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A method of calculating the normal vibrations of polymer molecules is presented in detail. The method is based on that used by Schachtschneider and Snyder in their analysis of polypropylene but has not heretofore been published. The factoring of the infinite matrix and reduction to the coordinates of the unit cell is justified in a manner based on the factoring of finite molecules. It is comparatively simple for anyone familiar with the method of calculating the normal vibrations of finite molecules to make the extension to polymer molecules by this method.

The geometry of polymer chains is discussed in connection with setting up the g matrix for the calculations. Some errors in the use of the geometric relationships of Shimanouti and Mizushima on the helical configuration of polymer chains are pointed out and supplementary relationships are presented.

Some arguments in favor of the valence force field for this type of calculation are discussed. The error inherent in using the equilibrium transformation between the valence and Urey-Bradley force field is pointed up and made more obvious in a calculation of the normal vibrations of trioxane. In this calculation the polyether force constants reported by Tadokoro for polyoxymethylene gave a very poor fit of the data. Transference of the valence force constants obtained in the trioxane data to polyacetaldehyde gave as good a fit for polyacetaldehyde as was obtained in the trioxane calculation.

The method developed in the first chapters of the thesis for the normal vibrational analysis of polymers is applied to polyacetaldehyde in the last chapter. It is not possible to adjust the force constants to fit the observed frequencies because of the large number of calculated frequencies and force constants compared to the small number of observed frequencies. It appears to be possible to make band assignments in agreement with the calculated frequencies if reasonable force constants are already available.

THE NORMAL VIBRATIONAL ANALYSIS
OF POLYACETALDEHYDE

by

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THE NORMAL VIBRATIONAL ANALYSIS OF POLYACTALDEHYDE

GENERAL THEORY

Introduction

Since Wilson's work in the 1930's, the analysis of molecular vibrations of small molecules has developed and formalized itself into standard rules and procedures. It was first applied only to gaseous spectra, but was extended in the 1940's to condensed systems and in the 1950's to polymers or long chain molecules. It will not be within the scope of this discussion to develop the theory from the Newtonian laws of motion but rather to assume the reader's familiarity with such standard texts as Wilson, Decius and Cross (63), Barrow (2), and Wu (64) and from this knowledge of the treatment of small molecules lead into the more specialized treatment of polymers.

It will be necessary, however, to review briefly the steps in the solution of the energy levels of polyatomic molecules in order to see the logical extension to polymer molecules. The starting point of any problem concerning the energy of a molecule is Schrodinger's famous equation,

$$H\Psi = W\Psi. \quad (1)$$

It is usual to apply the Born-Oppenheimer separation (4; 41, p. 259) based on the differences in magnitude of the various types of energies

$$H = H_e + H_v + H_r . \quad (2)$$

The Hamiltonian can be separated into the components of electronic, vibration and rotation. Since we are concerned here mostly with condensed systems, and the infrared spectra, the vibrational component will be of major interest. H will be used here to be equivalent to H_v or to $H_v + H_r$. Using the harmonic oscillator-rigid rotor model:

$$H = T + V \quad (3)$$

$$T = 1/2 \sum \dot{Q}_i^2 \quad (4)$$

$$V = 1/2 \sum_i \lambda_i Q_i^2 \quad (5)$$

Where the Q 's are the mass weighted generalized normal displacement coordinates. In a nonlinear molecule containing N atoms, there will be $3N - 6$ independent coordinates. The secular determinant can be expressed as $3N - 6$ equations, if internal coordinates are used to eliminate the translation and rotation zero modes. Wilson (63, p. 73) has shown that the secular determinant can be put in the form

$$| GF - E \lambda | = 0 \quad (6)$$

$$2T = \sum_{tt'} G_{tt'}^{-1} \dot{S}_t \dot{S}_{t'} \quad (7)$$

$$2V = \sum_{tt'} F_{tt'} S_t S_{t'} . \quad (8)$$

G^{-1} is called the inverse kinetic energy matrix, F is the force constant matrix. The capital letter will be used to imply they are factored, the small g and f signify unfactored matrices. The S 's are the symmetry coordinates which are generated from the internal displacement coordinates by use of the "Wigner crank" (63, p. 119) and

the character tables of group theory. The methods of group theory permit factoring large order secular determinants into blocks corresponding to various species of vibration, i. e. modes which are symmetric, antisymmetric or degenerate with respect to the major axis of symmetry.

The unsymmetrized (unfactored) g is calculated on the basis of an assumed geometric structure which determines the choice of internal coordinates. The nondegenerate symmetry coordinates can be generated by considering one coordinate at a time and operating on it with the operations of identity, rotation, reflexion, inversion and combinations of these. The appropriate character table is used and the Wigner crank applied. The degenerate symmetry species must frequently be determined by inspection or analogy with other molecules or simply ingenuity. Tables are included in the appendix for generating symmetry coordinates for molecules with C_n type symmetry for $n = 3$ to 9 . The transformation from internal coordinates to symmetry coordinates defines the U matrix which is used to symmetrize the g and f matrices.

$$S_m = U_{mn} s_n \quad (9)$$

$$G = U g U' \quad (10)$$

$$F = U f U' \quad (11)$$

The g elements are then calculated from the formulas of Decius (8) or Wilson et al (63, p. 55-61). A potential field is assumed and

transformed into terms of the internal coordinates chosen for the g matrix in order to set up the f matrix and make use of equation 6. The secular determinate is now factored into blocks whose number will equal the number of species in the character table used. The order of each block will be equal to the number of symmetry coordinates belonging to that particular species. The proof of the factoring, which will be discussed in more detail later, is given in Appendix XII of Wilson, Decius and Cross (63, p. 347-349) and is inherent in the methods of group theory (44). The solution of the secular equations must result in a set of force constants which are consistent with the infrared frequencies observed.

The criteria for infrared activity is that the vibration must produce a change in the dipole moment. It has been shown (63, p. 146 f and other textbooks) that only those species will be active which transform in the same manner as the translational vectors T_x , T_y , and T_z . In the character tables of reference 63, p 323-340, the species containing these vectors are indicated. It is then a simple matter to determine which of the fundamental vibrations are infrared active. It is not difficult, however, to determine to which species the translational vectors belong. If the major axis is designated as the z axis, the x and y axes are perpendicular, application of the symmetry operations will quickly reveal the species of each vector.

Proceeding now to a series of regularly spaced arrays, Halford

(22) has shown that for molecular crystals the same character tables may be used, but the group operations must be changed slightly. The so-called space group operations may include a translation along with the operations of the point groups. Thus translation plus identity as well as the simple identity becomes an invariant subgroup, translation plus reflexion becomes a glide plane, translation plus rotation is a screw axis. This means that an operation which sends an atom into its identical site in the next unit cell is considered to leave the atom unchanged.

The solution of running waves through an array gives two branches, the acoustical low frequency branch and the optical high frequency branch whose values will depend on the wave vector, k , (11, p. 55). Application of the Born-von Karman cyclic conditions (11, p. 50; 3) confines k to the region $\pm \pi/a$, where a is the lattice spacing. The optical branch is composed of those frequencies which result when k is set = 0. In molecular crystals the branches correspond to two types of motion, the lattice modes and the molecular modes. The lattice modes are of translatory origin and will compose the acoustical region of the spectrum. The primary concern here is with the infrared spectra arising from the distortions of the molecule whose center of mass and principal axes of inertia are at rest, i. e., the molecular modes. Making this separation the usual methods of group theory can be applied to some unit of the array. The unit may

or may not correspond to an x-ray unit cell, but implicit in the treatment is the assumption of the Born-von Karman cycle -- there is a periodic repetition of the molecular motions.

Infinite helical chains

There are three basic approaches to the normal vibrational analysis of infinite helical chains or polymers. The first approach is to extrapolate from low polymeric homologs starting with the monomers, dimers, etc. The method was originally developed by Kirkwood (27) and extended by Pitzer (42). Zbinden (65), using the concept of coupled oscillators, sets up the Newtonian equations of n oscillators leading to n homogeneous equations whose solution depend on whether the ends are free or fixed. Since the ends of the chain must necessarily be different from the center, the n frequencies ω_s can be calculated ignoring the ends or assuming they are identical to the link;

$$\text{for fixed ends: } \omega_s^2 = \omega_0 + 2 \omega'^2 (1 \pm \cos s\pi/n + 1) \quad (12)$$

$$\text{for free ends: } \omega_s^2 = \omega_0 + 2 \omega'^2 (1 \pm \cos s\pi/n). \quad (13)$$

The error is greater the smaller the chain; Kirkwood's calculations through hexane were not good but improving with each carbon unit. Selection rules and intensity depend on whether s is odd or even since it determines the symmetry. The ω_0 and ω' are found by plotting ω_s^2 versus the term in parentheses.

A similar approach but a different plot was used by Snyder and

Schachtscheider (46). The solution of the secular equation for a linear array of n identical coupled oscillators can be set up in terms of the g and f matrices whose elements are:

$$g_{ii} = g_0 \quad (14)$$

$$g_{i, i+1} = g_1 \quad (15)$$

$$g_{i, i+2} = g_2 \quad (16)$$

with f 's substituted for f in the f matrix. Generally g_j 's are small, i. e. interactions beyond the next nearest neighbor are negligible.

The matrix $H = GF$ has the elements

$$H_j = H_{i, i+j} = H_{i+j, i} = g_0 f_j + \sum_{k=1}^{\infty} g_k (f_{k+j} + f_{k-j}) \quad (17)$$

The eigenvalues for equation 6 are then

$$\lambda_m = 4\pi^2 c^2 \nu_m^2 = H_0 + 2 \sum_{k=1}^{\infty} H_k \cos k \phi_m \quad (18)$$

where ϕ_m , the phase difference between adjacent oscillators is given by

$$\phi_m = m \pi / n + 1 \quad (m = 1, 2, 3 \dots n) \quad (19)$$

The ν_m is a function of ϕ_m only and the problem is to assign m so that a curve of ν_m versus ϕ_m is common to all the bands.

Crystalline infinite chains

Infrared spectra of polymer molecules are of condensed systems which are hopefully crystalline. It is necessary to take a closer look at this system, since it cannot really be considered as isolated molecules as the first approach would imply nor it is a molecular crystal.

The following is based on the papers of Liang et al (30, 31, 32) and Tobin (60, 61).

Assume that the polymer molecules are infinitely long and are arranged in a single crystal. If there are p atoms per repeat unit in a unit cell containing m molecules of n repeat units each, there will be $3pmn - 3$ fundamentals per unit cell, since only the modes corresponding to the translation of the whole crystal can be subtracted. Tobin uses a whole unit cell in the analysis of polyethylene. It is then necessary to remove the three translational motions of the unit cell as a whole plus the $3(m-1)$ lattice vibrations of the polymer chains against each other within the unit cell and the m lattice rotations around the helical axis. The rotations perpendicular to the helical axis are restricted and become internal modes. There will then be a total of $3pmn - 4m$ vibrations which may be optically active. If only one chain in the unit cell is considered, there will be $3pn - 4$ ($m=1$) vibrations. It is obvious that the factor modes for the single chain must necessarily be the basis for the modes of the unit cell, whose increased number corresponds to the normal vibrations of two or more chains moving in or out of phase with each other.

The more usual treatment is to consider the polymer chain as an infinite one dimensional array and somehow reduce the infinite order to a more reasonable number such as that of the single chain unit cell. From this point on the term unit cell will be taken to mean

not the usual x-ray unit cell, but the section of a single chain which is contained within the x-ray unit cell ignoring all other chains.

The second approach to the normal vibrational analysis of the infinite helical chain was initiated by Higgs (23). If equations 14 - 18 are developed for the infinite chain, the g matrix elements can be represented as

$$g_{ta, ub} = g_{ab}^{(m)} \quad a, b = 1, 2, 3. \dots N \quad (20)$$

$$u, t = \text{integer}$$

$$m = u - t$$

the interaction between the a coordinate of one unit with the b coordinate of the mth unit further on. The symmetry coordinates

$$S_a(\phi) = (2\pi)^{-1/2} \sum_{t=-\infty}^{\infty} s_{ta} e^{it\phi} \quad (21)$$

are obtained from a Fourier transform of the internal coordinate s which factors

$$g_{ab}(\phi) = \sum_{t=-\infty}^{\infty} g_{ab}^{(m)} e^{-im\phi} \quad (22)$$

to the Nth order where N is the number of coordinates. The parallel modes are obtained from the solution of equation 6 for $\phi = 0$. The perpendicular modes are for $\phi = \pm \theta$ where θ is the internal angle of rotation. Only these modes are infrared active. The modes corresponding to $\phi = \pm 2\theta$ are Raman active. The G and F matrices of the form of (22) are used in equation 6, and solutions for the appropriate values of ϕ are found. Lin and Konig (33) generalize equation 18 without factoring and by proper choice of the Fourier transform

coefficients which is still complex manage to factor the secular determinate without applying the Born-von Karman conditions. Lawson and Crosby (29) use more than one unit cell in their cycle. Miyazawa (34, 35) uses trigometric instead of complex functions in order to adapt the method of Higgs to high speed computers.

The third approach to the problem is the one used in this dissertation. It considers the unit cell as an isolated molecule which interacts at the ends with the adjacent unit cells. Its convenience lies in the fact that the details are very similar to the treatment for small molecules, i. e. equations 1-11 hold with the exception that the U and U' differ slightly. In the method of Tadokoro (56 - 58) the character tables for generating the symmetry coordinates separate the degenerate species into complex components, and the space group operations are used in the "Wigner crank." The g and f elements follow equations 14 - 16 but the end group interaction demand the following conditions:

$$g_{n, 1} = g_{1, 2} \quad (23)$$

$$g_{n-1, 1} = g_{1, 3}$$

where n = the last monomer unit in the unit cell, i. e. nearest neighbors anywhere in the chain interact with each other identically, and next nearest neighbors also. This procedure gives an irreducible representation containing as many complex species as there are pairs of degenerate species. Since the solution of the secular

determinants of the orders involved in polymer molecules are possible only with computers, and since the use of complex numbers slows the speed of the computation appreciably, Tadokoro uses another unitary transformation $U_1 G U_1'$ to recombine the degenerate species. U_1 is very similar to U but contains trigometric functions of θ , the internal angle of rotation from one repeat unit into the next repeat unit. The order of the g and f matrices and the number of symmetry coordinates in this method is equal to $3pn - 4$ excluding redundancies.

The use of rectangular U matrices by Schachtschneider and Snyder (50) may be looked upon as setting up an infinite matrix and truncating it at the two ends of the unit cell. The g and f matrix is extended beyond the unit cell boundaries to include the coordinates in the adjacent unit cells which interact with the basic unit cell. The order of the g and f matrices will be greater than $3pn - 4$. Let the order be j and let $3pn - 4 = k$;

$$G = U_2 g U_1' \quad (24)$$

similarly for F , where U_2 and U_1 are $k \times j$ matrices and f and g are $j \times j$. U_2 is the transformation from the total internal coordinates being considered to the symmetry coordinates of the infinite chain. U_1 is the transformation only of the unit cell internal coordinates and contains zeros for the internal coordinates outside the unit cell. The U matrices are always real in this method.

The last approach will be developed further in the following

pages and applied specifically to polyacetaldehyde in the last chapter.

FACTORING AND REDUNDANCIES

The unitary transformation

The solvability of the secular determinant for small molecules will not depend on its factorability, but in practice it is common to factor any determinant greater than order two. In the case of polymers, it would be impossible to solve an infinite order secular determinant so that the key to the solution lies in the method of factoring.

As stated in the last chapter, the first approach does not involve the secular determinant of the polymer as such. In the second approach the factoring occurs as a natural result of the Fourier transformation and the choice of ϕ . The last approach requires the selection of a U matrix which will properly factor the g and f matrices resulting in the reduction of the final determinant into blocks of lower order.

It is useful to study more closely the transformation used by Tadokoro et al (56, 57) and Schachtschneider and Snyder (50). The details of the transformation will be studied as they would apply to polyacetaldehyde, although the example of Tadokoro is polyoxymethylene and that of Schachtschneider and Snyder is polypropylene.

In general, polymers fall into the space group $C(2m \pi/n)$ or

$D(2m \pi/n)$ depending on whether there is a symmetry axis perpendicular to the helical axis. There are p atoms in a monomer unit and n monomer units making t turns per unit cell. If n is odd there will be $(n-1)/2$ E species; if n is even there will be $n/2 - 1$ E species. For C type symmetry the A and one E species will be active in the infrared; both of these plus another E species will be active in the Raman spectra. For D type symmetry, the activity of the E species does not change but the totally symmetric A mode is active in the Raman and inactive in the infrared while the A_2 mode which is antisymmetric to a rotation around the perpendicular axis is just the opposite.

There are four repeat units in a unit cell of polyacetaldehyde. If the internal coordinates of a chemical repeat unit are chosen, the g and f matrices of Tadokoro can be represented as

$$g \text{ or } f = \begin{vmatrix} \alpha & \beta' & \gamma' & 0 \\ \beta & \alpha & \beta' & \gamma' \\ \gamma & \beta & \alpha & \beta' \\ 0 & \gamma & \beta & \alpha \end{vmatrix} \quad (1)$$

where α , β , γ , β' , and γ' are submatrices of order equal to the number of internal coordinates per repeat unit and represent the interaction of a repeat unit with itself (α), with its neighbor (β), and with its next nearest neighbor (γ). The second nearest neighbor interactions are generally negligible and are ignored. Rarely are there other than torsion interaction in γ . In equation 1, the

interaction between the first monomer unit and the last monomer unit within the cell is actually the interaction between the first monomer unit of one cell with the last monomer unit of the preceding cell. A complex unitary transformation UgU' factors g and f into n blocks with the degenerate E modes split into real and complex blocks. In order to make the equations suitable to machine computation, Tadokoro performs another transformation $U_1(UgU')U'_1$, where U_1 is real. The general form of U and U_1 are shown in Table 1. It should be noted that the multiplication by \bar{E} is misleading as it is shown in the original paper (56). Since for polyacetaldehyde, U is equal to the first four rows and columns of the general U , it is necessary to expand U to the order of the g and f matrix of polyacetaldehyde which is n times the number of internal coordinates chosen. Thus each U_{ij} as it is shown in the table is equal to a submatrix of the same order as α , β , etc., i. e. for polyacetaldehyde, it equals 23. This is the meaning of the multiplication by \bar{E} .

Taking a closer look at the transformation, it is easily shown that if $U_2 = U_1U$, the transformation can be performed in one step $U_2gU'_2$. The U_2 matrix, which is rather tedious to itemize but is simply the product of the two matrices in Table 1, is very reminiscent of the method of Miyazawa (34). Since both U' and U'_2 are complex, the use of complex numbers in the calculation is not completely eliminated.

Table 1. Transformation matrices of Tadokoro(56)

U matrix

	1	1	1	1	...	1	
	1	ϵ	ϵ^2	ϵ^3	...	ϵ^{n-1}	
	1	ϵ^2	ϵ^4	ϵ^6	...	$\epsilon^{2(n-1)}$	
N_1	1	ϵ^3	ϵ^6	ϵ^9	...	$\epsilon^{3(n-1)}$	\bar{E}
	
	
	1	ϵ^{n-1}	$\epsilon^{2(n-1)}$	$\epsilon^{(n-1)(n-1)}$	

 U_1 matrix

	1/2	1/2	1/2	1/2	...	1/2	
	1	$\cos\theta$	$\cos 2\theta$	$\cos 3\theta$...	$\cos(n-1)\theta$	
	0	$\sin\theta$	$\sin 2\theta$	$\sin 3\theta$...	$\sin(n-1)\theta$	
N_2	1	$\cos 2\theta$	$\cos 4\theta$	$\cos 6\theta$	\bar{E}
	
	
	1	$\cos(n/2-1)\theta$	$\cos(n/2-1)(n-1)\theta$	
	0	$\sin(n/2-1)\theta$	$\sin(n/2-1)(n-1)\theta$	

Substitute $1/2(n-1)$ for $n/2 - 1$ if n is odd

$\theta = 2m\pi/n$

N_1 and N_2 are normalization constants

\bar{E} = the unit matrix of the proper order

$\epsilon = e^{i\theta}$

The method of Schachtschneider and Snyder permits the use of real numbers exclusively. The transformation of equations I-24 uses rectangular U matrices which are not unitary in the ordinary sense but

$$U_2 U_1' = \bar{E} \quad (2)$$

where \bar{E} is the same order as the number of internal coordinates of the unit cell or the number of symmetry coordinates used. Instead of equation 1,

$$g \text{ or } f = \begin{array}{c} \left| \begin{array}{cccccc} a & \beta' & \gamma' & . & . & . \\ \beta & \boxed{a} & \boxed{\beta'} & \boxed{\gamma'} & . & . \\ \gamma & \beta & a & \beta' & \gamma' & . \\ . & \gamma & \beta & a & \beta' & \gamma' \\ . & . & \gamma & \beta & a & \beta' \\ . & . & . & \gamma & \beta & a \end{array} \right| \end{array} \quad (3)$$

The dotted lines indicate the unit cell.

The generation of the symmetry coordinates of the molecule in this method is analogous to the isolated molecule, i. e. application of the "Wigner crank." Since the character tables generally give complex elements for the E species, the avoidance of complex matrices is not achieved unless some other way is found to form the degenerate species. Complex numbers can always be expressed as

trigometric functions. For one dimensional species, the degenerate modes may be expressed as the real part and the coefficient of the imaginary part of the complex number. The tables of Appendix I are so derived except for the active mode of C_9 which is obtained by recognizing that it has a factor mode of C_3 . Thus for polyacetaldehyde which has C_4 symmetry the internal coordinates of Figure 1 can be represented by Table 2 with the s's oriented as indicated in the C_4 table. The equivalence of the internal coordinates applies only to the generation of the symmetry coordinates which can be represented for C_4 by

$$S_A = s_1 + s_2 + s_3 + s_4 \quad (5)$$

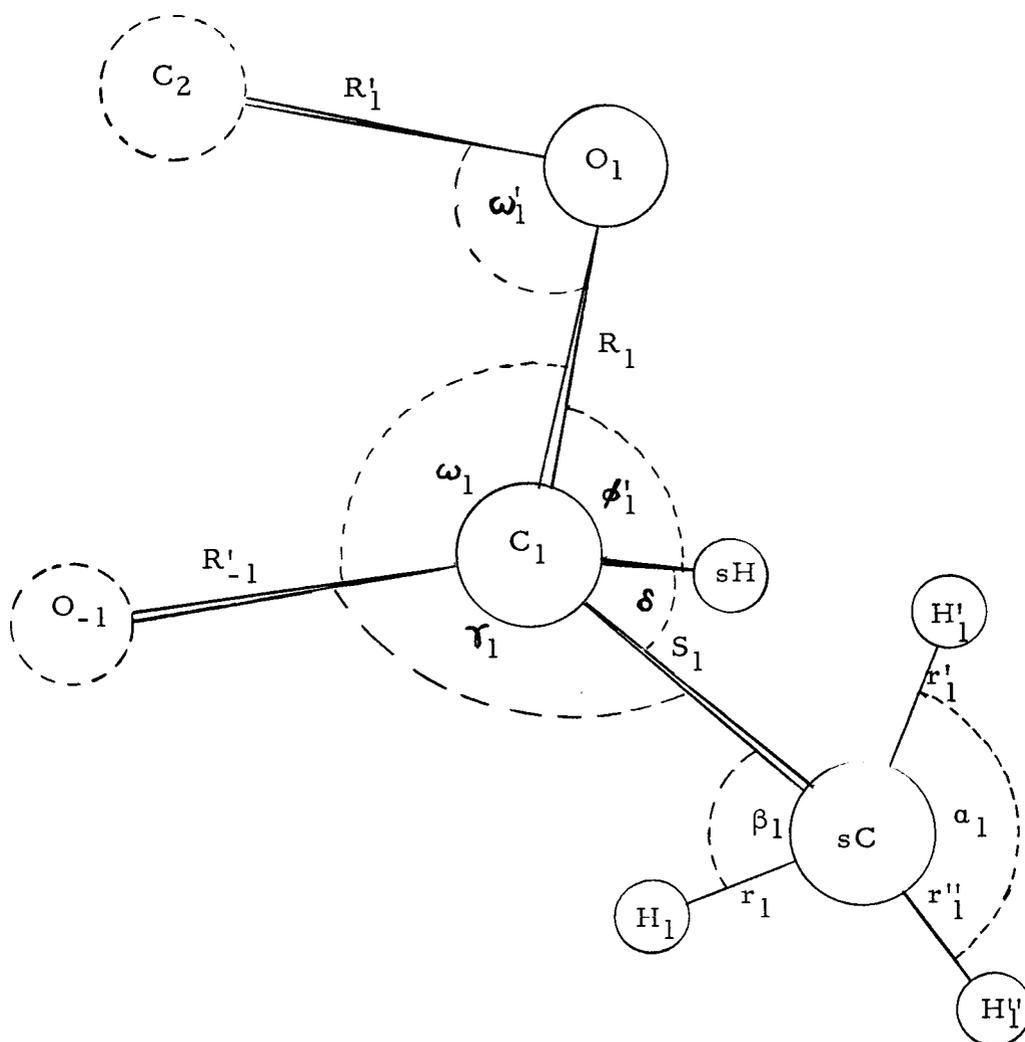
$$S_B = s_1 - s_2 + s_3 - s_4$$

$$S_E = s_1 - s_2 - s_3 + s_4$$

$$S_{E'} = s_1 + s_2 - s_3 - s_4$$

It is not necessary in using the tables of Appendix I that the repeat units be oriented in any fixed way, i. e. the use of the tables is not dependent on t but only on n . If t is greater than 1, all of the vectors will be changed proportionately and the resultant of each species will remain the same with respect to each other.

Equation 5 gives only the symmetry coordinates of the unit cell from which U_1 may be obtained by use of equation I-9. The same equation may be used to generate U_2 but now the symmetry equations of 5 must include the internal coordinates from the preceding and



σ = torsion of methyl side group around S

τ = torsion around C_1-O_1 bond

τ' = torsion around O_1-C_2 bond

Figure 1. The internal coordinates of a monomer unit of polyacetaldehyde.

Table 2. Internal coordinates of polyacetaldehyde for generating symmetry coordinates

	s_1	s_2	s_3	s_4
1	$R_1+R'_1$	$R_2+R'_2$	$R_3+R'_3$	$R_4+R'_4$
2	$R_1-R'_1$	$R_2-R'_2$	$R_3-R'_3$	$R_4-R'_4$
3	$r_1+r'_1+r''_1$	$r_2+r'_2+r''_2$	$r_3+r'_3+r''_3$	$r_4+r'_4+r''_4$
4	$2r_1-r'_1-r''_1$	$2r_2-r'_2-r''_2$	$2r_3-r'_3-r''_3$	$2r_4-r'_4-r''_4$
5	$r'_1-r''_1$	$r'_2-r''_2$	$r'_3-r''_3$	$r'_4-r''_4$
6	t_1	t_2	t_3	t_4

Coordinates of equivalent symmetry type

$$R = \gamma = \phi = \tau$$

$$R' = \gamma' = \phi' = \tau'$$

$$r = \alpha = \beta$$

$$r' = \alpha' = \beta'$$

$$r'' = \alpha'' = \beta''$$

$$t = S = \omega = \omega' = \sigma = \delta$$

Linear combinations of ω and ω' are used in the analysis of polyacetaldehyde and trioxane in this thesis.

succeeding cells. The coefficient of identical coordinates in adjacent cells must be identical. Since it is rare for interactions greater than next nearest neighbors to be effective, the symmetry coordinates to form U_2 of equation 3 may be expressed as:

$$S_A = s_{-3} + s_{-4} + s_1 + s_2 + s_3 + s_4 + s_{+1} + s_{+2} \quad (6)$$

$$S_B = s_{-3} - s_{-4} + s_1 - s_2 + s_3 - s_4 + s_{+1} - s_{+2}$$

$$S_E = -s_{-3} + s_{-4} + s_1 - s_2 - s_3 + s_4 + s_{+1} - s_{+2}$$

$$S_{E'} = -s_{-3} - s_{-4} + s_1 + s_2 - s_3 - s_4 + s_{+1} + s_{+2}$$

where the subscripted - and + refer to the preceding and succeeding unit cells respectively. The matrix U_2 is actually the infinite U_1 matrix, i. e. $U_1 - U_1 - U_1 \dots$. In practical application, however, it is found that the extra coordinates which do not interact with the unit cell do not affect the transformation. The order of the g and f matrix is approximately $3(n+4)p$. The far reaching torsion interactions may increase the number, but the isolated side group coordinates will decrease it somewhat. Thus for polyoxymethylene ($n=9$, $p=4$), polyacetaldehyde ($n=4$, $p=7$) and polypropylene ($n=3$, $p=9$), the number of internal coordinates necessary is between 130 and 140. The number in C-O chains is less than in C-C because of the insulating effect of the oxygen which eliminates many of the C-C-H angle interactions. The number will also vary because of the orientation, and judicious thought can decrease the number by as much as 10. When one is dealing with 130, however, ± 10 will not make much difference.

Indeed with machine computation, it is sometimes wise to have as many as the program will allow to serve as checks, since it will be impossible to hand check the solution. This leads naturally to the problem of redundancies.

Before proceeding to that section, however, something should be said concerning the proof of these transformations. The first proof is that they work, i. e. the g and f matrices are actually factored. Neither Miyazawa or Schachtschneider and Snyder justify their methods any further. It should be pointed out, however, that the use of the character tables insures the factoring because it is inherent in the theory of groups that the species will not mix. The U matrices of Schachtschneider and Snyder are not unitary in the strictest sense but their inability to meet all the test of unitary character does not affect their ability to meet the reasoning of Appendices XI and XII of Wilson, Decius and Cross (63, p. 341-349). Further discussion of this is reserved for Appendix II.

Redundancies and constraints

In choosing the internal coordinates and generating the symmetry coordinates and the U matrix, the question of redundancies arises. This is particularly troublesome in the case of polymer molecules. Decius'(9) discussion of complete sets and redundancies can be applied to polymer molecules keeping in mind that f for the polymer is

now 3a - 4 (using the notation of that reference). It is not easy to account for the redundancy even when it is easy to recognize the redundant coordinate.

In the case of the α and β angles of the methyl group in polyacetaldehyde, the sum is obviously fixed. A linear combination of the symmetry coordinates of each of these internal coordinates will then give a zero and a non-zero root. The combinations of the δ , ϕ , γ , and ω angles are not so easy. It must be remembered that only the ω not the ω' is included in the redundancy here. Many workers have simply eliminated one of the coordinates and permitted the eigenvectors to adjust accordingly, rather than use cumbersome linear combinations of all these angles. Gold et al (21) present a case for the necessity of linear combinations, i. e. the f and g matrices must possess a singularity for every redundancy. Another way of stating this is that the UU' must equal \bar{E} whose order is no greater than the degrees of freedom of the molecule. Their justification is that in a space of n dimensions, n+1 equations cannot be independent. Hubbard (25) fortifies their argument by showing that the force constants which have been derived without using singular f and g matrices are not transferable from molecule to molecule and are not constant for every U matrix transformation.

Rigina and Godnev (43) present a justification of the more common practice of not using singular f and g matrices. By use of

LaGrangian undetermined multipliers (7, p. 67) a system of equations

$$df/dx_i (x_1, x_2, \dots, x_n) = 0 \quad (7)$$

may be added to any new conditions of the type

$$g (x_1, x_2, \dots, x_n) = 0 \quad (8)$$

if coefficients are inserted to make equations 7 and 8 consistent.

Freeman (17) gives an example of a nonsingular f which is physically

realizable but somewhat artificial. But a study of the solution of

such molecules as propane shows there is considerable mixing of the

symmetry coordinates so that fixing the methylene angle or any simi-

lar condition is misleading.

The question still remains whether the solution of the secular determinant gives force constants which are dependent on the choice of the U matrix, e. g. the use of singular f and g matrices. Symmetry coordinates of polyacetaldehyde for redundancies of angles around a single point to satisfy this condition are

$$S_A = \sum \alpha + \beta \quad (9)$$

$$S_A = \sum \alpha - \beta$$

$$S_A = \sum \omega + \gamma' + \gamma + \phi' + \phi + \delta$$

$$S_A = \sum \omega - \delta$$

$$S_A = \sum 2\omega - \gamma' - \gamma - \phi' - \phi + 2\delta$$

with similar combinations for the E species. The symbols are identified in Figure 1.

Equations 9 are only applicable to the Schachtschneider and

Snyder treatment. It is more difficult to handle the redundancies in the use of the unitary matrices of Miyazawa but relationships analogous to equations 9 can be derived. The method of Higgs requires that the redundancies be removed before solution. The use of homologous series requires that all of the treatment be consistent, i. e. if the methylene angle is included in one homolog, it should be in all the molecules for that series.

The above redundancies are tedious but obvious. There exists other redundancies in the case of polymer molecules and even cyclic molecules which are not so obvious and may actually be constraints (5).

Applying the Decius (9) formula to trioxane $(\text{CH}_2\text{O})_3$ with 12 atoms, $f = 36 - 6 = 30$ vibrations. Then with $a = 12$, $b = 12$, $\mu = 1$, $a_1 = 6$, there will be 12 bond stretches, 18 bond angles, and 6 torsion angles giving six redundant coordinates. It is immediately obvious that one of the angles around each carbon atom is redundant, giving three; but what about the other three? There is a geometric theorem which will make these clear, i. e. the sum of the angles of a polygon equals the number of sides minus 2 times 180° . In other words the sum of the angles of a polygon is dependent on the number of sides only. It should then be obvious that it will be impossible to increase all the angles of trioxane without increasing some or all of the C-O bond lengths. Attempts to decrease the C-O-C angles without

changing the O-C-O angles will also change the torsion angles. It is difficult to combine angles and stretches, and fortunately it is unnecessary. Calculations on propane show that the frequencies and force constants are independent of the U matrix, if the choice of the internal coordinates are the same. It is necessary to include all possible types of internal coordinates in order to have the force constants transferable.

The situation is very similar in polymer molecules. Shimanouchi and Mizushima (54) have derived relationships showing that for the six parameters: bond length (r), bond angle (ϕ), torsion angle (τ), helical radius (ρ), internal rotation angle (θ), and repeat distance (d), only three are independent. Since the application of the Born-von Karman cyclic conditions fix θ and d or rather the sum of the θ 's and the sum of the d 's, (the unit cell cannot increase and there can be no resultant twist around the helical axis), only one of the other parameters is independent. The skeletal angles here are analogous to the ring angles of trioxane. The torsional angles of the polymer are of some interest, for these are most sensitive to the conformation of the helix and may give information about the stability of the crystalline form. They have been included, but it will not be possible to learn very much at this stage of the analysis.

Summary

The problem of the normal vibrational analysis of polymers can be approached from three basic viewpoints. The use of homologous series to extrapolate to infinite chains is tedious, demanding much experimental data and is frequently impossible since complete series are rarely obtainable. Also the method does not allow for differences in chain conformation nor does it permit complete analysis of the x-ray unit cell. The method of Higgs using complex Fourier transformation of an infinite series is not convenient to machine solution and cannot handle the redundancies. These arguments are also valid in the method of Tadokoro, although the solution of the secular determinant has been programmed for the computer. The method of Snyder and Schachtschneider is readily adapted to machine solution and is very similar to the treatment of small molecules while permitting extension to all the complexities of polymer molecules. It is also fairly simple to program for machine computation the construction of the g matrix and the factoring of the f and g matrices for insertion into the secular determinant program using this method. The details of these will be the subject of the next two chapters.

THE GEOMETRIC CONFIGURATION AND THE G MATRIX

When a suitable choice of internal coordinates has been made for the unit cell (Figure 1), the g matrix elements may be calculated. Schachtschneider has provided a program to calculate the g elements by the formulas of Wilson, Decius and Cross (63, p. 55-65) for the matrix of equation II-3. The program requires only that each atom in the polymer be located in a common cartesian coordinate system and that the masses be known. Each internal coordinate is then computed through the displacement vector:

$$s_i = \sum_{a=1}^N \bar{s}_{ia} \cdot \bar{\rho}_a \quad (1)$$

where s is the internal coordinate, \bar{s} is the associated vector for the atom displaced, $\bar{\rho}$ is the cartesian displacement vector. The B matrix is then defined by:

$$s_i = \sum_{t=1}^{3N} B_{it} x_t \quad (2)$$

where the x 's are the cartesian coordinates, and g is computed from

$$g_{tt'} = \sum_{i=1}^{3N} \mu_i B_{ti} B_{t'i} \quad t, t' = 1, 2, \dots, N \quad (3)$$

where N is the total number of internal coordinates; μ = reduced mass.

The atoms are numbered in any order. Associated with each atom are its three cartesian coordinates which make up a 3 by N X matrix and its mass. The internal coordinates are numbered and coded as to type (bond stretch, angle bend, etc.) and atoms involved. The U matrix or matrices along with the number of modes in each

symmetry species are necessary, if a factored G is desired. This is all the information the program requires to construct a G matrix for equation I-6.

The problem becomes a geometric one, but first it is necessary to decide how many internal coordinates to use of the preceding and succeeding cells. If the choice of internal coordinates for the chemical repeat unit of polyacetaldehyde are chosen as shown in Figure 1, the α , β , and γ matrices can be represented by Table 3a, b, and c. A study of these tables shows that in the case of the g matrix, one monomer unit reacts with 17 internal coordinates of the succeeding monomer unit (the number of rows containing elements in the β matrix). Conversely it interacts with nine internal coordinates of the preceding monomer unit (the number of columns containing elements in the β matrix). All of these must be included in the calculations. Also the γ matrix interactions of five in the second succeeding and one in the second preceding must be included and any of the extra f matrix interactions (Table 4a and b). The total in this case is 125. The f and g matrices must be of the same order. All of the atoms which make up these internal coordinates must be included in the calculations.

Shimanouchi and Mizushima (54) have derived mathematical expressions for the helical configuration of a polymer chain as a function of the angle of rotation, translational distance and distance

Table 3a. α submatrix of abbreviated g matrix of polyacetaldehyde

	r_1	t_1	S_1	R_1	R'_1	a_1	β_1	ϕ_1	δ_1	γ_1	ω_1	ω'_1	σ_1	τ_1	τ'_1	
r_1	g															
r'_1	g															
r''_1	g															
t_1		g														
S_1		g	g													
R_1		g	g	g												
R'_1				g	g											
a_1						g										
β_1							g									
ϕ_1								g								
δ_1									g							
γ_1										g						
ω_1											g					
ω'_1												g				
σ_1													g			
τ_1														g		
τ'_1															g	

Symmetric

g indicates non-zero interaction between coordinates at head of column and left of row.

Table 3b. β submatrix of abbreviated g matrix of polyacetaldehyde

	r_1	t_1	S_1	R_1	R'_1	α_1	β_1	ϕ_1	δ_1	γ_1	ω_1	ω'_1	σ_1	τ_1	τ'_1
t_2					g							g		g	g
S_2					g							g		g	g
R_2					g							g		g	g
R'_2					g							g		g	g
β_2					g							g		g	g
ϕ_2				g	g		g		g	g	g	g	g	g	g
ϕ'_2					g							g		g	g
δ_2					g							g		g	g
γ_2					g		g		g	g	g	g	g	g	g
γ'_2					g							g		g	g
ω_2				g	g		g		g	g	g	g	g	g	g
ω'_2					g							g		g	g
σ_2				g	g		g		g	g	g	g	g	g	g
τ_2				g	g		g		g	g	g	g	g	g	g
τ'_2					g							g		g	g

Table 3c. γ submatrix of abbreviated g matrix of polyacetaldehyde
the column headings are the same as above

ϕ_3															g
γ_3															g
ω_3															g
σ_3															g
τ_3															g

all other terms are zero except for the equivalence of the β_2 angles

between two successive atoms which are permuted into each other by the screw operation. It is necessary to emphasize that the two atoms so related need not be neighboring atoms on the skeletal chain (6) and that the bond lengths and bond angles as used by Shimanouchi are not necessarily the bond length and angle in the chemical sense. The importance of this derivation is that of the parameters associated with atoms arranged in a helical polymer: r , d , ϕ , θ , τ , and ρ , (Figure 2) only three are independent. In general it is true that if two points are related to each other by three independent parameters, all other parameters are functions of these first three.

Consider Figure 2, if A can be transformed in A' by a rotation of θ around the cylinder axis and a translation of d up the same axis then the following applies (54). If X represents the coordinate system with x directed along the line joining A to A', y in the plane of this line and the line joining A to the preceding A', and z chosen to keep the system right-handed then:

$$X_{i-1} = AX_i + B \quad (4)$$

$$A = \begin{vmatrix} -\cos \phi & -\sin \phi & 0 \\ \sin \tau \cos \phi & -\cos \tau \cos \phi & -\sin \tau \\ \sin \tau \sin \phi & -\cos \tau \sin \phi & \cos \tau \end{vmatrix}$$

$$B = \begin{vmatrix} r \\ 0 \\ 0 \end{vmatrix}$$

Similarly if Ξ is the coordinate system with ξ axis on the projection of point A to the cylinder axis, ζ along the cylinder axis and η

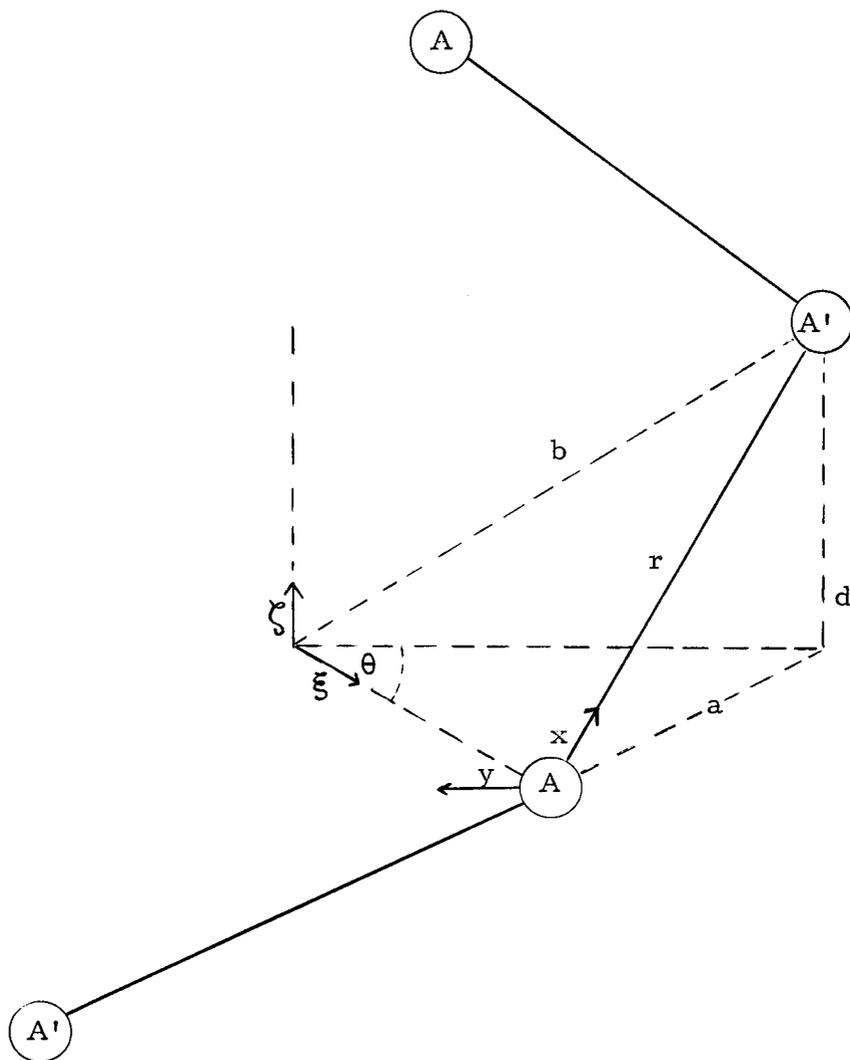


Figure 2. Identification of helical parameters.

chosen to keep the system right-handed then:

$$\vec{H}_{i-1} = N \vec{H}_i + L \quad (5)$$

$$N = \begin{vmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

$$L = \begin{vmatrix} 0 \\ 0 \\ d \end{vmatrix}$$

Shimanouchi shows that N and A are related to each other by a similarity transformation; therefore, the trace of N = trace A. Thus from Figure 2 and equations 4 and 5:

$$r^2 = a^2 + d^2 \quad (6)$$

$$\rho^2 = b^2 + d^2 = r^2 + b^2 - 2rb \cos \phi / 2 \quad (7)$$

$$a^2 = 2 \rho^2 (1 - \cos \theta) \quad (8)$$

$$r^2 = 2 \rho^2 (1 - \cos \theta) + d^2; \quad \rho^2 = (r^2 - d^2 / 2(1 - \cos \theta)) \quad (9)$$

$$1 + 2 \cos \theta = \cos \tau - \cos \tau \cos \phi - \cos \phi \quad (10)$$

Equation 9 shows that ρ is uniquely determined from r , d , and θ .

Equation 7 can be rearranged so that ϕ is a function of ρ , r , and d ;

therefore τ in equation 10 is determined when r , d , and θ are

fixed. It is possible always to rearrange the equations to solve for

any one of the parameters in terms of any other three. Thus, if A

and A' are successive atoms on a chain, such as carbon atoms, there

will only be one unit cell length for any set of r , θ , and ϕ (6).

These equations have been derived without requiring that A and A' be two successive carbon atoms joined by a single bond. They are

equally valid if A is joined to A' by an intermediate point or atom B. Consider the chain A-B shown in Figure 3. If the A-B distance and the A-B-A angle are equal to the B-A distance and the B-A-B angle, A and B must lie on the surface of the same cylinder. The A-A distance must be equal to the B-B distance. A must spiral around a cylinder of radius determined by its r , θ , and ϕ . But if B is related in the said manner to A, it must also lie on a cylinder of the same radius since it will have the same r , θ , and ϕ .

If the A's are carbon atoms, the B's may be carbon or oxygen and the same statements would be true. A polymer having a monomer unit (-CR₂CR₂-) or (-CR₂O-) must have all of the skeletal atoms on the surface of the same cylinder, but the screw operation is not necessarily applicable in passing from one atom to the next on the chain.

Now consider a structure having three atoms on the skeletal chain per monomer (-CR₂CR₂CR₂-) as indicated by the dotted lines in Figure 3. If the first carbon of each unit is on the surface of a cylinder of radius ρ , the second carbon can lie on a cylinder ρ' , and the third carbon on a cylinder ρ'' ; where $\rho' < \rho < \rho''$. The screw operation is applicable in passing from A to A, but not from A to any atom in between. If these are carbon atoms, the question of staggered and trans configuration discussed by Corradini and Pasquon (6) arises. The θ angle first discussed must still be the angle of rotation

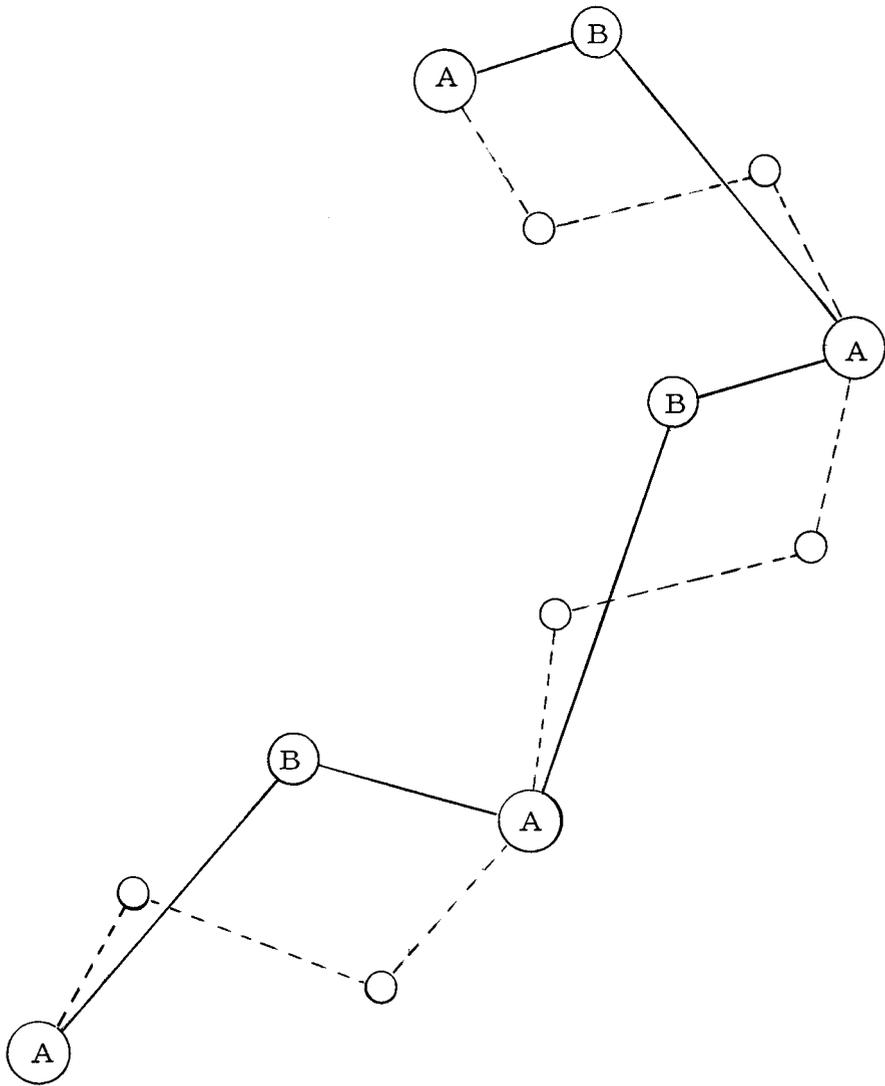


Figure 3. Types of helical chains.

required to transform the first carbon of the first monomer unit to the first carbon of the second monomer unit; and the r must be the distance between these carbon atoms. The ϕ angle must be the angle between the lines joining the first carbon atoms of three successive monomer units.

If the position of the A type atoms in Figure 3 are chosen consistent with the unit cell data, the B type atoms must be determined by the fact that they are a bond length distance from the neighboring A atoms and lie on the surface of the cylinder on which these carbons lie.

If there are two or more atoms between the positions of the reference atoms, the problem becomes more difficult. A series of equations can be written relating the positions of the intermediate atoms to the reference atoms and to each other. Since there are $3n$ parameters for n atoms, and $3n$ equations necessary to solve the problem exactly, the solution for more than one intermediate atom is best solved on a computer.

The problem is simplified for carbon-carbon chains and carbon-oxygen chains since the bond distance between the atoms is constant and so is the bond angle. If the unit cell length c , the number of turns per unit cell t , and the number of chemical repeat units are known, equation 9 can be used to solve for ρ , where $d = c/n$ and $\theta = 2t\pi/n$. Let A_i and B_i be the cartesian coordinates of an axis system with z

along the helical axis and x the perpendicular from the initial atom to the z axis. The initial atom A will have the coordinates $\rho, 0, 0$.

Then if the prime refers to the second monomer unit;

$$A'_1 = \begin{vmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{vmatrix} A_i + \begin{vmatrix} 0 \\ 0 \\ d \end{vmatrix} \quad (11)$$

$$\sum_{i=1,3} (B_i - A_i)^2 = R_{ab}^2$$

$$\sum_{i=1,3} (B_i - A'_i)^2 = R_{a'b}^2$$

$$\sum_{i=1,2} B_i^2 = \rho^2$$

R_{ab} is the distance from A to B and $R_{a'b}$ is the distance from A' to B .

The Newton-Raphson iteration (24, p. 447-453) can be used to program these equations for computer solution.

For an A-B type chain an additional check can be included making use of the cosine law:

$$\sum_{i=1,3} (A_i - B_i)(A'_i - B_i) = R_{ab}R_{a'b} \cos \phi \quad (12)$$

For A-B-C type chains, the R_a , R_b , R_c distances must be determined from knowledge or assumption of the configuration. Since carbon bonds are generally assumed to be trans or gauche to the penultimate preceding bond, only the two distances from these configurations need be considered.

It may or may not be obvious that there will be two solutions to the equations even though there are more equations than unknowns.

The solutions will correspond to the B type atoms above and below the line joining the A type atoms (Figure 3). The two positions are related by a rotation perpendicular to the helical axis.

Computer programs in Fortran II for calculating the cartesian coordinates of the intermediate atom and the side groups and for generating the atoms of the successive repeat units from the initial monomer unit are included in Appendix III. These are meant to serve only as examples. It is a short mental but laborious manual step to writing a program for the construction of the X matrix of the Schachtschneider programs.

The methyl side group is orientated staggered to the polypropylene chain, but it may be either staggered or eclipsed in the case of polyacetaldehyde. The choice of orientation effects the frequencies. In order to understand these effects, propane was calculated using an eclipsed configuration of the methyl groups to the methylene group. The results are discussed in Chapter 5.

THE POTENTIAL FIELD AND THE F MATRIX

There are three types of potential fields used in normal vibrational analyses - the central force field (CFF), the valence force field (VFF) and the Urey-Bradley force field (UBFF). The VFF is more generally popular, because it is in terms of the internal coordinates used in the g matrix, and because it has proved to be more satisfactory than the others in most cases. Dr. Schachtschneider has provided machine programs for symmetrizing the f matrix in VFF terms. The f matrix is actually entered in the secular determinant program as a vector. This is a programming technicality which is unimportant here.

From Table 4a and b the internal coordinate from the preceding and succeeding cells interacting with the unit cell are determined in the same manner as the g matrix. Many of these will, of course, be the same as those in the g matrix, but there will generally be additional ones depending on how far reaching the effect of the field. Interactions between stretches and bond angles have been included for completeness. These are frequently undeterminable since the number of force constants far exceeds the number of frequencies observed. Schachtschneider and Snyder (47) have reported transferable force constants for the n -parafin series, polyethylene and polypropylene (48, 50, 51, 52). Their values have been used as the initial values where

Table 4a. α submatrix of f matrix of polyacetaldehyde

	r_1	t_1	S_1	R_1	R'_1	α_1	β_1	ϕ_1	ϕ'_1	δ_1	γ_1	γ'_1	ω_1	ω'_1	σ_1	τ_1	τ'_1	
r_1	K																	
r'_1	F																	
r''_1	F																	
t_1		K																
S_1			K	F														
R_1			F	K														
R'_1				F'	K													
α_1						H												
α'_1						F												
α''_1						F												
β_1			F	F			H											
β'_1			F	F			F											
β''_1			F	F			F											
ϕ_1			F	F'			f	H										
ϕ'_1			F	F			f'	F	H									
δ_1			F	F			f ^g	F	F	H								
γ_1			F	F'			f ^e	F	f	F	H							
γ'_1			F	F	F'		f ^c	f	F	F	F	H						
ω_1			F	F	f		f ^g	F	F	F	F	F	H					
ω'_1			F'	F'	F'			f	F		h	F'	F	H				
σ_1															H			
τ_1																	H	
τ'_1																		H

Table 4b. β submatrix of f matrix of polyacetaldehyde (same column headings)

S_2																			F'
R_2					F														
β_2					F														
β'_2					F														
β''_2					F														
ϕ_2					F			h'^c	h^c										F'
ϕ'_2					F'			h''	h'										
δ_2					F			f'	f'										
γ_2				f'	F						h'	h	h'	F'					
γ'_2					F'						h''	h'		h					
ω_2				f	F							h'	f'	f					
ω'_2					f'									f'					

Elements must be subscripted with the coordinates of the column and row in which they appear.

applicable in the calculations on trioxane and polyacetaldehyde. The force constants of the carbon-oxygen chain were converted from the UBFF force constants of Tadokoro et al (58) using a transformation of the type indicated in equations 4 and 6 for a system shown in Figure 4c. These values calculated from the relationships listed in Table 5 were used as the initial force constants in the trioxane analysis, the results of which were then the starting values for polyacetaldehyde.

Some discussion concerning the choice of potential fields is in order, and it will be the purpose of this chapter to justify the choice of the VFF used in the analysis. A very practical reason has already been mentioned; the coordinates are the same as those used in the g matrix. Another practical reason is that the machine program available could use the f matrix in this form directly. There are other justifications which are discussed below.

Consider a charged particle in the field of another charged particle, the potential will vary according to the distance and force of each of the particles with respect to each other. The central force field is an expression based on this simple classical field. Since the advent of Schrodinger wave mechanics, it is postulated that the field around a nucleus chemically bonded to another will not be isotropic. The electron density in the region joining the two nuclei will be greater than outside this region. If the nucleus is bound to two other nuclei, there will be a preferred orientation of the nuclei with respect

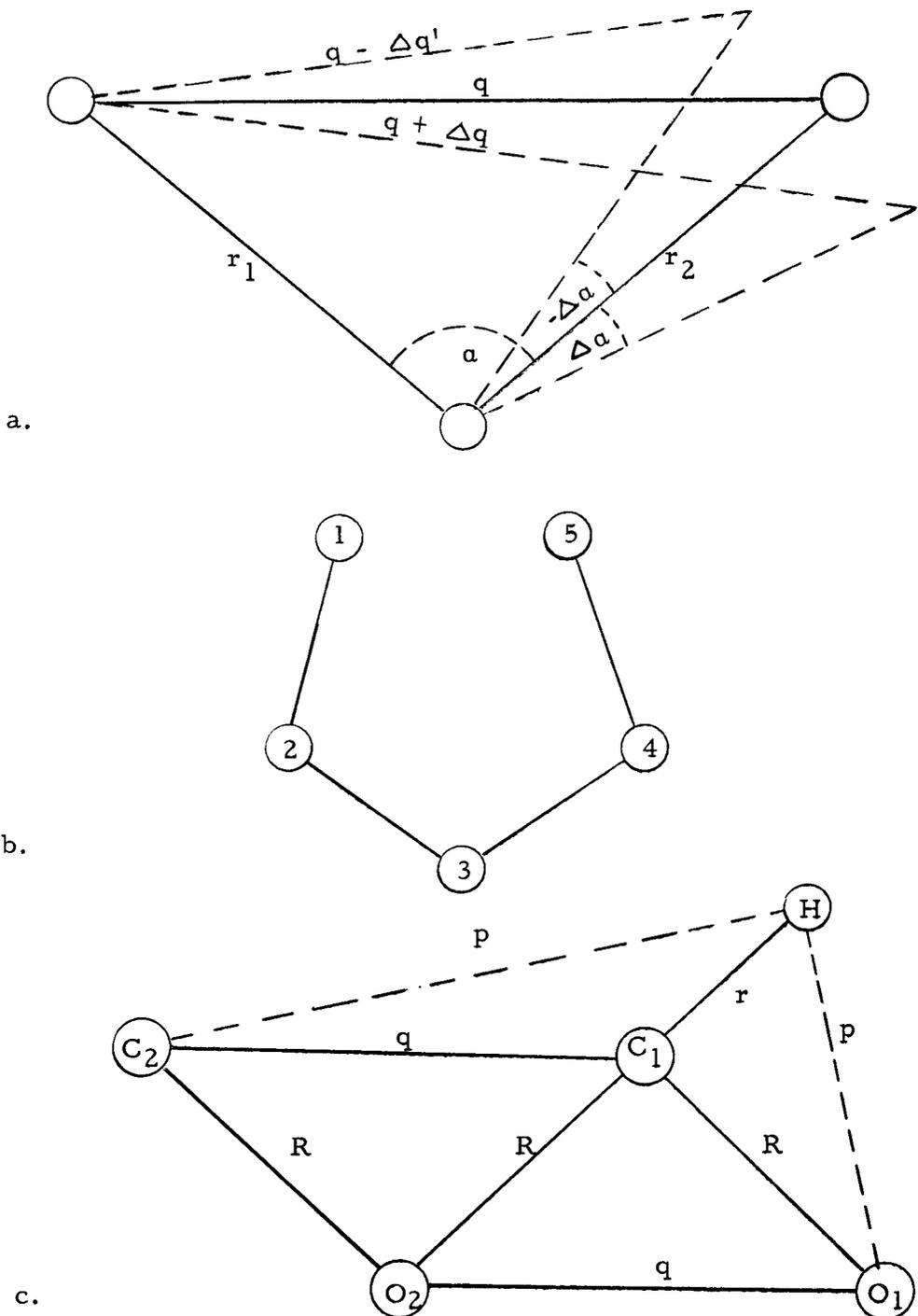


Figure 4. Systems for potential field consideration

Table 5. VFF force constants from UBFF force constants

$$\begin{aligned}
 K_r &= K_{CH} + 2c^2 F_{OH} \\
 H_\gamma &= H_{OCH} + e^2 F_{OH} \\
 K_R &= K_{CO} + d^2 F_{OH} + a^2 (F_{OO} + F_{CC}) \\
 H_\omega &= K_{OCO} + b^2 F_{OO} \\
 H_{\omega'} &= K_{COC} + b^2 F_{CC} \\
 F_{d\phi} &= ce F_{OH} \\
 F_{dR} &= dc F_{OH} \\
 F_{\phi R} &= de F_{OH} \\
 F_R &= a^2 F_{OO} \\
 F'_R &= a^2 F_{CC} \\
 F_{R\omega} &= ba F_{OO} \\
 F'_{R\omega} &= ba F_{CC}
 \end{aligned}$$

Force constants on left are VFF, on right UBFF, symbols are defined below; UBFF force constants are in $\text{mdyn}/\text{A}^\circ$, VFF force constants must be converted to $\text{mdyn}/\text{A}^\circ$ for stretches, mdyn/rad for stretch-bond interaction, and $\text{mdyn}/\text{A}^\circ/\text{rad}^2$ for bending force constants.

$$\begin{aligned}
 a &= R \cos \theta / q \\
 b &= R^2 \sin \theta / q \\
 c &= (r + R \cos \theta) / p \\
 d &= (R + r \cos \theta) / p \\
 e &= R r \sin \theta / p \\
 &\text{see Figure 4c} \\
 \theta &= \text{tetrahedral angle}
 \end{aligned}$$

$$\begin{aligned}
 K_{CO} &= 3.075 \\
 H_{COC} &= 0.55 \\
 H_{OCO} &= 0.34 \\
 F_{CC} &= 0.42 \\
 K_{CH} &= 3.95 \\
 F_{OO} &= 0.80 \\
 H_{OCH} &= 0.225 \\
 F_{OH} &= 0.70
 \end{aligned}$$

Reference 58

to each other depending on the type of binding. The valence force field is an expression of this type of field.

Neither of these alone completely describes the field, however, since both types of forces are applicable. An atom in a molecule is subject to the electrostatic potential of every other atom in the molecule (and indeed to every other atom everywhere) as well as the electronic forces of the atom(s) to which it is bound. The UBFF expresses the potential more adequately by combining the CFF and VFF. The result of which is to increase the already-too-many force constants. The UBFF field traditionally uses only the diagonal elements of its f matrix, but it is treated here in a manner analogous to the VFF and CFF.

For the system in Figure 4a, the potential field can be expressed:

$$\text{VFF} = \begin{vmatrix} \Delta r_1 & \Delta r_2 & \Delta a \end{vmatrix} \begin{vmatrix} K_v & f_v & h_v \\ f_v & K_v & h_v \\ h_v & h_v & H_v \end{vmatrix} \begin{vmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta a \end{vmatrix} \quad (1)$$

$$\text{CFF} = \begin{vmatrix} \Delta r_1 & \Delta r_2 & \Delta q \end{vmatrix} \begin{vmatrix} K_c & f_c & f'_c \\ f_c & K_c & f'_c \\ f'_c & f'_c & F_c \end{vmatrix} \begin{vmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta q \end{vmatrix} \quad (2)$$

$$\text{UBFF} = \begin{vmatrix} \Delta r_1 & \Delta r_2 & \Delta a & \Delta q \end{vmatrix} \begin{vmatrix} K_u & f_u & h_u & f'_u \\ f_u & K_u & h_u & f'_u \\ h_u & h_u & H_u & k_u \\ f'_u & f'_u & k_u & F_u \end{vmatrix} \begin{vmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta a \\ \Delta q \end{vmatrix} \quad (3)$$

The transformation between the fields is generally expressed as

$$\text{VFF} = T_c \text{CFF} T_c' = T_u \text{UBFF} T_u' \quad (4)$$

The transformation matrices T_c and T_u is derived from the equilibrium geometric of the system. Here

$$T_c = \begin{vmatrix} 1 & 0 & s_{12} \\ 0 & 1 & s_{21} \\ 0 & 0 & t \end{vmatrix} \quad (5)$$

$$T_u = \begin{vmatrix} 1 & 0 & 0 & s_{12} \\ 0 & 1 & 0 & s_{21} \\ 0 & 0 & 1 & t \end{vmatrix} \quad (6)$$

$$\text{where } s_{12} = (r_1 - r_2 \cos \alpha) / q \quad (7)$$

$$s_{21} = (r_2 - r_1 \cos \alpha) / q$$

$$t = (r_1 r_2 \sin \alpha) / q$$

A particular force constant such as the angle bending, H_v , can be used in the three fields if it is known in one by simply deriving the following relationships based on the invariance of the potential field:

$$H_v = t^2 F_c = H_u + t^2 F_u + t k_u \quad (8)$$

It can quickly be shown that this is consistent with a change in α keeping r_1 and r_2 constant by differentiating the cosine law:

$$q^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos \alpha \quad (9)$$

$$dq = s_{12} dr_1 + s_{21} dr_2 + t d\alpha \quad (10)$$

Examining the system shown in Figure 6a more closely for a change in α with r_1 and r_2 constant, note that a change of α to $\alpha + \Delta\alpha$ changes q to $q + \Delta q$ and α to $\alpha - \Delta\alpha$ changes q to $q - \Delta q'$. Compare these changes.

$$(q + \Delta q)^2 = 2r^2(1 - \cos(\alpha + \Delta\alpha)) \quad (11)$$

$$(q - \Delta q')^2 = 2r^2(1 - \cos(\alpha - \Delta\alpha))$$

assuming $r_1 = r_2 = r$.

Taking the square root of both sides of the equal sign and adding to obtain

$$\begin{aligned} (\Delta q - \Delta q' + 2q)/(2r^2)^{1/2} = \\ (1 - \cos(\alpha + \Delta\alpha))^{1/2} + (1 - \cos(\alpha - \Delta\alpha))^{1/2} \end{aligned} \quad (12)$$

Use the sum and difference formulas of the cosine:

$$\cos(\alpha + \Delta\alpha) = \cos\alpha \cos\Delta\alpha - \sin\alpha \sin\Delta\alpha \quad (13)$$

$$\cos(\alpha - \Delta\alpha) = \cos\alpha \cos\Delta\alpha + \sin\alpha \sin\Delta\alpha$$

$$\text{and let } u = 1 - \cos\alpha \cos\Delta\alpha \text{ and } v = \sin\alpha \sin\Delta\alpha \quad (14)$$

Substitute for q from equation 9 and rearrange

$$(\Delta q - \Delta q')/(2r^2)^{1/2} = (u + v)^{1/2} + (u - v)^{1/2} - 2(1 - \cos\alpha)^{1/2} \quad (15)$$

Expand by the binomial theorem using only the first three terms

$$(\Delta q - \Delta q')/(2r^2)^{1/2} = 2u^{1/2} - v^2/4u^{3/2} - 2(1 - \cos\alpha)^{1/2} \quad (16)$$

Remembering equation 13:

$$\begin{aligned} (\Delta q - \Delta q')/(2r^2)^{1/2} = 2(1 - \cos\alpha \cos\Delta\alpha)^{1/2} - 2(1 - \cos\alpha)^{1/2} \\ - (\sin\alpha \sin\Delta\alpha)^2/4(1 - \cos\alpha \cos\Delta\alpha)^{3/2} \end{aligned} \quad (17)$$

Since $\alpha \sim 0$, $\sin\Delta\alpha \sim \Delta\alpha$ and $\cos\Delta\alpha \sim 1$,

$$\Delta q' - \Delta q = (r/8^{1/2}) \Delta\alpha^2 (1 - \cos\alpha)^{1/2} \quad (18)$$

The difference then between the differences in the changes of q when $\Delta\alpha$ is + or -, is second order with respect to $\Delta\alpha$ and is a function of r and α , but it is not zero. The purpose of this derivation is to point out that although it is possible to write down transformations such as equations 5 and 6, the transformations are not strictly

applicable. The transformations between the three force fields are not linear except at the equilibrium position. It is analogous to mapping a spherical world on a flat surface. A Mercades projection has its usefulness but approaches physical reality only very near the equator. The three force fields are also useful in handling various problems, but one is probably closer to physical reality than the others. In our understanding of atoms and molecules, the UBFF seems to be the closest to the potential actually experienced by the molecule. The torsional forces are generally thought to result from the repulsion of atoms in positions analogous to 1 and 4 in Figure 6b. It is not easy, however, to relate this distance to known parameters of the molecule.

Formulas for the g matrix elements use the coordinates of the VFF. Since the f matrix must be in terms of the same coordinates as the g matrix, it is simplest to set up the potential using the VFF. The CFF has never been very satisfactory even in triatomic molecules and is less so in larger molecules. The additional parameters introduced by the UBFF are not justified in terms of the data available. Use of the simplified UBFF is not as satisfactory in many cases as use of the simplified VFF (47). Even in terms of VFF there are always more force constants to be determined than observed frequencies for a molecule of any size. For each non-bonded parameter in UBFF, there must be at least one additional equation relating it to the other parameters and at least four or more additional force constants.

Then there is the question of which non-bonded parameters to include. Consider the system of Figure 6b, if q_{13} and q_{14} are included in the force field, why not q_{15} ? When a methyl-type group is staggered to a methylene-type group, what determines the choice of interacting atoms? The complexity of the problem increases, if one includes all possible effective interactions not only because of their number, but also because of the difficulty of defining their relationship to each other.

THE MACHINE PROGRAM AND
SOME INTERESTING FINITE MOLECULES

THE MACHINE PROGRAM

Dr. J. H. Schachtschneider provided a vibrational secular equation program coded in Fortran II which diagonalizes the G and F matrices separately and then obtains the solution to

$$GFL = L\Lambda \quad (1)$$

L is related to the eigenvectors of the G and F matrices. Λ is a diagonal matrix whose elements are the eigenvalues of the secular determinant.

$$\Lambda = \lambda_i \quad (2)$$

$$\lambda_i = 4\pi^2 c^2 \omega_i^2 / N \quad (3)$$

Generally force constants are assumed and the frequencies calculated from them. It is then necessary to adjust the force constants to give the best fit of the frequencies observed. The difference

$$\lambda_{\text{obs.}} - \lambda_{\text{calcd.}} = \Delta\lambda_i \quad (4)$$

can be related to the changes necessary in the force constants by

$$\Delta\lambda_i = \sum_j \sum_k \sum_l (L_o)_{ki} (L_o)_{li} Z_{klj} \phi_j \quad (5)$$

where Z is the vector form of the F matrix and ϕ 's are the force constants,

$$F_{kl} = \sum_j Z_{klj} \phi_j \quad (6)$$

When these changes are incorporated in equation I-6

$$G(F_0 + \Delta F) - \lambda E = 0 \quad (7)$$

and new λ can be calculated. This process is repeated until no significant improvement in the frequencies is achieved from changes in the force constants.

A regression routine is also included such that each force constant is entered one at a time to test its effect on the fit. If the force constant has less than a set level of effect, it is dropped. If the effect is within the given significance level, its variation is tested and the possible range of values which will not significantly affect the frequencies is computed. This is printed as the error in the force constant value.

PROPANE

This molecule has been thoroughly studied by Schachtschneider and Snyder (46, 47) and Gayles (19). The molecule is considered to have both methyl groups staggered to the methylene group. The analysis here is to compare the differences in the force constants for an eclipsed configuration of the methyl groups for the purpose of understanding the effect of differences in the g matrix with no change in symmetry. In light of the disagreement of Gold et al (21) and Rigina and Godnev (43), a unitary matrix with as many singularities as redundancies in the f and g was also used on the staggered configuration to observe the differences in the resulting force constants. Table 6

and 7 show the results of this study.

There was no change in the frequencies or force constants resulting from a change in the U matrix for the same f and g matrices of propane. The changes in the frequencies resulting from the use of an eclipsed configuration are worth some discussion.

In the A_1 species the fourth frequency is mainly the symmetric α angles decreasing. A literal interpretation of this is that the repulsion of the methylene group would be greater in the eclipsed configuration and this frequency would increase as it does. There seems to be no reason for the decrease in the ninth frequency representing the ω angle decreasing, for a decrease here would also increase the separation of the methyl and methylene hydrogens; but it would also decrease the distance between the odd hydrogen on each methyl group.

The increases in the third and fourth frequencies of the B_1 modes are again expected as these represent the α and β angles moving in and out of phase. The decrease in the fifth frequency represents the methylene hydrogens moving toward one of the methyl groups which is now more difficult than in the staggered configuration. The sixth and seventh frequencies are a combination of the α , β , and γ which explains the small difference from the staggered configuration for the decrease in the repulsion of one pair of hydrogen interactions may be offset by the increase in another pair.

The increase in the sixth frequency of the B_2 modes is expected

Table 6. Propane frequencies

	<u>Observed</u>	<u>Staggered</u>	<u>Eclipsed</u>	<u>Description</u>
A_1				
1	2976.73	2966.4	2970.1	r^-
2	2961.74	2882.4	2892.6	r^+
3	2887.02	2856.4	2860.9	d^+
4	1476.00	1471.1	1505.9	$a +$
5	1462.00	1445.8	1443.9	$a + \beta + \gamma + \delta$
6	1391.88	1377.7	1386.2	$\gamma + \delta + a$
7	1157.51	1150.8	1157.3	β
8	869.34	870.4	850.9	R
9	369.20	381.7	350.4	ω
B_1				
1	2968.16	2962.9	2961.2	r^-
2	2887.02	2881.7	2889.9	r^+
3	1464.04	1464.8	1504.7	$a + \beta + \gamma + \delta$
4	1378.01	1367.1	1425.4	$a + \gamma$
5	1338.39	1341.8	1273.9	$a + \beta + \gamma$
6	1053.79	1045.9	1028.4	$a + \beta + \gamma$
7	921.73	923.7	900.0	β
B_2				
1	2972.61	2965.2	2965.7	r
2	2968.16	2921.2	2915.3	d
3	1471.95	1463.9	1456.2	a
4	1191.50	1184.7	1193.9	$\beta + \tau + \gamma$
5	748.13	746.9	748.3	$\gamma + \tau$
6		221.2	362.0	τ
A_2				
1		2964.3	2963.8	r
2		1459.0	1466.1	a
3		1278.8	1230.1	$\gamma + \tau$
4		903.4	1042.9	$\beta + a$
5		200.3	346.3	τ

Observed frequencies are from Gayles (19).

Description is for the eclipsed calculation using the notation of Schachtschneider and Snyder (46, 47) and is similar to that used for trioxane and polyacetaldehyde.

Table 7. Force constants for propane calculation.

<u>Description</u>	<u>Initial</u>	<u>Calculated</u>	<u>Gayles</u>
K_r	4.703	4.703*	5.113684
F_r	.038	.038*	.011006
K_d	4.545	4.545*	5.066316
F_d	.015	.015*	.059411
K_R	4.745	4.745*	4.798390
F_R	.138	.138*	.063900
$F_{R\beta} = F_{R\gamma}$.120	.217	.250078
$F'_{R\gamma}$	-.164	.032	
$F_{R\omega}$.279	1.034	.351400
H_d	.541	.541*	.597881
H_β	.606	.606*	.665218
F_β	-.051	-.051*	-.045143
H_γ	.665	.665*	.697092
F_γ	-.014	-.014*	-.024204
F'_γ	.015	.015*	.007845
$F_{r\omega}$	-.074	-.074*	-.014135
H_ω	.944	.944*	1.069890
$f_{\beta\omega}^g = f_{r\omega}^g$	-.076	.054	-.058400
$f_{\beta t} = f_{\beta r} = f_{\gamma t}$.063	.198	.063744
$f_{\beta\omega}^t = f_{r\omega}^t$.043	-.160	.106615
$h_{\beta r}^e = h_{\gamma}^e$.012	.018	.106615
$h_{\beta r}^c = h_{\gamma}^c$.010	.121	
$h_\beta^e = h_{\beta r}^e = h_\gamma^e$.022	.030	.044853
$h_\beta^c = h_{\beta r}^c = h_\gamma^c$.014	.021	-.043071
H_δ	.519	.519*	.618030

*fixed in this calculation

The initial force constants are from the staggered configuration. The calculated force constants are for the eclipsed configuration. Gayles (19) calculated values for the unperturbed frequencies.

as this represents the τ frequency which is favored since any change in position would tend to decrease the potential energy.

The decrease in the third frequency of the A_2 modes is somewhat unexpected, but might be thought of as representing a rotation of the methyl and methylene in the same direction. The increases in the fourth and fifth frequencies are again explainable as the increased tendency of the hydrogens to move away from each other.

The overall fit for the staggered configuration is better than twice as good as for the eclipsed configuration, but the really unacceptable result of the eclipsed calculation is the unreasonable value for the $F_{R\omega}$ interaction. One would not expect an off-diagonal force constant to have a value greater than 0.5. A second calculation holding no force constants fixed showed no improvement in the frequencies but changed the H_β to 0.665. The error range was fantastically high. It is necessary to hold major force constants fixed in turn in order to obtain reasonable ranges for the errors in the force constants.

SYM-TRIOXANE

Analysis

The vibrational spectra of sym-trioxane has been reported by Stair and Nielsen (55), who have also assigned the bands observed in both the infrared (gas and liquid states from 3200 to 390 cm^{-1}) and

Raman (liquid and crystalline states from 3020 to 300 cm^{-1}) spectra. The crystalline unit cell contains two molecules rotated 60° to each other. It belongs to the C_{3v}^6 space group and every fundamental of the molecule should be split for the unit cell. The analysis here uses the C_{3v} point group of a single molecule and fits to the gaseous spectra (the 307 Raman line is also included). Using the coordinates designated in Figure 5, the symmetry species are shown in Table 8.

Table 8. Symmetry species for sym-trioxane.

C_{3v}	E	$2C_3$	$3C_2$	n_T	n_r	n_R	n	n	n	n	'n	
A_1	1	1	1	8	2	1	1	2	1	1	1	T_z
A_2	1	1	-1	4	0	1	0	2	0	0	1	R_z
E	2	-1	0	12	2	2	1	4	1	1	2	T_x, T_y, R_x, R_y

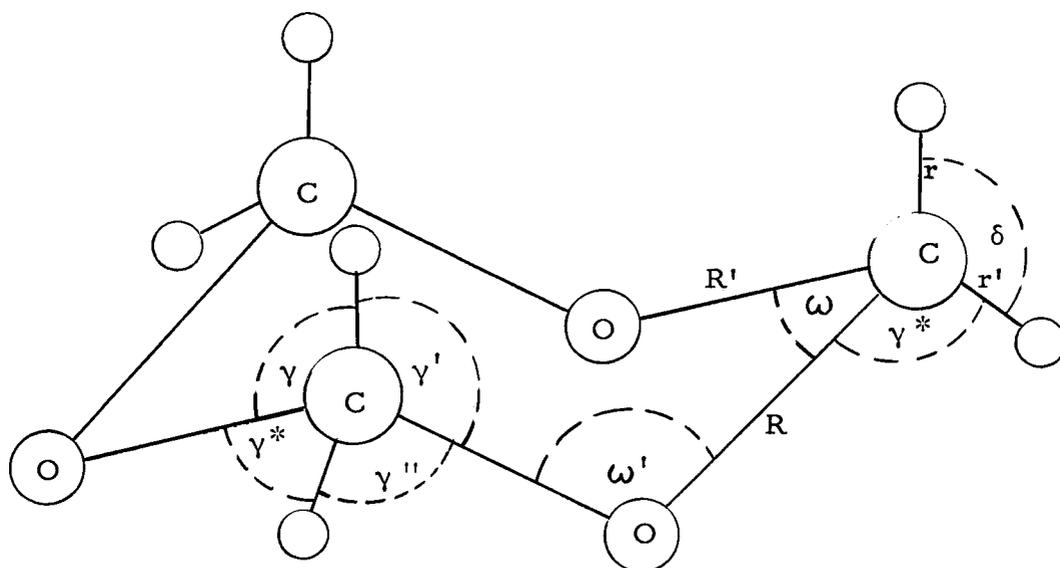
Using the table C_3 of the Appendix I, the species may be represented as

$$S_A = s_1 + s_2 + s_3 \quad (8)$$

$$S_E = 2s_1 - s_2 - s_3$$

$$S_{E'} = s_2 - s_3$$

Since there are 12 atoms in a single molecule of trioxane, the normal vibrations will have 30 modes consisting of $7A_1$, $3A_2$, and $10E$. The redundancies as discussed in Chapter Two will involve one for the angles around the C atom and one for the ring stretches, bendings and torsional distortions. Because of the peculiarity of the torsional modes, the species containing the minus sign will appear in the



τ = torsion around R

τ' = torsion around R'

Figure 5. Internal coordinates of sym-trioxane.

Table 9. Symmetry coordinates for trioxane

 A_1

$$\begin{aligned}
S_1 &= A(r - r') \\
S_2 &= A(r + r') \\
S_3 &= A(\delta) \\
S_4 &= A(\gamma + \gamma' - \gamma^* - \gamma'') \\
S_5 &= A(\gamma + \gamma' + \gamma^* + \gamma'') \\
S_6 &= A(R + R') \\
S_7 &= A(-\omega + \omega') \\
S_8 &= A(\omega + \omega') \\
S_9 &= A(\tau - \tau')
\end{aligned}$$

 A_2

$$\begin{aligned}
S_{10} &= A(\gamma - \gamma' - \gamma^* + \gamma'') \\
S_{11} &= A(\gamma - \gamma' + \gamma^* - \gamma'') \\
S_{12} &= A(R - R') \\
S_{13} &= A(\tau - \tau')
\end{aligned}$$

 E

$$\begin{aligned}
S_{14} &= E(r - r') \\
S_{16} &= E(R + R') \\
S_{18} &= E(R - R') \\
S_{20} &= E(\delta) \\
S_{22} &= E(\gamma + \gamma' + \gamma^* + \gamma'') \\
S_{24} &= E(\gamma - \gamma' - \gamma^* + \gamma'') \\
S_{26} &= E(\gamma + \gamma' - \gamma^* - \gamma'') \\
S_{28} &= E(\gamma - \gamma' + \gamma^* - \gamma'') \\
S_{30} &= E(\omega + \omega') \\
S_{32} &= E(\omega - \omega') \\
S_{34} &= E(r + r') \\
S_{36} &= E(\tau + \tau') \\
S_{38} &= E(\tau - \tau') \\
S_{15} &= E'(r - r') \\
S_{17} &= E'(R + R') \\
S_{19} &= E'(R - R') \\
S_{21} &= E'(\delta) \\
S_{23} &= E'(\gamma + \gamma' + \gamma^* + \gamma'') \\
S_{25} &= E'(\gamma - \gamma' - \gamma^* + \gamma'') \\
S_{27} &= E'(\gamma + \gamma' - \gamma^* - \gamma'') \\
S_{29} &= E'(\gamma - \gamma' + \gamma^* - \gamma'') \\
S_{31} &= E'(\omega + \omega') \\
S_{33} &= E'(\omega - \omega') \\
S_{35} &= E'(r + r') \\
S_{37} &= E'(\tau + \tau') \\
S_{39} &= E'(\tau - \tau')
\end{aligned}$$

A_1 modes. By convention (63, p. 60) the increase in the torsion angle is taken in the clockwise sense of the projections of the bonds, when this is reflexed through the symmetry plane the direction is reversed. The A_1 and E modes are both infrared and Raman active; the A_2 modes are inactive.

The abbreviated f matrix is shown in Table 10. The initial force constants used in the calculation were obtained where appropriate from the saturated hydrocarbon force constants of Snyder and Schachtschneider (47, p. 131) and from Tadokoro (58, p. 707) using the transformations indicated in Table 5. The final force constants listed were obtained by fitting to the assignments of Stair and Nielsen.

Discussion

The fit of the first calculation was 4.1%. The range of error in the ring stretches and bendings was considerably higher than that for the other force constants. They also differ quite markedly from the initial force constants which were obtained from the transformation of the UBFF force constants of Tadokoro. The interaction constants between the ring stretches and bendings were also high. This is probably because of the interdependency of these force constants due to the redundancy conditions. The torsional force constant which was entered as the ethane torsion constant of Schachtschneider and

Table 10. Abbreviated f matrix for trioxane

	r	R ₁	R' ₁	δ ₁	ω ₁	ω' ₁	γ ₁	τ ₁
r	K _d							
r'	F _d							
R ₁	F	K						
R' ₁	F	F	K					
R ₂			F'					
R' ₂			F'					
δ ₁	F	F	F	H				
ω ₁	F	F	F	F	H			
ω' ₁	F	f'	F'	f	F	H'		
ω ₂			f'		h	f		
ω' ₂						h'		
ω ₃		f'	f		h			
ω' ₃	F	F'	f	f'	F	h'		
γ ₁	F	F	F'	f	F	f'	H	
γ' ₁	F	F'	F	f	F	f	F'	
γ ₂	F'	F	F'	f	F	f'	F	
γ' ₂	F'	F'	F	f	F	f	f	
γ ₃			f		h	f	h ^e	
γ' ₃						f'	h ^e	
γ ₄			f		h'	f	h'	
γ' ₄						f'	h ^c	
γ ₅							h ^e	
γ' ₅		f			h		h ^e	
γ ₆							h ^c	
γ' ₆		f			h'		h ^c	
τ								H

The force constants are subscripted with the coordinates of the row and column in which they appear.

Table 11. Force constants of sym-trioxane

<u>Number</u>	<u>Description</u>	<u>Initial</u>	<u>Calculated</u>
1	K_d	4.756	4.298
2	F_d	.016*	.016
3	F_{dR}		-.461
4	K_R	4.421	5.757
5	F_R	.503	.503
6	H_S	.550*	.584
7	$F_{d\omega}$		-.872
8	$F_{R\omega}$.539	.756
9	$F''_{R\omega}$.180
10	$F_{d\gamma}$.473	-.473
11	$F_{R\gamma}$.540	.540
12	H_ω	1.810	1.238
13	F_ω	.043*	.043
14	$F_{\gamma\omega}$	-.124*	-.124
15	H_γ	.906	.806
16	F_γ	-.016*	-.016
17	F'_γ	.023*	.023
18	H'_ω	1.724	1.390
19	$F'_{R\omega}$.290	.415
20	F'_R	.286	.286
21	H_γ	.024*	.131
22	$F''_{R\omega}$.1 *	.1
23	$f^g_{\gamma\omega}$	-.058*	-.058
24	h^e_γ	-.002*	0.
25	h^c_γ	-.003*	0.
26	h^e_ω	.01 *	.01
27	h'^e_γ	.012*	-.094
28	h'^c_γ	.01 *	0.

*from Snyder and Schachtschneider (47)

Snyder turned out to be closer to the torsional constant of cyclohexane reported by Takahashi (59). The decrease in the methylene force constant and increase in the interaction constants involving the hydrogen and oxygen coordinates may reflect some attraction between the oxygen and hydrogen which does not occur in the hydrogen and carbon compounds.

The assignments of Stair and Nielsen were based on the shape of the band envelopes, comparison with cyclohexane, and intuition. Trioxane is an oblate top with the unique moment of inertia greater than the two equal ones. For this case the β parameter of Gerhard and Dennison (20) is about $-1/3$. Reference to that work shows that the only theoretical difference between the shape of the parallel and perpendicular bands is the spacing between the P and R branch. Stair and Nielsen calculated a spacing of 15 cm^{-1} for the perpendicular bands and 25 for the parallel. A difference of 10 cm^{-1} is difficult to distinguish. The intensity of the Q branch also shows no large differences for this type of molecule. If then the bands are assigned on the basis of the calculations, it is possible to improve the fit by about 1%. Some justification for the reassignment is found in the recent work of Snyder and Schachtschneider (52) and Takahashi(59) on cyclohexane. Both these papers assign the higher r^- frequency to the A mode rather than the E. The A modes involving the methylene rock in cyclohexane differ by about 200 to 300 cm^{-1} whereas the

assignments of Stair and Nielsen for these modes in trioxane differ by about 500 cm^{-1} . The 1477 and 1496 overlap so that the normal vibrational calculation is probably a better criteria than any other for distinguishing between the A and E modes. Stair and Nielsen suggested 1474 for the A mode which is closer to 1477 than to 1496. It is possible to increase K_r to 4.546, the value used by Schachtschneider and Snyder, and H_ω to 1.39, = H'_ω and thereby decrease the interaction constant $F_{d\omega}$ to -.4 without changing the goodness of the fit by more than 0.1%, if the band assignments are changed; the error increases appreciably if the original assignments are used. The best criteria for making band assignments would be a polarized spectra of a single crystal of trioxane, since the difference in polarization is probably the most distinguishing difference between the A and E modes. Table 12 shows the assignments of Stair and Nielsen under the heading Observed. The calculated frequencies fitted to these are listed in the second column. The suggested reassignments are in the third column, the fit is 2.6% here.

Table 12. Frequencies of sym-trioxane.

<u>Observed</u>	<u>Calculated</u>	<u>Reassignment</u>	<u>Description</u>
A ₁			
2853	2944.7	3031	r ⁻
2792	2774.7	2792	r ⁺
1496	1476.4	1477	δ
975	996.7	1050	γ + τ + ω + R
943	940.6	943	ω + γ + R + δ
752	711.2	752	ω + τ + γ
524	445.4	460	τ + γ + ω
A ₂			
	1379.2		γ
	1160.0		γ + R
	1127.0		γ
E			
3031	2939.0	2853	r ⁻
2753	2767.8	2753	r ⁺
1477	1497.0	1496	δ
1408	1431.0	1408	γ
1305	1335.4	1305	γ
1175	1210.2	1175	R + γ + ω
1072	1003.6	1072	R + ω
1050	917.2	975	γ + τ
460	502.1	524	ω + τ
307*	305.4	307	τ

*Raman line

POLYACETALDEHYDE

Analysis

Natta et al (38) reported the x-ray data for polyacetaldehyde giving the space group as $I4_1/a$ with $a = 20.01\text{\AA}$, $c = 4.78\text{\AA}$ and four chains per x-ray unit cell. Since only a single chain is used in this analysis, the C_4 space group applies. There are 28 atoms in a unit cell of polyacetaldehyde; $3N-4$ for polymer molecules indicates 80 normal modes divided into $19A + 21B + 20E$. Since we have chosen 23 internal coordinates per monomer unit and each monomer unit is displaced for every symmetry operation except the identity, there will be 23 symmetry coordinates for each mode generated by substituting the sets of internal coordinates listed in Table 2 into equations II-5 and 6 to obtain U_1 and U_2 respectively. There are then four redundancies in A, two in B and three in E (each E is doubly degenerate). Again the redundancies involve the angles around each carbon atom and the skeletal stretches, bendings and torsional distortions. The non-degenerate skeletal redundancies will both appear in the A block since these are symmetric with a quarter turn around the helical axis. They may be thought of as resulting in a twist around the axis which is forbidden in this analysis since it would change the unit cell.

Though there are theoretically 39 infrared active modes (A + E),

there are only 18 observed frequencies reported by Novak and Whalley (39, 40). The spectra has also been reported by Furukawa et al (18). Both authors have generously supplied us with full scale copies of their spectra.

The spectra are of crystalline polyacetaldehyde, but it is not possible to obtain single crystals of polymer. There will be no clues as to which are the A and E modes from the band shapes; and there will be much overlapping of bands because of the splitting of the fundamental frequencies and because there are many modes similar to each other. With so few frequencies it was not possible to decrease the perturbation low enough for the machine program to fit the force constants to the frequencies. This is probably because of the large interdependency of the force constants with each other. It is necessary in this case to calculate the frequencies using the best values of force constants known and making the assignments on the basis of these calculations. Some assistance on assignments can be obtained by comparison with polypropylene data (48, 51, 52). Polyacetaldehyde has a similar relationship to polypropylene as trioxane has to cyclohexane.

The initial force constants are listed in Table 13. Numbers 6, 7, 11, 14, 15, 18, 24, 25, 26, 27, and 34 were obtained from the trioxane calculation. K_t is estimated from the value given by Snyder and Schachtschneider (47) taking into account the fact that the C-H

Table 13. Force constants used in the calculation of polyacetaldehyde

<u>No.</u>	<u>Description</u>	<u>Value</u>	<u>No.</u>	<u>Description</u>	<u>Value</u>
1	K_r	4.699	21	$F_{S\gamma}$.2
2	F_r	.043	22	$F_{S\omega}$.4
3	K_t	4.726	23	$F_{R\beta}$.1
4	K_S	4.337	24	$F_{R\phi}$.54
5	F_{RS}	.101	25	$F_{R\gamma}$.54
6	K_R	5.7	26	$F_{R\omega}$.756
7	F_R	.503	27	$F'_{R\omega}$.415
8	H_α	.541	28	F_γ	-.021
9	H_β	.645	29	F_ω	-.043
10	F_β	-.012	30	F_ϕ	-.041
11	H_ϕ	.805	31	$F_{\phi\delta}$	-.014
12	H_δ	3.667	32	$F_{\gamma\omega}$	-.124
13	H_γ	.900	33	$F'_{\gamma\omega}$	-.124
14	H_ω	1.264	34	F'_R	.286
15	H'_ω	1.390	35	$F_{\delta\gamma}$	-.12
16	H_σ	.130	36	$F_{\delta\omega}$	-.12
17	H_τ	.130	37	$F'_{\delta\omega}$	-.12
18	$F_{S\beta}$.2	38	$F_{\phi\gamma}$	-.12
19	$F_{S\phi}$.2	39	$F_{\phi\omega}$	-.12
20	$F_{S\delta}$.2	40	$F_{\phi\omega}$	-.12

stretch in trioxane is lower than for cyclohexane. The C-C-O angle bending constant was given the C-C-C angle value of that reference. All other values were obtained or estimated from these authors.

The calculated frequencies are listed in Table 14. The observed frequencies which most closely correspond to the calculated are listed in the second column. The description refers to the dominant mode in the eigenvector. None of the modes are entirely free of the others in the calculation. The fit of the calculated frequencies to the observed is about 3.6%.

The calculations were carried out for the methyl group oriented both gauche and eclipsed to the skeletal chain in an attempt to decide whether the calculations would be a criteria for the orientation of the side chain. The results of both calculations were identical.

Discussion

At first it might be thought that with 39 calculated frequencies and only 18 observed, it would be difficult not to find a good fit of the frequencies. This is not entirely true. If the original force constants for the polyether coordinates obtained from the transformation of the Urey-Bradley force constants reported by Tadokoro for polyoxymethylene are used in the calculations instead of first fitting them to the trioxane spectra, the 1380, 1335, 1187, and 810 frequencies are hard to assign. These calculations also predict a modes in the range of

Table 14. Frequencies of polyacetaldehyde.

<u>Calculated</u>	<u>Assigned</u>	<u>Description</u>	<u>Calculated</u>	<u>Description</u>
A			B	
2962.5	2980	r ⁻	2962.0	r ⁻
2961.4		r ⁻	2961.3	r ⁻
2950.6	2920	t	2946.9	t
2883.9	2860	r ⁺	2883.9	r ⁺
1465.9		a + ϕ + σ	1499.0	ϕ + σ
1464.3		a ⁻	1463.9	a ⁻
1461.4	1445	a ⁻	1463.3	a ⁻
1413.2	1400	a ⁺	1416.0	a ⁺
1371.0	1380	δ + σ + ϕ	1373.5	a + δ + ϕ
1337.3	1187	δ + σ + ϕ	1175.7	β + δ + R
1164.4	1130	β + τ + ω	1160.8	β + δ + a
1108.7	1085	δ + S	1059.8	β + a
965.8	935	β ⁻	945.4	β + σ
928.3	845	β ⁻	913.0	β + S
750.4		σ	796.1	σ
576.7	620	σ + ω	628.7	ω + ϕ + τ
406.0	490	τ + ω + ϕ	466.8	σ + τ
369.8		a	308.5	a + τ
162.2		ω + a	206.6	ω + τ
			118.5	τ
			57.4	τ
E				
2962.2	2980	r ⁻		
2961.3		r ⁻		
2948.8	2920	t		
2883.9	2860	r ⁺		
1477.1		ϕ + σ + a		
1464.0	1445	a		
1462.5		a		
1412.3	1400	a		
1363.7	1335	δ + a + ϕ		
1213.1		β + R + τ		
1141.3	1130	σ + ϕ + δ		
1089.9	1040	β + a + δ		
977.8	970	β + a		
912.6	935	β + σ		
749.0	810	σ		
635.7	620	a + τ		
486.3	450	a + ω + τ		
300.9		a + ω		
190.9		τ		
52.4		τ		

1500 - 1700 which is difficult to accept. Using the fitted force constants from trioxane, all of the observed bands can be reasonably assigned. The α modes fall in the upper 1400 region which is expected. At first glance the methyl torsion modes appear to fall in the right range also. Fateley and Miller (15, 16) predict the single rotor CH_3 group on acetaldehyde to fall in the 100 - 300 range with the E modes higher than the A mode. The methyl rotor on $\text{CH}_3\text{CHOCH}_2$ ring is between 167 - 426 according to these authors. Glancing at Table 14, one would expect the methyl torsion to dominate the 162.2 in A, 206.6 in B, and 300.9 in E. Instead the 750.4 in A, 796.1 in B, and 749.0 in E are predominately methyl torsion with some contributions to other frequencies. It is difficult to decide whether this is because of the small displacement approximation inherent in the calculation which is not necessarily true for a freely rotating methyl side group or whether the cause is due to the high mixing of the normal modes and the method of defining the torsion coordinates. The torsion angle here is defined as the sum of the torsional displacements of each of the methyl hydrogens with respect to one of the atoms attached to the skeletal carbon. Since it involves so many of the atoms, there is much interaction of this mode with the others.

The fact that the calculations for the methyl group oriented gauche to the skeletal chain is identical to the results when the methyl group is eclipsed to the chain is at first surprising. At least in these

calculations, unlike propane, there can be no criteria from which to judge the orientation of the side group. The methyl group hydrogens are generally staggered to other hydrogens or carbons but they may be eclipsed to oxygen atoms and form hydrogen bonds. It might have been possible, however, if enough confidence in the transferability of the force constants existed, to fix the major force constants and permit the force constants between the α and β interacting with the γ , δ , ϕ , and ω to perturb to fit the frequencies. Their final values might be a clue to the side group orientation. In these calculations these force constants were set equal to zero. If time permitted it would have been wiser to first fit the trioxane data to the polyoxymethylene calculations before attempting the polyacetaldehyde. There would have been more transfer of force constants between the trioxane and polymethylene. This would have given more confidence in the values of the polyether force constants.

More spectral data either from Raman studies or isotopic spectra might be helpful at this stage to help determine the significance of the force constants. Although it would not be possible to make the neat calculations according to the Teller-Redlich product rule (7, p. 202-204) because of the intermixing of the modes, some calculations according to the sum rule of Decius and Wilson (10) would not be too difficult since isotopic substitution does not change the symmetry. In any case both rules would give a prediction of the direction of

change of frequencies and some clues to the significance of the force constant values.

In this calculation it has only been possible to fit the polyacetaldehyde spectra only as well as it was possible to fit the trioxane spectra. It could be hoped that a better fit of the trioxane spectra and more certainty of the polyether force constants would give a better fit of the polyacetaldehyde spectra. The method of carrying out the analysis is now established; it now remains to obtain enough data to ascertain the transferability of the force constants.

SUMMARY

A method for analyzing the normal vibrations of polymer molecules is developed in detail. The details of the treatment are set up in a manner analogous to the treatment of finite molecules so that the same computer programs can be used for either system.

The normal vibrational analysis was made on propane using a staggered configuration normally assumed for this molecule to ascertain the effect of the U matrix on the force constants. No change in the force constants were found whether or not the redundancies are explicit or implicit in the U matrix as long as the same set of internal coordinates are used. Calculations were also made on the eclipsed configuration of the methyl group to the methylene group to determine the sensitivity of the frequencies to the g matrix. Certain frequencies were found to change, especially those involving the α modes. The fit to the observed frequencies was not quite as good, 1.6% compared to 0.67% for the staggered configuration. Some of the values of the interaction force constants were unreasonably high, especially the interaction between the carbon stretch and angle bending.

A normal vibrational analysis was made on trioxane to obtain force constants for the analysis of polyacetaldehyde. The initial polyether force constants for this analysis were obtained from a transformation of Urey-Bradley force constants used in the calculation

of polyoxymethylene by Tadokoro(58). Other force constants were obtained or estimated from Schachtschneider and Snyder (52). The final fit of the calculated frequencies to the assignments of Stair and Nielsen (55) was 4.1%. Some of the interactions force constants were unreasonably high. These could be reduced somewhat by reassignments based on the calculations. The fit of the new calculations to the reassigned frequencies was 2.8%. Further attempts to fit the frequencies would not be fruitful without more certainty of the assignments.

The method for calculating the normal vibrations of polymers was applied to polyacetaldehyde. It was not possible to fit its observed frequencies to better than the final fit of trioxane using the polyether force constants obtained from that analysis. The calculations do permit assignment of all of the reported frequencies (39). It was not possible in these calculations to distinguish between the staggered and eclipsed orientation of the methyl side group. The validity of the assignments is subject to further verification since the number of observed frequencies is much less than the number of calculated frequencies.

A discussion of the conformation of polymer chains offers an approach to determining the Cartesian coordinates necessary in the calculation of the g matrix. Some errors in the usual use of the equations of Shimanouchi and Mizushima (54) are pointed out and a

correction is suggested.

Tables for generating real symmetry species of C_n type helices are included for use in polymer analyses.

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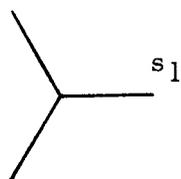
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APPENDICES

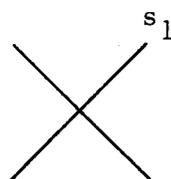
APPENDIX I

Tables for generating symmetry coordinates. The resultant vector is indicated if the coordinates are oriented in the same manner as the accompanying diagram. Numbering is counterclockwise. $\theta = 2\pi/n$

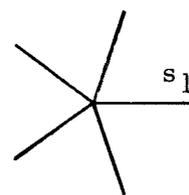
C_3	s_1	s_2	s_3	
A	1	1	1	
E	2	-1	-1	(x)
		1	-1	(y)



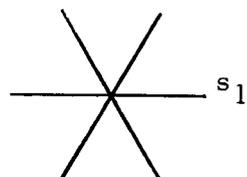
C_4	s_1	s_2	s_3	s_4	
A	1	1	1	1	
B	1	-1	1	-1	
E	1	-1	-1	1	(x)
	1	1	-1	-1	(y)



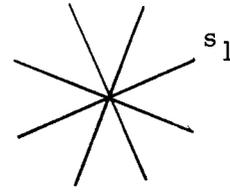
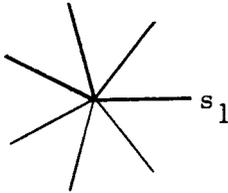
C_5	s_1	s_2	s_3	s_4	s_5	
A	1	1	1	1	1	
E_1	1	$\cos\theta$	$\cos 2\theta$	$\cos 2\theta$	$\cos\theta$	(x)
		$\sin\theta$	$\sin 2\theta$	$-\sin 2\theta$	$-\sin\theta$	(y)
E_2	1	$\cos 2\theta$	$\cos\theta$	$\cos\theta$	$\cos 2\theta$	
		$\sin 2\theta$	$-\sin\theta$	$\sin\theta$	$-\sin 2\theta$	



C_6	s_1	s_2	s_3	s_4	s_5	s_6	
A	1	1	1	1	1	1	
B	1	-1	1	-1	1	-1	
E_1	2	1	-1	-2	-1	1	(x)
		1	1		-1	-1	(y)
E_2	2	-1	-1	2	-1	-1	
		-1	1		-1	1	

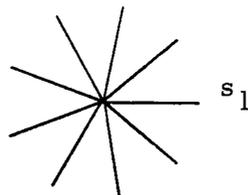


C_7	s_1	s_2	s_3	s_4	s_5	s_6	s_7	
A	1	1	1	1	1	1	1	
E_1	1	$\cos\theta$ $\sin\theta$	$\cos 2\theta$ $\sin 2\theta$	$\cos 3\theta$ $\sin 3\theta$	$\cos 3\theta$ $-\sin 3\theta$	$\cos 2\theta$ $-\sin 2\theta$	$\cos\theta$ $-\sin\theta$	(x) (y)
E_2	1	$\cos 2\theta$ $\sin 2\theta$	$\cos 3\theta$ $-\sin 3\theta$	$\cos\theta$ $-\sin\theta$	$\cos\theta$ $\sin\theta$	$\cos 3\theta$ $\sin 3\theta$	$\cos 2\theta$ $-\sin 2\theta$	
E_3	1	$\cos 3\theta$ $\sin 3\theta$	$\cos\theta$ $-\sin\theta$	$\cos 2\theta$ $\sin 2\theta$	$\cos 2\theta$ $-\sin 2\theta$	$\cos\theta$ $\sin\theta$	$\cos 3\theta$ $-\sin 3\theta$	



C_8	s_1	s_2	s_3	s_4	s_5	s_6	s_7	s_8	
A	1	1	1	1	1	1	1	1	
B	1	-1	1	-1	1	-1	1	-1	
E_1	1	1	-1	-1	-1	-1	1	1	(x)
	1	1	1	1	-1	-1	-1	-1	(y)
E_2	1	1	-1	-1	1	1	-1	-1	
	1	-1	-1	1	1	-1	-1	1	
E_3	1	0	-1	$\sqrt{2}$	-1	0	1	$-\sqrt{2}$	
	1	$-\sqrt{2}$	1	0	-1	$\sqrt{2}$	-1	0	

C_9	s_1	s_2	s_3	s_4	s_5	s_6	s_7	s_8	s_9	
A	1	1	1	1	1	1	1	1	1	
E_1	2	2	-1	-1	-1	-1	-1	-1	2	(x)
			1	1	1	-1	-1	-1		(y)
E_2	1	$\cos 2\theta$ $\sin 2\theta$	$\cos 4\theta$ $\sin 4\theta$	$\cos 3\theta$ $-\sin 3\theta$	$\cos\theta$ $-\sin\theta$	$\cos\theta$ $\sin\theta$	$\cos 3\theta$ $\sin 3\theta$	$\cos 4\theta$ $-\sin 4\theta$	$\cos 2\theta$ $-\sin 2\theta$	
E_3	2	-1	-1	2	-1	-1	2	-1	-1	
		1	-1		1	-1		1	-1	
E_4	1	$\cos 4\theta$ $\sin 4\theta$	$\cos\theta$ $-\sin\theta$	$\cos 3\theta$ $\sin 3\theta$	$\cos 2\theta$ $-\sin 2\theta$	$\cos 2\theta$ $\sin 2\theta$	$\cos 3\theta$ $-\sin 3\theta$	$\cos\theta$ $\sin\theta$	$\cos 4\theta$ $-\sin 4\theta$	



APPENDIX II

Proof of the reduction of the F and G matrices of an infinite chain

The proof will deal with the F matrix but applies equally to the G matrix. The potential function is always

$$2V = \sum_{tt'} s_{t'} f_{tt'} s_t \quad (1)$$

where t and $t' = 1, 2, \dots, \infty$

and f has the form of equation II-3:

$$f = \begin{vmatrix} \alpha & \beta' & \gamma' & \delta' & . & . \\ \beta & \alpha & \beta' & \gamma' & \delta' & . \\ \gamma & \beta & \alpha & \beta' & \gamma' & \delta' \\ \delta & \gamma & \beta & \alpha & \beta' & \gamma' \\ . & \delta & \gamma & \beta & \alpha & \beta' \\ . & . & \delta & \gamma & \beta & \alpha \end{vmatrix} \quad (2)$$

Generally δ and farther interactions are zero. If equation 2 is multiplied on the right and left by a row and column vector of the infinite chain internal coordinates in the form $s_{n\alpha} \ s_{n\beta} \ s_{n\gamma} \ s_{n\delta} \ \dots$ where the coordinates are grouped so that $s_{n\alpha}$ are the internal coordinates of the first monomer unit of the n th repeat unit; $n = 1, 2, \dots, N$, the number of repeat units in the chain. Inspection of the

multiplication shows that the f_s ' will reduce to a column vector of which each element will be a summation involving terms containing γ' , β' , α , β , γ , each multiplied in consecutive order by the s 's of the internal coordinates. The summation of equation 1 will consist therefore of

$$s_t' f_{tt'} s_t = N(\text{sum of terms}) s_{n\alpha} + N(\text{sum of terms}) s_{n\beta} + N(\text{sum of terms}) s_{n\gamma}, \text{etc.} \quad (3)$$

The number of terms in the parenthesis of equation 3 will depend on how far the neighboring interactions are extended. The number of terms on the right side of equation 3 will depend on the number of monomer units per repeat unit.

If symmetry coordinates can be generated such that

$$s_{t'} = \sum_k U_{t'k}^{-1} S_k \quad (4)$$

$$s_t' = \left(\sum_{k'} U_{tk'}^{-1} S_{k'} \right)' \quad (5)$$

then the infinite matrix f is reduced to the order kk' which is chosen to be finite.

$$F_{kk'} = \sum_{tt'} U_{kt'} U_{k't}^{-1} f_{tt'} \quad (6)$$

The normalization constant of U will be $1/\sqrt{Np}$; where N is the number of repeat units above and p is the sum of the squares of the elements in a single repeat unit and will differ for each row. A single term in equation 3 will be converted by the unitary transformation into terms similar to

$$N(1/\sqrt{Np} s_{n\gamma'} + 1/\sqrt{Np} s_{n\beta'} + 1/\sqrt{Np} s_{n\alpha} + 1/\sqrt{Np} s_{n\beta} + 1/\sqrt{Np} s_{n\gamma}) \quad (7)$$

where $n' = n - 1$.

It is immediately obvious that the terms are independent of the number of repeat units; and equation 1 is equivalent to a multiplication with $t = 1$ to ∞ , and $t' = 1$ to the total number of internal coordinates in a repeat unit.

In practice it becomes obvious that all terms involving coordinates which do not interact with the repeat unit under consideration drop out of the final multiplication. The symmetry of $F_{kk'}$ will be the same as $f_{tt'}$, as long as $U_{kt'}U_{k't} = \bar{E}$, the identity matrix of the order k and is not dependent on U' actually being the transpose of U . Equation 7 is an actual term for the case of four monomer units per repeat unit with $\delta = 0$.

APPENDIX III

Programs coded in Fortran II for generating the cartesian coordinates of helical polymers with tetrahedral geometry.

Program to calculate the skeletal atom positions of A-B type chain

```

C      X, Y, Z ARE CARTESIAN COORDINATES OF REFERENCE
C      ATOM: AN = NO. OF TURNS PER UNIT CELL; AM = NO.
C      OF MONOMER UNITS PER UNIT CELL; D=CELL LENGTH /
C      AM; S=BOND LENGTH
      DIMENSION A(3, 3)
12     READ INPUT TAPE 5, 1, X, Y, Z, S, D
      1     FORMAT (5F12.6)
      READ INPUT TAPE 5, 11, AN, AM
11     FORMAT (2F12.6)
      I=0
      B=2. *1.333333*S*S
      A=B-D*D
      TH=2. *3.1415927*(AN/AM)
      SINTH=SINF(TH)
      COSTH=COSE(TH)
      C=2. (1. - COSTH)
      R=SQRTE(A/C)
      PRINT 10, TH, SINTH, COSTH
10     FORMAT (8H1 TH=F12.6, 10X6HSINTH=F12.6, 10X6HCOS
      TH=F12.6)
      X2=R*COSTH
      Y2=R*SINTH
      Z2=D
      WRITE OUTPUT TAPE 6, 20, X, Y, Z, S, D, R
20     FORMAT (1H06(4XF12.6))
      2     PHI = X*X-2. *R*X+R*R+Y*Y+Z*Z-S*S
      PSI = X*X+Y*Y-2. *Y2*Y+Y2*Y2+Z*Z-2. *Z2*Z+Z2*Z2-S*S
      -2. *X2*X+X2*X2
      CHI = X*X+Y*Y-R*R
      I=I+1
      WRITE OUTPUT TAPE 6, 6, I, X, Y, Z
      6     FORMAT (I4, 3(3XF12.6))
      IF(ABS(F(PHI))-1.) 15, 17, 17
15     IF (ABS(F(PSI))-1.) 16, 17, 17

```

```

16 IF (ABSF(CHI)-1.) 7, 17, 17
17 WRITE OUTPUT TAPE 6, 9, PHI, PSI, CHI
  9 FORMAT (5H PHI=F12.6, 6H PSI=F12.6, 6H CHI=F12.6)
  GO TO 12
  7 A(1, 1) = 2. *X-2. *R
    A(1, 2) = 2. *Y
    A(1, 3) = 2. *Z
    A(2, 1) = 2. *X-2. *X2
    A(2, 2) = 2. *Y-2. *Y2
    A(2, 3) = 2. *Z - 2. * Z2
    A(3, 1) = 2. *X
    A(3, 2) = 2. *Y
    A(3, 3) = 0
    D = A(1, 1)*A(2, 2)*A(3, 3)+A(2, 1)*A(3, 2)*A(1, 3)+A(3, 1)*A(2,
      3)*A(1, 2)-A(3, 1)*A(2, 2)*A(1, 3)-A(3, 2)*A(2, 3)*A(1, 1)-A(3, 3)
      *A(1, 2)*A(2, 1)
    DH = -PHI*A(2, 2)*A(3, 3)-PSI*A(3, 2)*A(1, 3)-CHI*A(2, 3)*A(
      1, 2)+CHI*A(2, 2)*A(1, 3)+A(3, 2)*A(2, 3)*PHI+A(3, 3)*A(1, 2)*
      PSI
    DK = -A(1, 1)*PSI*A(3, 3)-A(2, 1)*CHI*A(1, 3)-A(3, 1)*A(2, 3)
      *PHI+A(3, 1)*PSI*A(1, 3)+CHI*A(2, 3)*A(1, 1)+A(3, 3)*PHI*A(
      2, 1)
    DL = -A(1, 1)*A(2, 2)*CHI-A(2, 1)*A(3, 2)*PHI-A(3, 1)*PSI*A(
      1, 2)+A(3, 1)*A(2, 2)*PHI+A(3, 2)*PSI*A(1, 1)+CHI*A(1, 2)*A(2,
      1)
    EH = DH/D
    EK = DK/D
    EL = DL /D
    SUM = EH*EH+EK*EK+EL*EL
    IF (SUM-1. E-12) 5, 5, 3
  3 IF (I-100) 4, 4, 5
  4 X = X+EH
    Y = Y+EK
    Z = Z+EL
    GO TO 2
  5 C = ((R-X)*(X2-X)-Y*(Y2-Y)-Z*(Z2-Z))/(S*S)
    WRITE OUTPUT TAPE 6, 8, X, Y, Z, C
  8 FORMAT (3H X=F12.6, 4H Y=F12.6, 4H Z=F12.6, 6H
    COS=F12.6)
    GO TO 12
  END

```

Program to calculate the positions of atoms attached to skeletal chain:

```

C      X0, Y0, Z0 ARE COORDINATES OF SKELETAL ATOM TO
C      WHICH SIDE ATOMS ARE ATTACHED; X1, Y1, Z1 ARE CO-
C      ORDINATES FOR THE PRECEDING SKELETAL ATOM;X2,
C      Y2, Z2 ARE FOR THE SUCEEDING SKELETAL ATOM;X, Y,
C      Z ARE THE COORDINATES TO BE CALCULATED;BL IS
C      THE BOND LENGTH OF THE SIDE ATOM TO THE SKELE-
C      TAL ATOM;BL1 IS THE SKELETAL BOND LENGTH;N=1 IF
C      NEW SKELETAL POSITIONS ARE TO BE READ IN
      DIMENSION A(3, 3)
12     READ INPUT TAPE 5, 21, N
21     FORMAT (I2)
22     IF (N) 13, 14, 30
30     READ INPUT TAPE 5, 1, X0, Y0, Z0, X1, Y1, Zi, X2, Y2, Z2,
      BL1
      1  FORMAT (6F12. 6/4F12. 6)
13     READ INPUT TAPE 5, 5, X, Y, Z, BL
      5  FORMAT (4F12. 6)
      WRITE OUTPUT TAPE 6, 20, X, Y, Z, BL
20     FORMAT (1H0 4(3XF12. 6))
      I=0
      C1=-0. 333333*BL1*BL
      C3=BL*BL
2     A(1, 1)=X1-X0
      A(1, 2)=Y1-Y0
      A(1, 3)=Z1-Z0
      A( 2, 1)=X2-X0
      A(2, 2)=Y2-Y0
      A(2, 3)=Z2-Z0
      BX=X-X0
      BY=Y-Y0
      BZ=Z-Z0
      A(3, 1)=2. *BX
      A(3, 2)=2. *BY
      A(3, 3)=2. *BZ
      I=I+1
      PHI=A(1, 1)*BX+A(1, 2)*BY+A(1, 3)*BZ-C1
      PSI=A(2, 1)*BX+A(2, 2)*BY+A(2, 3)*BZ-C1
      CHI=BX*BX+BY*BY+BZ*BZ-C3
      IF (ABSF(PHI)-1. ) 15, 17, 17
15     IF (ABSF(PSI)-1. ) 16, 17, 17
16     IF (ABSF(CHI)-1. ) 7, 17, 17
17     WRITE OUTPUT TAPE 6, 9, PHI, PSI, CHI
      9  FORMAT (5H PHI=F12. 6, 6H  PSI=F12. 6, 6H  CHI=F12. 6)

```

```

GO TO 12
7 D=A(1, 1)*A(2, 2)*A(3, 3)+A(2, 1)*A(3, 2)*A(1, 3)+A(3, 1)*A(2, 3)
  *A(1, 2)-A(3, 1)*A(1, 3)*A(2, 2)-A(3, 2)*A(2, 3)*A(1, 1)-A(3, 3)*
  A(1, 2)*A(2, 1)
  DH=-PHI*A(2, 2)*A(3, 3)-PSI*A(3, 2)*A(1, 3)-CHI*A(2, 3)*A(1,
  2)+CHI*A(2, 2)*A(1, 3)+A(3, 2)*A(2, 3)*PHI+A(3, 3)*A(1, 2)*PSI
  DK=-A(1, 1)*PSI*A(3, 3)-A(2, 1)*CHI*A(1, 3)-A(3, 1)*A(2, 3)*
  PHI+A(3, 1)*PSI*A(1, 3)+CHI*A(2, 3)*A(1, 1)+A(3, 3)*PHI*A(2,
  1)
  DL=-A(1, 1)*A(2, 2)*CHI-A(2, 1)*A(3, 2)*PHI-A(3, 1)*PSI*A(1,
  2)+A(3, 1)*A(2, 2)*PHI+A(3, 2)*PSI*A(1, 1)+CHI*A(1, 2)*A(2, 1)
  EH=DH/D
  EK=DK/D
  EL=DL/D
  SUM=EH*EH+EK*EK+EL*EL
  IF (SUM-1. E-12) 18, 3, 3
3 IF (I-100)4, 4, 18
4 X=X+EH
  Y=Y+EK
  Z=Z+EL
  WRITE OUTPUT TAPE 6, 6, I, X, Y, Z
6 FORMAT (I3, 3(3XF12. 6))
  GO TO 2
18 WRITE OUTPUT TAPE 6, 8, X, Y, Z
  8 FORMAT (3H X=F12. 6, 4H Y=F12. 6, 4H Z=F12. 6)
  GO TO 12
14 CALL EXIT
  END

```

```

C PROGRAM TO GENERATE REPEAT UNITS OF POLYMER
C DIMENSION X(20), Y(20), Z(20), MOL(4), ATOM(11)
C X, Y, Z ARE COORDINATES OF ONE ATOM OF FIRST
C MONOMER UNIT, MOL IS MOLECULE IDENTIFICATION,
C ATOM IS ATOM IDENTIFICATION, C IS UNIT CELL LENG
C TH, AN IS NUMBER OF TURNS PER UNIT CELL, AM IS
C NUMBER OF MONOMER UNITS PER UNIT CELL, IND IS
C 1 IF NEW MOLECULE IS TO BE ENTERED
1 READ 2, MOL, C, AN, AM
2 FORMAT (4A6, 3F12. 6)
3 PRINT 4, MOL, C, AN, AM
4 FORMAT (1H1, 4A6, 3F12. 6)
5 READ 6, IND, ATOM
6 FORMAT (I6, 11A6)
  IF (IND) 1, 7, 1

```

```
7 PRINT 70, ATOM
70 FORMAT (1H0, 5X, 11A6)
   TH=3.1415927*(AN/AM)
   D=C/AM
8 READ 9, X(1), Y(1), Z(1)
9 FORMAT (3F12.6)
   SINTH=SINF(TH)
   COSTH=COSF(TH)
   M=AM+3.
12 DO 13 I=1, M
   X(I+1)=X(I)*COSTH- Y(I)*SINTH
   Y(I+1)=X(I)*SINTH+Y(I)*COSTH
13 Z(I+1)=Z(I)+D
14 PRINT 15, (I, X(I), Y(I), Z(I), I=1, M)
15 FORMAT (I10, 3F20.6)
   GO TO 5
   END
```

Note: PRINT = WRITE OUTPUT TAPE 6