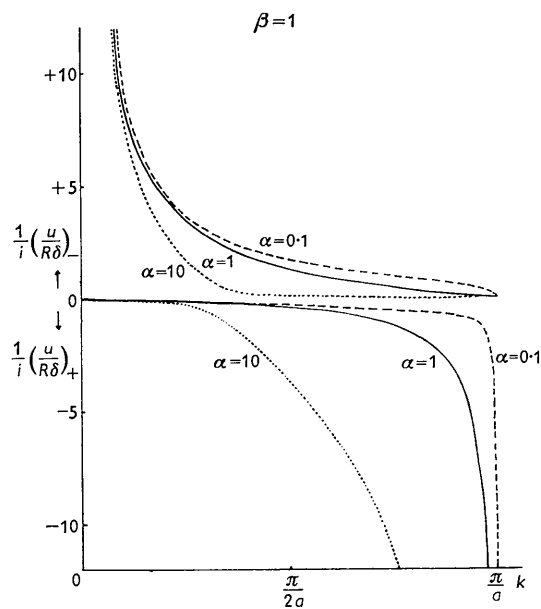


Fig. 11.

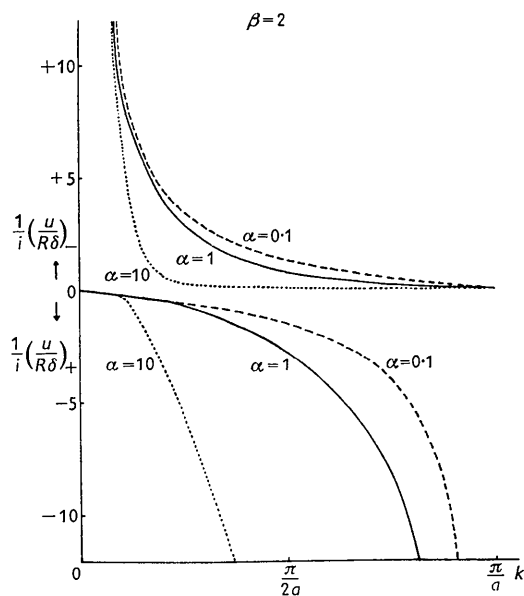


Fig. 12.

Figs. 10–12. The amplitude ratio curves corresponding to the dispersion curves plotted in Figs. 7–9.

are reversed. Here the vibration in the 'plus' branch is purely translational, while in the 'minus' branch purely rotational. The increase of either parameter  $\alpha$  and  $\beta$  lengthens those ranges in which one type of vibration is predominant.

#### *Secular equation and dispersion curves for longitudinal vibrations*

Since a general translational displacement of a molecule can always be resolved into three perpen-

dicular components, two transverse and one longitudinal relative to the chain axes, the results obtained in the previous paragraphs should be complemented by considering also the case of longitudinal translational displacements. If again we restrict the problem to two degrees of freedom, allowing translational displacements along the chain direction (longitudinal displacements) and angular displacements about an axis perpendicular to the equilibrium plane of the molecules we find that (i) longitudinal displacement

can generate only translational vibrations, (ii) angular displacements can generate only rotational vibrations, i.e. we find that the two types of vibrations are uncoupled. The first statement is demonstrated in Fig. 13 which shows that unequal longitudinal displacements of the neighbours can not generate rotational vibrations about an axis perpendicular to the chain direction.

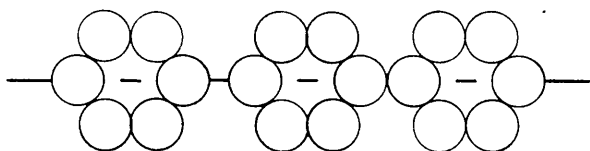


Fig. 13. Unequal longitudinal displacements of the neighbours can not generate rotational vibrations about an axis perpendicular to the chain direction.

placements of the two neighbours alone cannot generate rotational vibrations. With regard to the second statement we may note that in Fig. 4 the motion generated by the angular displacements is purely transverse. Correspondingly in the present case the two equations of motion of the  $j$ th molecule take the form:

$$M\ddot{u}_j = (c_1 + c_2)(u_{j+1} + u_{j-1} - 2u_j) \quad (28)$$

$$I\ddot{\delta}_j = -c_2 R^2 (\delta_{j+1} + \delta_{j-1} + 4\delta_j). \quad (29)$$

These two independent equations can be satisfied by two travelling plane waves. For the possible frequencies we get the following expressions

$$\omega_t^2 = (4(c_1 + c_2)/M) \sin^2 \frac{1}{2}ka \quad (30)$$

$$\omega_r^2 = (4c_2 R^2/I) (\cos^2 \frac{1}{2}ka + \frac{1}{2}). \quad (31)$$

The first expression represents purely translational (longitudinal) the second purely rotational vibrations. The translational branch of the dispersion curve is a sine curve (see Fig. 14) while the rotational branch

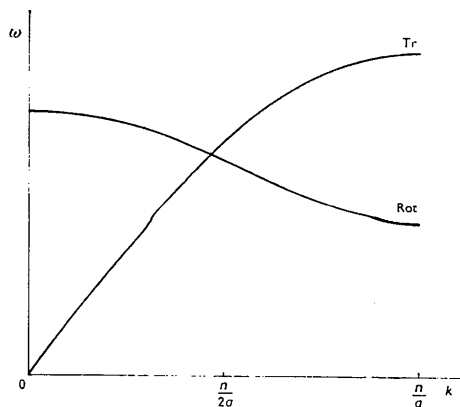


Fig. 14. Dispersion curves for longitudinal vibrations of a linear chain of identical ring-shaped molecules.

is of similar shape as the dotted 'plus' branch in Fig. 7.

## B. Lattice vibrations of a dimolecular chain

The results obtained for the monomolecular chain can be extended to the dimolecular chain i.e. to a linear chain having two different (or at least differently orientated) molecules in the unit cell. We take again close-packed ring-shaped molecules, but this time two different types (see Fig. 15). The parameters ( $M$ ,  $I$  and  $R$ ) of the two types of molecules will be distinguished by the indices 1 and 2. Furthermore the molecules themselves will be numbered in such a way that odd indices ( $2j-1, 2j+1$  etc.) correspond to type-1 molecules, and even indices ( $2j-2, 2j, 2j+2$  etc.) to type-2 molecules. Again we restrict the problem to two degrees of freedom: a transverse translational vibration in the equilibrium plane of the molecules and a rotational vibration around an axis perpendicular to this plane. Only vibrations of small amplitude will be admitted.

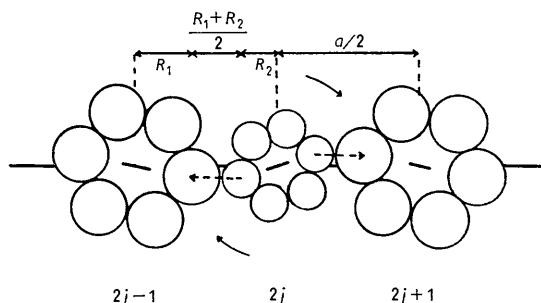


Fig. 15. Instantaneous positions of three neighbours in a vibrating linear chain consisting of two types of ring-shaped molecules.

From the mathematical point of view the problem of the dimolecular chain differs in two respects from that of the monomolecular chain. First, separate equations of motion have to be derived for the two types of molecules, which increases the number of the equations of motion from two to four. Second, the horizontal distances between the centres of the nearest atoms of neighbouring molecules in equilibrium

$$R_h = (R_1 + R_2)/2 \quad (32)$$

are not equal to the distances of these atomic centres from the centres of their parent molecules ( $R_1$  and  $R_2$  respectively).

Accordingly, using similar arguments to those for a monomolecular chain, the moment acting on the  $(2j+1)$ th type-1 molecule in the anti-phase angular displacement of the neighbours (similar to the one shown in Fig. 5 for a monomolecular chain) may be conveniently given the form

$$Q_{2j+1}^h = -c_2 R_1 (R_1 + R_2) \delta_{2j+1}. \quad (33)$$

A similar expression may be used for the moment acting on the type-2 molecules in the same arrangement.



Using the above assumptions the two equations of motion of the  $(2j+1)$ th molecule can be written:

$$M_1 \ddot{u}_{2j+1} = (c_1 + c_2)(u_{2j+2} + u_{2j} - 2u_{2j+1}) - c_2 R_2 (\delta_{2j+2} - \delta_{2j}) \quad (34)$$

$$I_1 \ddot{\delta}_{2j+1} = c_2 R_1 (u_{2j+2} - u_{2j}) - c_2 R_1 [R_2 (\delta_{2j+2} + \delta_{2j}) + (3R_1 + R_2) \delta_{2j+1}] \quad (35)$$

and similarly those of the  $2j$ 'th type-2 molecule:

$$M_2 \ddot{u}_{2j} = (c_1 + c_2)(u_{2j+1} + u_{2j-1} - 2u_{2j}) - c_2 R_1 (\delta_{2j+1} - \delta_{2j-1}) \quad (36)$$

$$I_2 \ddot{\delta}_{2j} = (c_2 R_2 (u_{2j+1} - u_{2j-1}) - c_2 R_2 [R_1 (\delta_{2j+1} + \delta_{2j-1}) + (3R_2 + R_1) \delta_{2j}]) \quad (37)$$

We try to solve these four equations by the four travelling plane waves

$$u_{2j+1} = u_1 \cdot \exp i[\omega t - (2j+1)\frac{1}{2}ka] \quad (38)$$

$$\delta_{2j+1} = \delta_1 \cdot \exp i[\omega t - (2j+1)\frac{1}{2}ka] \quad (39)$$

$$u_{2j} = u_2 \cdot \exp i[\omega t - 2j\frac{1}{2}ka] \quad (40)$$

$$\delta_{2j} = \delta_2 \cdot \exp i[\omega t - 2j\frac{1}{2}ka] \quad (41)$$

The first wave corresponds to transverse translational, the second to rotational vibrations, both waves propagating through type-1 molecules only. Similarly the third and fourth waves propagate only through type-2 molecules, and they are also of transverse translational and rotational character respectively. Substituting these four waves in equations (34)–(37) we get after rearranging and simplifying: (see equation (42)). These four homogeneous equations are only compatible if the determinant of the coefficients vanishes, i.e. if (see equation (43)). This fourth-order equation in  $\omega^2$  is the secular equation of the di-molecular chain. Since it is the characteristic equation of a Hermitian matrix, its four roots are real for all values of  $k$  so that the dispersion curve of the di-molecular chain has four real branches.

$$\begin{cases} [M_1 \omega^2 - 2(c_1 + c_2)]u_1 + [2(c_1 + c_2) \cos \frac{1}{2}ka]u_2 + [2ic_2 R_2 \sin \frac{1}{2}ka]\delta_2 & = 0 \\ [2(c_1 + c_2) \cos \frac{1}{2}ka]u_1 + [M_2 \omega^2 - 2(c_1 + c_2)]u_2 + [2ic_2 R_1 \sin \frac{1}{2}ka]\delta_1 & = 0 \\ -[2ic_2 R_2 \sin \frac{1}{2}ka]u_1 - [2ic_2 R_1 \sin \frac{1}{2}ka]u_2 + [I_1 \omega^2 - c_2 R_1 (3R_1 + R_2)]\delta_1 - [2c_2 R_1 R_2 \cos \frac{1}{2}ka]\delta_2 & = 0 \\ -[2ic_2 R_2 \sin \frac{1}{2}ka]u_1 - [2c_2 R_1 R_2 \cos \frac{1}{2}ka]\delta_1 + [I_2 \omega^2 - c_2 R_2 (3R_2 + R_1)]\delta_2 & = 0 \end{cases} \quad (42)$$

$$\begin{vmatrix} [M_1 \omega^2 - 2(c_1 + c_2)] & 2(c_1 + c_2) \cos \frac{1}{2}ka & 0 & 2ic_2 R_2 \sin \frac{1}{2}ka \\ [2(c_1 + c_2) \cos \frac{1}{2}ka] & [M_2 \omega^2 - 2(c_1 + c_2)] & 2ic_2 R_1 \sin \frac{1}{2}ka & 0 \\ 0 & -2ic_2 R_1 \sin \frac{1}{2}ka & [I_1 \omega^2 - c_2 R_1 (3R_1 + R_2)] & -2c_2 R_1 R_2 \cos \frac{1}{2}ka \\ -2ic_2 R_2 \sin \frac{1}{2}ka & 0 & -2c_2 R_1 R_2 \cos \frac{1}{2}ka & [I_2 \omega^2 - c_2 R_2 (3R_2 + R_1)] \end{vmatrix} = 0 \quad (43)$$

First we determine the four fundamental frequencies of the chain by solving the secular equation for  $k=0$ . In this particular case equation (43) reduces to

$$\begin{vmatrix} M_1 \omega^2 - 2(c_1 + c_2) & 2(c_1 + c_2) & 0 & 0 \\ 2(c_1 + c_2) & M_2 \omega^2 - 2(c_1 + c_2) & 0 & 0 \\ 0 & 0 & I_1 \omega^2 - c_2 R_1 (3R_1 + R_2) & -2c_2 R_1 R_2 \\ 0 & 0 & -2c_2 R_1 R_2 & I_2 \omega^2 - c_2 R_2 (3R_2 + R_1) \end{vmatrix} = 0 \quad (44)$$

which can be factorized into the product of two second order determinants

$$\begin{vmatrix} M_1 \omega^2 - 2(c_1 + c_2) & 2(c_1 + c_2) \\ 2(c_1 + c_2) & M_2 \omega^2 - 2(c_1 + c_2) \end{vmatrix} \times \begin{vmatrix} I_1 \omega^2 - c_2 R_1 (3R_1 + R_2) & -2c_2 R_1 R_2 \\ -2c_2 R_1 R_2 & I_2 \omega^2 - c_2 R_2 (3R_2 + R_1) \end{vmatrix} = 0 \quad (45)$$

each yielding a quadratic equation in  $\omega^2$ .

Since the first factor in equation (45) contains only the masses of the molecules, its two roots are associated with purely translational vibrations. These two roots yield the two fundamental frequencies

$$\omega_{10}^2 = 0 \quad (46)$$

and

$$\omega_{20}^2 = 2(c_1 + c_2)(M_1 + M_2)/(M_1 M_2) \quad (47)$$

The fundamental frequency  $\omega_{10}$  corresponds to a translational motion in which all molecules in the chain move in phase. Since this is equivalent to the translation of the whole chain there is no restoring force, so that the frequency has to be zero. On the other hand the fundamental frequency  $\omega_{20}$  corresponds to a translational motion in which the two molecules in the unit cell vibrate in antiphase though each one is still in phase with all molecules of the same type. This can be shown by substituting  $k=0$  and  $\omega_{20}$  in the first equation of (42). From this equation we get the following amplitude ratio for the translational vibrations of the two molecules:

$$u_1/u_2 = -M_2/M_1 \quad (48)$$

The negative sign indicates the translational vibrations of the two molecules in the unit cell are in antiphase.

On the other hand, since the second factor in equation (45) contains only the moments of inertia of the

two molecules, its two roots are associated with purely rotational vibrations. These two roots yield the fundamental frequencies

$$\left. \begin{aligned} \omega_{30}^2 \\ \omega_{40}^2 \end{aligned} \right\} = \frac{c_2}{2} \left\{ \frac{R_1(3R_1+R_2)}{I_1} + \frac{R_2(3R_2+R_1)}{I_1} \right. \\ \left. \pm \left( \left[ \frac{R_1(3R_1+R_2)}{I_1} - \frac{R_2(3R_2+R_1)}{I_2} \right]^2 + \frac{16R_1^2R_2^2}{I_1I_2} \right)^{\frac{1}{2}} \right\}. \quad (49)$$

The fundamental frequency  $\omega_{30}$  associated with the positive sign in front of the square root corresponds to the in-phase rotational vibrations, while the fundamental frequency  $\omega_{40}$  associated with the negative sign corresponds to the antiphase rotational vibrations of the two molecules in the unit cell. This can again be checked by substituting  $k=0$  and the two frequencies  $\omega_{30}$  and  $\omega_{40}$  in either the third or the fourth equation of (42).

By putting  $M_1=M_2$ ,  $I_1=I_2$  and  $R_1=R_2$  in the expressions of the four fundamental frequencies of the dimolecular chain we find that the two in-phase fundamental frequencies of the dimolecular chain  $\omega_{10}$  and  $\omega_{30}$  reduce to the two fundamental frequencies of the monomolecular chain associated with  $k=0$  (see equations (14) and (15)), while the two anti-phase fundamental frequencies of the dimolecular chain  $\omega_{20}$  and  $\omega_{40}$  reduce to the two limiting frequencies of the monomolecular chain corresponding to  $k=\pi/a$  (see equations (22) and (23)).

Now we solve the secular equation of the dimolecular chain (equation (43)) for  $k=\pi/a$ . In this case the secular equation reduces to

$$\begin{vmatrix} M_1\omega^2 - 2(c_1 + c_2) & 0 & 0 & 2ic_2R_2 \\ 0 & M_2\omega^2 - 2(c_1 + c_2) & 2ic_2R_1 & 0 \\ 0 & -2ic_2R_1 & I_1\omega^2 - c_2R_1(3R_1 + R_2) & 0 \\ -2ic_2R_2 & 0 & 0 & I_2\omega^2 - c_2R_2(3R_2 + R_1) \end{vmatrix} = 0 \quad (50)$$

which can be factorized into the product of two second-order determinants:

$$\begin{aligned} & \begin{vmatrix} M_1\omega^2 - 2(c_1 + c_2) & 2ic_2R_2 \\ -2ic_2R_2 & I_2\omega^2 - c_2R_2(3R_2 + R_1) \end{vmatrix} \\ \times & \begin{vmatrix} M_2\omega^2 - 2(c_1 + c_2) & 2ic_2R_1 \\ -2ic_2R_1 & I_1\omega^2 - c_2R_1(3R_1 + R_2) \end{vmatrix} = 0 \end{aligned} \quad (51)$$

each yielding a quadratic equation in  $\omega^2$ . The two roots of the first quadratic equation are

$$\left. \begin{aligned} \omega_1^2 \\ \omega_2^2 \end{aligned} \right\} = \frac{1}{2} \left\{ \frac{2(c_1 + c_2)}{M_1} + \frac{c_2R_2(3R_2 + R_1)}{I_2} \right. \\ \left. \pm \left( \left[ \frac{2(c_1 + c_2)}{M_1} - \frac{c_2R_2(3R_2 + R_1)}{I_2} \right]^2 + \frac{16c_2^2R_2^2}{M_1I_2} \right)^{\frac{1}{2}} \right\}. \quad (52)$$

Since both  $\omega_1$  and  $\omega_2$  depend on  $M_1$  as well as on  $I_2$ , both frequencies are associated with mixed normal modes in which transverse translational vibrations of the type-1 molecules are coupled with rotational vibrations of the type-2 molecules. Substituting  $\omega_1$  and  $\omega_2$  in the first equation of (42) we find that the amplitude ratio is positive imaginary for the one frequency and negative imaginary for the other, indicating that in the one mixed normal mode the rotational vibration is ahead of the transverse translational vibration by  $\pi/2$  while in the other normal mode it is the other way round.

Similarly the second determinant in equation (51) yields a quadratic equation with the roots

$$\left. \begin{aligned} \omega_3^2 \\ \omega_4^2 \end{aligned} \right\} = \frac{1}{2} \left\{ \frac{2(c_1 + c_2)}{M_2} + \frac{c_2R_1(3R_1 + R_2)}{I_1} \right. \\ \left. \pm \left( \left[ \frac{2(c_1 + c_2)}{M_2} - \frac{c_2R_1(3R_1 + R_2)}{I_1} \right]^2 + \frac{16c_2^2R_1^2}{M_2I_1} \right)^{\frac{1}{2}} \right\}. \quad (53)$$

Again we find that both frequencies  $\omega_3$  and  $\omega_4$  are associated with mixed normal modes similar to those associated with the frequencies  $\omega_1$  and  $\omega_2$  (see equation (52)) only the rôles of the two molecules are reversed. For  $\omega_3$  and  $\omega_4$  rotational vibrations of the type-1 molecules are coupled with translational vibrations of the type-2 molecules, the phase differences

between the two types of vibrations being  $\pm\pi/2$  respectively.

The characteristics of the normal modes associated with general values of  $k$  within the range  $(0, \pi/a)$  can be derived from the mathematical form of the amplitude ratios without solving explicitly the secular equation for intermediate  $k$  values. Since out of the four equations in (42) only three are linearly independent, one of the four amplitudes, say  $\delta_1$ , can be chosen arbitrarily, and the other three amplitudes can be expressed in terms of this arbitrarily chosen  $\delta_1$  amplitude and of the molecular parameters. Thus we get from the first three equations of (42) by Cramer's rule

$$u_1 = \begin{vmatrix} 0 & 2(c_1 + c_2) \cos \frac{1}{2}ka & 2ic_2R_2 \sin \frac{1}{2}ka \\ [-2ic_2R_1 \sin \frac{1}{2}ka] \delta_1 & M_2\omega^2 - 2(c_1 + c_2) & 0 \\ -[I_1\omega^2 - c_2R_1(3R_1R_2)] \delta_1 & -2ic_2R_1 \sin \frac{1}{2}ka & -2c_2R_1R_2 \cos \frac{1}{2}ka \\ \hline M_1\omega^2 - 2(c_1 + c_2) & 2(c_1 + c_2) \cos \frac{1}{2}ka & 2ic_2R_2 \sin \frac{1}{2}ka \\ 2(c_1 + c_2) \cos \frac{1}{2}ka & M_2\omega^2 - 2(c_1 + c_2) & 0 \\ 0 & -2ic_2R_1 \sin \frac{1}{2}ka & -2c_2R_1R_2 \cos \frac{1}{2}ka \end{vmatrix} \quad (54)$$

We can show without actually expanding this determinant that the ratio  $u_1/R_1\delta_1$  is finite imaginary everywhere in the  $(0, \pi/a)$  range, except at  $k=0$  where it might be zero or infinite. Accordingly in the general normal modes the type-1 molecules carry out both translational and rotational vibrations with a constant  $\pm \pi/2$  phase difference. Similar result can be derived for the amplitude ratio  $u_2/R_2\delta_2$ . On the other hand we find that the amplitude ratios  $u_1/u_2$  and  $\delta_1/\delta_2$  are positive or negative real numbers for any value of the wave vector. Thus the translational vibrations of the two molecules in the unit cell are either in-phase or anti-phase and so are their rotational vibrations.

To sum up, the general normal modes of our di-molecular chain are mixed modes, in which the vibration of both types of molecules has translational as well as rotational components. The phase relationships between the two types of vibrations of the same molecule as well as between similar vibrations of neighbouring molecules are fixed, and they remain unchanged in the entire  $(0, \pi/a)$  range. On the other hand the contribution of the translational and rotational vibrations to the normal modes changes continuously along each branch of the dispersion curve. The characteristics of the particular normal modes associated with  $k=0$  and  $k=\pi/a$  have already been dealt with when calculating the corresponding frequencies.

### Discussion

Though the characteristics of the normal modes of monomolecular and dimolecular chains have been derived only for the particular model of ring-shaped molecules the results can be extended to centrosymmetrical molecules of more general shape. In fact when the molecular form factor  $\beta$  was given values different from unity we tacitly allowed already for departures from the ring-shape.

With regard to the forces, the assumption of only next-neighbour interaction is probably correct in view of the rapid decline of the intermolecular forces with distance. But the assumption of harmonic restoring forces is a rather coarse approximation. Nevertheless, it is expected that the introduction of a more complex force pattern will not basically alter the mixed character of the general normal modes.

In setting up equations of motion for our linear molecular chains three independent force and torque constants ( $c_1$ ,  $c_2$  and  $c_3$ ) were introduced, though in the actual calculations we used only two of them ( $c_1$  and  $c_2$ ) attributing to  $c_3$  a fixed value based on analogy arguments. However, the use of only two independent constants can be justified in a more rigorous way. It can be shown that we can ignore the

central force, i.e. take  $c_1=0$ , without affecting either the general shape of the dispersion curves and amplitude ratios in Figs. 7-12, or the continuous change in the character of the mixed normal modes along the fundamental range and the rules governing their phase relationships. Nor will our results will be fundamentally altered by taking  $c_3$  as an independent parameter instead of a fixed value. This means that an alternative approach to the problem would be to assume only non-central forces acting between the nearest atoms of neighbouring molecules and torque giving rise to the anti-phase rotational vibrations. This assumption would involve only two independent constants (corresponding to our  $c_2$  and  $c_3$ ) and would yield similar results to those derived above.

Finally it is expected that the results obtained for linear molecular chains will have relevance to the vibrations of three-dimensional molecular crystals along particular directions, in the same way that the theoretical dispersion curves calculated for linear monatomic lattices (Born & Kármán, 1912) can be compared with dispersion curves determined experimentally from the thermal diffuse scattering of monatomic cubic crystals along directions of high symmetry (e.g. Walker, 1956).

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