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# Exact solution of the vibration problem for the carbon-60 molecule

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## Abstract

Utilizing the icosahedral symmetry of the  $C_{60}$  molecule by amalgamating two methods, we solve the vibrational eigenfrequency problem for carbon-60 to obtain exact algebraic expressions for the characteristic polynomials of the vibration. The inter-atomic interaction consists of four force constants, two for bond-stretching and two for angle-oscillation. © 1997 Elsevier Science B.V.

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## 1. Introduction

Since the discovery of the fullerene molecules, numerous papers have been published discussing the chemical, physical and mathematical problems related to these molecules. In particular, there were several papers [1] on the theoretical studies of the vibrational motion of the  $C_{60}$  molecule. Because the vibration problem requires the diagonalization of a  $180 \times 180$  matrix with elements which are functions of the force constants, vibrational eigenfrequencies of  $C_{60}$  have been computed only numerically for several choices of the spring constants. In the present paper, by utilizing the symmetry properties of the  $C_{60}$  molecule, we are able to solve the vibration problem of  $C_{60}$  exactly and analytically. Explicit characteristic polynomials for the eigenfrequencies, one for each irreducible representation of the symmetry group of the molecule, are obtained. We adopt in the present calcu-

lation a potential function which contains a set of four force constants, two for bond-stretching and two for angular motion between pairs of neighboring bonds. The bond-stretching introduces an interaction between neighboring atoms, but the angular oscillations generate non-nearest-neighbor interactions among atoms.

## 2. Method

The solution of the vibration problem of carbon-60 can be greatly simplified by taking advantage of the symmetry properties of the molecule. Two possible approaches may be used.

It was emphasized [2] that the symmetry group of  $C_{60}$  possesses an Abelian subgroup. The irreducible representation of this subgroup is one-dimensional, and can be characterized by an integer  $m$ . (See below, Section 3.) The molecule also has inversion symme-

try with eigenvalues  $p = \pm 1$ . Thus, given  $m$  and  $p$ , the displacements of the six atoms located at the vertices of one hexagon are sufficient to determine the displacements of all 60 atoms. Utilizing this symmetry, we can drastically reduce the order of the vibration matrix from 180 to 18. However, analytic computation of the determinant for this reduced  $18 \times 18$  matrix remains beyond our present computational power.

The vibration problem may also be simplified if all irreducible basis vectors with respect to the symmetry group of the molecule can be found. With respect to an irreducible basis set, which transforms according to the  $\mu$  representation of the symmetry group, the vibration matrix can be reduced to an order  $d_\mu$  (= the degeneracy of the irreducible representation). For  $C_{60}$  vibrations, the largest  $d_\mu$  is 8 (see Eq. (1) below). The calculation of such a ( $d_\mu \times d_\mu$ ) secular determinant should be quite feasible. The construction of irreducible basis vectors from arbitrary vectors can be achieved by using the projection operator method. However, this approach suffers from the drawbacks that (i) the complete  $180 \times 180$  vibration matrix has to be constructed, and (ii) it is cumbersome to identify the  $d_\mu$  linearly independent rows (or columns) in the  $180 \times 180$  projection matrices.

The method used in this paper for solving the  $C_{60}$  vibration problem is the amalgamation of the two ideas discussed above. First, we shall obtain the reduced  $18 \times 18$  vibration matrix, thereby avoiding the difficulties (i) and (ii) above. The projection operators are then constructed in the reduced 18-dimensional vector space to project out irreducible basis vectors for the various irreducible representations. Thus, secular determinants of order  $d_\mu$  are obtained, the largest of which has an order of 8.

### 3. Symmetry of the $C_{60}$ molecule

The  $C_{60}$  molecule, being a truncated icosahedron, is invariant under the symmetry group  $I \times Z_2$  where  $I$  is the icosahedral group and  $Z_2$  is the two-element group consisting of the inversion operator  $P$  and the identity. The 180 components of the displacement vectors of the 60 carbon nuclei from their equilibrium positions generate a 180-dimensional representation of the 120-element group  $I \times Z_2$ . Using the character table of this group, we can reduce this 180-dimensional rep-

Table 1  
The irreducible representations for each  $(mp)$

$(mp)$	$R_1$	$R_3$	$R_{3'}$	$R_4$	$R_5$
$(\pm 2, +)$			4	6	8
$(\pm 1, +)$		4		6	8
$(0, +)$	2	4	4		8
$(\pm 2, -)$			5	6	7
$(\pm 1, -)$		5		6	7
$(0, -)$	1	5	5		7

resentation to a sum of 48 irreducible representations of  $I \times Z_2$ ,

$$[2R_{1+} \oplus 4R_{3+} \oplus 4R_{3'+} \oplus 6R_{4+} \oplus 8R_{5+}] \\ \oplus [R_{1-} \oplus 5R_{3-} \oplus 5R_{3'-} \oplus 6R_{4-} \oplus 7R_{5-}]. \quad (1)$$

The first bracket contains 24 even-parity irreducible representations and the second contains 24 odd-parity ones.

The symmetry group  $I \times Z_2$  contains an Abelian subgroup  $h$ ,  $h = \{\rho^0, \rho^1, \rho^2, \rho^3, \rho^4\}$ , where  $\rho$  is an element of  $I$  representing a rotation through an angle  $2\pi/5$ . The irreducible representations of this Abelian subgroup are one-dimensional, and are characterized by an integer  $m$  (in analogy with the quantum number  $m$  for the rotation group),

$$\rho = \eta^{-m}, \quad m = -2, -1, 0, 1, 2, \\ \eta = \exp(2\pi i/5). \quad (2)$$

Since  $[\rho, P] = 0$ , where  $P$  is the inversion operator with eigenvalues  $p = \pm 1$ , the  $180 \times 180$  vibration matrix  $M (\equiv V - \omega^2 T)$  can be transformed into a block-diagonal form with each diagonal block  $M_{mp}$  belonging to only one  $(mp)$ , with  $M_{mp} = M_{-mp}$  due to the symmetry between  $m$  and  $-m$ . The irreducible representation content for each  $M_{mp}$  can be found from the character table and is exhibited in Table 1.

The 60 carbon atoms in  $C_{60}$  can be symmetrically divided [2] into ten sets, each consisting of  $60/10 = 6$  atoms (see Fig. 1). We label the 60 atoms by three numbers  $(n_1, n_2, n_3)$ .  $n_1 = \pm 1$  denotes whether the atom is in the upper or lower hemisphere;  $n_2$ , ranging from 0 to 4, designates the azimuthal sector which the atom is in; and  $n_3 = I, II, \dots, VI$  specifies atoms in the set. For the basic set of atoms,  $n_1 = +1$ ,  $n_2 = 0$ . Thus, for a given  $m$  and parity  $p$ , knowing the displacement

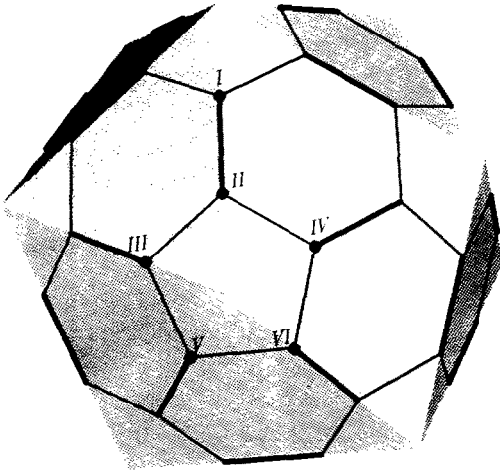


Fig. 1. The bond arrangement for C<sub>60</sub>. The heavy and thin lines represent respectively the double and single bonds. The six atoms forming the basic set are indicated.

vectors for the 6 atoms in the basic set is enough to determine the displacements for all 60 atoms. For example, if atom *X* is in the basic set with  $n_1 = +1$ ,  $n_2 = 0$ ,  $n_3 = x$  and atom *X'* is labeled by  $(1, 2, x' = x)$ , the displacement vectors of these two atoms are related by  $D_{X'} = D_X \eta^{-2m}$ . However, care must be taken when *X'* is in the lower hemisphere. For instance, if  $X = (1, 0, x)$  and  $X' = (-1, 0, x)$  are antipodes, then

$$D_{X'} = pD_X, \tag{3}$$

where *p* is the parity eigenvalue. With the local coordinate systems to be defined below, Eq. (3) implies that

$$a_{X'} = pa_X, \quad b_{X'} = pc_X, \quad c_{X'} = pb_X. \tag{4}$$

Notice that the displacement vectors for atoms outside the basic set are all complex quantities if  $m \neq 0$ .

#### 4. The vibration matrix

The displacement vector *D* of each atom is specified with respect to a local coordinate system defined at the atom's equilibrium site. We designate the three unit base vectors for atomic site *X* as  $(\hat{a}_X, \hat{b}_X, \hat{c}_X)$ , with  $\hat{a}_X$  along the double bound,  $\hat{b}_X$  and  $\hat{c}_X$  along the single bonds, in a counterclockwise sense (Fig. 2). Thus,

$$D_X = a_X \hat{a}_X + b_X \hat{b}_X + c_X \hat{c}_X. \tag{5}$$

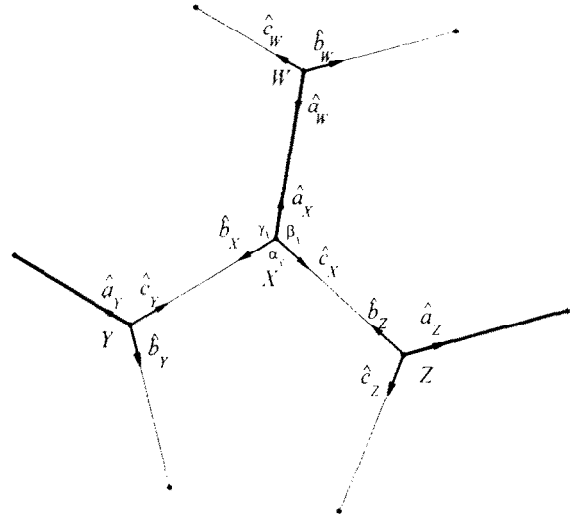


Fig. 2. The atom *X* surrounded by atoms *W*, *Y* and *Z* in the C<sub>60</sub> molecule. The three unit base vectors  $(\hat{a}, \hat{b}, \hat{c})$  and three bond angles  $(\alpha, \beta, \gamma)$  are shown for each atom.

Notice that these unit base vectors are *not* mutually orthogonal. The angles between the bonds for a given atom will be denoted in the clockwise sense by  $\alpha_X, \beta_X, \gamma_X$  (Fig. 2). At equilibrium,  $\alpha = 3\pi/5, \beta = \gamma = 2\pi/3$ , and the dot-products between base vectors of the same atom and of neighboring atoms can be easily obtained.

The kinetic and potential energies of the C<sub>60</sub> molecule can all be expressed in terms of the  $3 \times 6 = 18$  displacement-components of the atoms in the basic set for each (*mp*). Thus, with the concept of basic set, the order of the vibration matrix is reduced from 180 down to 18. Since the kinetic and potential energies for the whole molecule are ten times that of the atoms in the basic set due to icosahedral symmetry, it is only necessary to compute the energies of atoms and bonds pertaining to the basic set.

Consider first the kinetic energy. Write the kinetic energy of atom *X* as *T<sub>X</sub>*. Then

$$T_X = \frac{1}{2} \dot{D}_X^* \cdot \dot{D}_X = \frac{1}{2} (\dot{a}_X^*, \dot{b}_X^*, \dot{c}_X^*) \tau \begin{pmatrix} \dot{a}_X \\ \dot{b}_X \\ \dot{c}_X \end{pmatrix}, \tag{6}$$

where the mass of the carbon atom is set to unity for convenience, and  $\tau$  is a  $3 \times 3$  matrix,

$$\tau = \begin{pmatrix} 1 & -\frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & 1 & \frac{1}{4}(1-r) \\ -\frac{1}{2} & \frac{1}{4}(1-r) & 1 \end{pmatrix}.$$

The dots represent derivatives with respect to time. If all the atomic coordinates oscillate with frequency  $\omega$  ( $\equiv \sqrt{\lambda}$ ), then

$$T_X = \frac{1}{2} \lambda (a_X^*, b_X^*, c_X^*) \tau \begin{pmatrix} a_X \\ b_X \\ c_X \end{pmatrix}. \quad (7)$$

The kinetic energy  $T$  of the six carbon atoms in the basic set can thus be written in the form

$$T = \frac{1}{2} \lambda \tilde{\psi}^* \mathbf{K} \psi, \quad (8)$$

where  $\psi$  is an 18-entry column matrix formed from components of  $\mathbf{D}$ ,  $\tilde{\psi}$  is its transpose,

$$\tilde{\psi} = (a_I, b_I, c_I, a_{II}, b_{II}, \dots, b_{VI}, c_{VI}), \quad (9)$$

and  $\mathbf{K}$  is a block-diagonal matrix with six blocks of  $\tau$  along its main diagonal.

The potential energy of  $C_{60}$  consists of terms which arise from (i) the change in lengths of single bonds and double bonds between neighboring atoms, and (ii) the change in angles between adjacent bonds for each atom. Since the  $C_{60}$  molecule is topologically a trivalent polyhedron, there are three potential energy terms due to angular motion for each atom.

#### 4.1. Potential energy for bond-stretching

There are  $3 \times 60/2 = 90$  bonds between pairs of neighboring atoms in  $C_{60}$ . Of the  $90/10 = 9$  bonds pertaining to each set of atoms, there are three double bonds and six single bonds. The double and single bonds assigned to the basic set are respectively,  $\{(I, II), (IV, VIII), (VI, IX)\}$  and  $\{(I, VII), (II, III), (II, IV), (III, V), (V, VI)\}$ , as exhibited in Fig. 3.

The vibrational potential energy due to bond-stretching between neighboring atoms  $X$  and  $U$  is of the general form

$$V_{XU} = \frac{1}{2} k (\Delta L)^2, \quad (10)$$

where  $k$  is the spring constant appropriate for the  $XU$  bond. (The spring constants,  $k_S$  and  $k_D$ , for single and double bonds are assumed to be different.)  $\Delta L$ , the change in bond-length from its equilibrium length

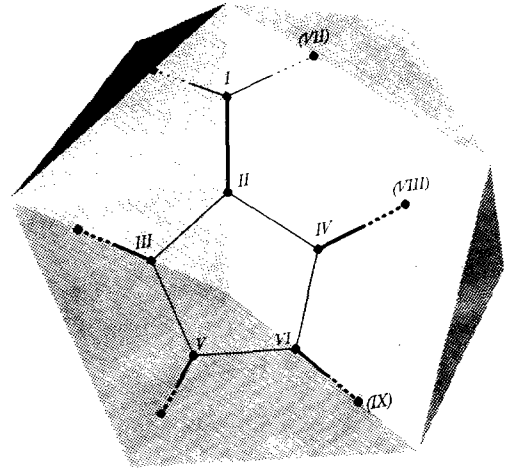


Fig. 3. The six atoms ( $n_1 = +1, n_2 = 0, n_3 = I, II, \dots, VI$ ) and nine bonds (three double and six single) pertaining to the basic set for  $C_{60}$ .

$L$ , can be computed from the displacement vectors of atoms  $X$  and  $U$ ,

$$(\Delta L) = [(\mathbf{D}_X - L\hat{\epsilon}_X - \mathbf{D}_U) \cdot (\mathbf{D}_X - L\hat{\epsilon}_X - \mathbf{D}_U)]^{1/2} - L, \quad (11)$$

where  $\hat{\epsilon}_X$  is the unit base vector along the  $XU$  bond at  $X$ ,

$$(\Delta L)^2 = (\Delta L)^* (\Delta L), \quad (12)$$

which, for  $|\mathbf{D}| \ll L$ , becomes

$$(\Delta L)^2 = [(\mathbf{D}_X - \mathbf{D}_U) \cdot \hat{\epsilon}_X]^* \cdot [(\mathbf{D}_X - \mathbf{D}_U) \cdot \hat{\epsilon}_X]. \quad (13)$$

(The complex conjugations in Eqs. (12) and (13) are required because  $\mathbf{D}$  can be complex.) Hence

$$V_{XU} = \frac{k}{2} (\tilde{\mathbf{D}}_X, \tilde{\mathbf{D}}_U)^* \begin{pmatrix} R_{XX} & R_{XU} \\ \tilde{R}_{XU} & R_{UU} \end{pmatrix} \begin{pmatrix} \mathbf{D}_X \\ \mathbf{D}_U \end{pmatrix}, \quad (14)$$

where

$$\mathbf{D}_X = \begin{pmatrix} a_X \\ b_X \\ c_X \end{pmatrix}, \quad \mathbf{D}_U = \begin{pmatrix} a_U \\ b_U \\ c_U \end{pmatrix}, \quad (15)$$

The  $R$ 's in Eq. (14) are  $3 \times 3$  matrices with constant elements which depend only on the geometry of the molecule.

The total potential energy for the three double bonds and six single bonds in the basic set can be readily

assembled from the parts  $V_{XU}$ . Notice that three of these bonds,  $\{(I, VII), (IV, VII)$  and  $(VI, IX)\}$ , end in atoms  $(VII, VIII, \text{ and } IX)$  which do not belong to the basic set. Nevertheless, their displacement vectors can be related to those in the basic set of atoms. For instance,

$$D_{VII} = \eta^m D_I, \quad D_{IX} = p\eta^3 D'_V, \quad (16)$$

where the primed displacement vector  $D'$  has *transposed*  $b, c$  components,

$$D'_V = (a_V, c_V, b_V). \quad (17)$$

Thus the total stretching potential energy for bonds in the basic set may be written in the form

$$\tilde{\psi}^* V_{\text{str}} \psi, \quad (18)$$

where  $\tilde{\psi} = (a_I, b_I, c_I, a_{II}, b_{II}, \dots, b_{VI}, c_{VI})$  as in (9), and  $V_{\text{str}}$  is a  $6 \times 6$  block-matrix with each block a  $3 \times 3$  matrix, which can be formed from the matrices  $R$  in (14).

#### 4.2. Potential energy for angular motion

The change in angles between the three bonds for a given atom  $X$  gives rise to a potential energy

$$V_{\text{angle}} = L^2 \left[ \frac{1}{2} k_\alpha (\delta\alpha)^* (\delta\alpha) + \frac{1}{2} k_\beta (\delta\beta)^* (\delta\beta) + \frac{1}{2} k_\gamma (\delta\gamma)^* (\delta\gamma) \right], \quad (19)$$

where the three terms correspond to the three angular degrees of freedom. The elastic force constants for angles  $\beta$  and  $\gamma$  are set to be equal due to symmetry. The factor  $L^2$  is inserted so as to give all force constants (stretching and angular motion) the same dimension.

Consider the angular motion for the angle  $\alpha$ , i.e., the first term in Eq. (19), of atom  $X$ . With reference to Fig. 2, the distances  $(L_{XY}, L_{XZ}, L_{YZ})$  between atoms  $X$  and  $Y$ ,  $X$  and  $Z$ , and  $Y$  and  $Z$ , can be easily computed for small displacements. We have

$$\begin{aligned} L_{XY} &\approx L + \hat{b}_X \cdot (D_Y - D_X), \\ L_{XZ} &\approx L + \hat{c}_X \cdot (D_Z - D_X), \\ L_{YZ} &\approx [L^2 (\hat{b}_X - \hat{c}_X)^2 \\ &\quad + 2L (\hat{b}_X - \hat{c}_X) \cdot (D_Y - D_Z)]^{1/2}. \end{aligned} \quad (20)$$

With displacement vectors  $D$  in Eq. (20) expressed in terms of base vectors, we obtain  $\delta\alpha$ , the change in the angle  $\alpha$ ,

$$\begin{aligned} \delta\alpha &= -\frac{\sqrt{2(5+r)}}{40L} [2(5+r)a_X - 10b_X - 10c_X \\ &\quad - (5+r)a_Y + 10b_Y - (5+r)a_Z + 10c_Z], \end{aligned} \quad (21)$$

with  $r \equiv \sqrt{5}$ . Thus the potential energy due to the change in angle  $\alpha$  for atom  $X$  can be written in matrix form as

$$\begin{aligned} V_{\text{angle } \alpha} &= L^2 \frac{1}{2} k_\alpha (\delta\alpha)^* (\delta\alpha) \\ &= L^2 \frac{1}{2} k_\alpha (D_X, D_Y, D_Z)^* \\ &\quad \cdot \begin{pmatrix} A_{XX} & A_{XY} & A_{XZ} \\ A_{YX} & A_{YY} & A_{YZ} \\ A_{ZX} & A_{ZY} & A_{ZZ} \end{pmatrix} \begin{pmatrix} D_X \\ D_Y \\ D_Z \end{pmatrix}, \end{aligned} \quad (22)$$

where the exhibited nine elements of the matrix  $A$  are themselves  $3 \times 3$  submatrices, each of which is formed from the coefficients in Eq. (21).

The potential energies due to the change in angles  $\beta$  and  $\gamma$  for atom  $X$  can be similarly computed.

Using the basic modules such as (22), we can now put together the potential energy due to angular motion for the six atoms in the basic set. Again, as in the calculation of the potential energy for bond-stretching, if displacement vectors of atoms not belonging to the basic set appear, replacements like (16) must be made. Thus, the potential energy is expressible in terms of the displacement vectors of the basic set atoms only.

By combining the potential energies due to bond-stretching and angular motion, the total potential energy can be written as

$$V = V_{\text{str}} + V_{\text{angle}} = \frac{1}{2} \tilde{\psi}^* V \psi, \quad (23)$$

where  $\tilde{\psi} = (a_I, b_I, c_I, a_{II}, b_{II}, \dots, b_{VI}, c_{VI})$  as before. The  $18 \times 18$  potential matrix  $V$  is rather cumbersome; its elements are linear functions of the four force constants  $(k_S, k_D, k_\alpha, k_\beta)$  and are also dependent on  $(mp)$  because displacements of atoms not pertaining to the basic set are involved (see Eq. (16)).

The vibration matrix  $M$  for given  $(mp)$  is then

$$M = V - \lambda K, \quad (24)$$

where  $\lambda \equiv \omega^2$ . Because of the symmetry  $M_{mp} = M_{-mp}$ , we only need to diagonalize six (instead of 10)  $M_{mp}$  matrices. This is for  $p = \pm 1$ , and  $m = 0, 1, 2$ .

### 5. Vibrational characteristic polynomials

The characteristic polynomial  $P_{mp}$  for given  $m$  and  $p$  may, in theory, be obtained by expanding the determinant of the vibration matrix  $M_{mp}$ . Then, by factoring  $P_{mp}$ , polynomials  $Q_{\mu p}$  belonging to different irreducible representations in Eq. (1) can hopefully be found. In fact, from Table 1, we expect to obtain

$$\begin{aligned} P_{0\pm} &= Q_{1\pm}Q_{3\pm}Q_{3'\pm}Q_{5\pm}, \\ P_{1\pm} &= Q_{3\pm}Q_{4\pm}Q_{5\pm}, \\ P_{2\pm} &= Q_{3'\pm}Q_{4\pm}Q_{5\pm}. \end{aligned} \quad (25)$$

(The degrees in  $\lambda$  of these polynomials can be read out directly from Eq. (1).) However, in practice, this procedure cannot possibly be implemented due to the enormous size of the vibration matrix. Even with the aid of a computer, it would not be possible to evaluate the determinant of a  $18 \times 18$  matrix as complex as one like  $M_{mp}$ .

In order to extract from  $M_{mp}$  the characteristic polynomial for a given irreducible representation  $R_\mu$  without fully expanding the  $18 \times 18$  determinant, we take advantage of the projection technique in group theory.

The projection matrix  $\mathcal{P}^{(\mu)}$  for a given irreducible representation  $R_\mu$  of the symmetry group  $I \times Z_2$  can be easily constructed using standard procedures [3],

$$\mathcal{P}^{(\mu)} = \frac{n_\mu}{g} \sum_s [\chi^{(\mu)}(S)]^* \mathcal{O}_s, \quad (26)$$

where  $g$ , the order of the group, is 120.  $n_\mu$  and  $\chi^{(\mu)}$  are respectively the dimension and the character of the irreducible representation  $R_\mu$ .  $\mathcal{O}_s$  is the representation matrix for the group element  $S$ . The summation runs through all elements of the group.  $\mathcal{P}^{(\mu)}$  is Hermitian.

To find the proper linear combinations of the displacements of the six atoms in the basic set which form bases for the ten irreducible representations in Eq. (1), we need to construct appropriate projection operators in this 18-dimensional sub-space of displacements. These operators in the reduced space can be obtained from the full projection operators,  $\mathcal{P}^{(\mu)}$ , given by (26) in the following way.

Denote by  $\Psi$  the  $180 \times 1$  column matrix for the displacements of the 60 atoms. The first 18 elements of  $\Psi$  represent the displacement of the six atoms in the basic set, i.e.,  $\psi$  of Eq. (9). The rest of the elements in

$\Psi$ , being displacements of atoms in the other sets, are all expressible in terms of the components of  $\psi$ . Thus,

$$\tilde{\Psi} = [\psi, \eta^m \psi, \eta^{2m} \psi, \dots, p\eta^{4m} \psi'], \quad (27)$$

where  $\psi' \equiv (\psi \text{ with } b, c \text{ components interchanged})$ . Now,

$$\mathcal{P}^{(\mu)} \Psi = \Phi, \quad (28)$$

where  $\Phi$  is also a  $180 \times 1$  column matrix. Denote the first 18 elements of  $\Phi$  by  $\varphi$ . The linear relationship between  $\varphi$  and  $\psi$  thus provides us with the projection matrix  $\varphi^{(\mu)}$  in the reduced 18-dimensional vector space, i.e.,

$$\varphi = \varphi^{(\mu)} \psi. \quad (29)$$

Notice that the projection matrix  $\varphi^{(\mu)}$  obtained has an order of 18 and a rank  $\mu$  (= the dimension of the irreducible representation  $R_\mu$ ) which is less than 18. Thus, there can only be  $\mu$  columns (or rows) of  $\varphi^{(\mu)}$  that are linearly independent.

Designate by  $\tilde{\varphi}^{(\mu)}$  the  $18 \times \mu$  matrix formed by deleting the linearly dependent columns of  $\varphi^{(\mu)}$ . Delete also the corresponding rows in  $M_{mp}$  and designate the remaining  $\mu \times 18$  matrix by  $\tilde{M}_{mp}$ . The characteristic polynomial  $Q_{\mu p}$  for the irreducible representation  $R_\mu$  and parity  $p$  is then given by the determinant of the matrix product  $\tilde{M}_{mp} \tilde{\varphi}^{(\mu)}$ , which has the order  $\mu$ ,

$$Q_{\mu p} = \det[\tilde{M}_{mp} \tilde{\varphi}^{(\mu)}]. \quad (30)$$

The characteristic polynomials for all irreducible representations can thus be computed. Some of the polynomials are exhibited below.  $Q_{4\pm}$  and  $Q_{5\pm}$  are rather lengthy and will be given elsewhere. We have

$$Q_{1+} = 2\lambda^2 + \lambda(-4k_D + (-5+r)k_S) + 2(3-r)k_D k_S,$$

$$Q_{1-} = \lambda - 3(3+r)k_\beta,$$

$$\begin{aligned} Q_{3+} &= \lambda(12\lambda^3 + \lambda^2[-3(5+r)k_S - 30k_\alpha \\ &\quad + 2(-125 + 3r)k_\beta] + \lambda\{[4(63 + 10r)k_S \\ &\quad - 2(-265 + 13r)k_\alpha]k_\beta + 8(78 + 11r)k_\beta^2\} \\ &\quad + [-16(29 + 9r)k_S - 32(25 + 4r)k_\alpha]k_\beta^2 \\ &\quad - 8(29 + 9r)k_\beta^3), \end{aligned}$$

$$\begin{aligned}
Q_{3-} = & \lambda(-12\lambda^4 + \lambda^3[24k_D - 3(-15+r)k_S \\
& + 30k_\alpha - 2(-61+15r)k_\beta] \\
& + \lambda^2\{-3[k_S(25k_D - 3rk_D + 10k_S) \\
& + (18k_D + 25k_S - 5rk_S)k_\alpha] \\
& + 2[-95k_D + 21rk_D - 196k_S + 58rk_S \\
& + (-134 + 42r)k_\alpha]k_\beta + 2(-111 + 43r)k_\beta^2\} \\
& + \lambda\{3k_Dk_S[-2(-6+r)k_S + (35-11r)k_\alpha] \\
& - 4[k_S(-126k_D + 39rk_D - 53k_S + 15rk_S) \\
& + 2(-44k_D + 12rk_D - 85k_S + 32rk_S)k_\alpha]k_\beta \\
& + [192k_D - 64rk_D + 478k_S - 194rk_S \\
& + (456 - 200r)k_\alpha]k_\beta^2\} \\
& + 12k_\beta\{6k_Dk_S[(-3+r)k_S + 2(-5+2r)k_\alpha] \\
& + [k_S(-9k_D + 3rk_D - 14k_S + 6rk_S) \\
& + 2(-14k_D + 6rk_D - 25k_S + 11rk_S)k_\alpha]k_\beta\},
\end{aligned}$$

$$\begin{aligned}
Q_{3'+} = & 12\lambda^4 + \lambda^3[-30k_S - 15(5+r)k_\alpha \\
& - 4(50+3r)k_\beta] \\
& + \lambda^2\{30(5+r)k_Sk_\alpha + [18(19+r)k_S \\
& + 4(295+68r)k_\alpha]k_\beta + 4(186+35r)k_\beta^2\} \\
& + \lambda\{-40(41+10r)k_Sk_\alphak_\beta \\
& + [-8(103+21r)k_S \\
& - 16(265+86r)k_\alpha]k_\beta^2 - 4(103+21r)k_\beta^3\} \\
& + 32(65+22r)k_\alpha k_\beta^2(2k_S + k_\beta),
\end{aligned}$$

$$\begin{aligned}
Q_{3'-} = & -12\lambda^5 + \lambda^4[24k_D - 6(-10+r)k_S \\
& + 15(5+r)k_\alpha - 4(-28+3r)k_\beta] \\
& + \lambda^3\{3(-35+3r)k_Dk_S \\
& + 15(-5+r)k_S^2 + [-6(16+r)k_D - 30(10+r)k_S]k_\alpha \\
& + [2(-85+21r)k_D + 2(-251+43r)k_S - 472k_\alpha]k_\beta \\
& + 2(-51+11r)k_\beta^2\} + \lambda^2\{-3(-37+7r)k_Dk_S^2 \\
& + [-3(-115+7r)k_Dk_S + 300k_S^2]k_\alpha \\
& + \{-6(-109+31r)k_Dk_S - 16(-32+7r)k_S^2 \\
& + [-32(-19+4r)k_D - 12(-155+11r)k_S]k_\alpha\}k_\beta \\
& + [-44(-3+r)k_D \\
& - 2(-179+41r)k_S - 16(-19+4r)k_\alpha]k_\beta^2)
\end{aligned}$$

$$\begin{aligned}
& + \lambda(60(-5+r)k_Dk_S^2k_\alpha + \{192(-3+r)k_Dk_S^2 \\
& + [24(-85+23r)k_Dk_S + 160(-10+r)k_S^2]k_\alpha\}k_\beta \\
& + \{96(-3+r)k_Dk_S - 128k_S^2 \\
& + [128(-3+r)k_D + 8(-125+29r)k_S]k_\alpha\}k_\beta^2) \\
& - 480(-3+r)k_Dk_S^2k_\alphak_\beta \\
& - 80(-9k_D + 3rk_D - 4k_S)k_Sk_\alphak_\beta^2.
\end{aligned}$$

*Remarks.* (i) Notice that both  $Q_{3+}$  and  $Q_{3-}$  contain a root of  $\lambda = 0$ . Thus, for each parity,  $\lambda = 0$  occurs three times (for  $m = +1, 0, -1$ ), corresponding to the translation ( $p = -1$ ) or rotation ( $p = +1$ ) of the molecule as a whole.

(ii) Simple expressions for the eigenfrequency are obtainable only for representations  $R_{1\pm}$ . They are ( $\omega = \sqrt{\lambda}$ )

$$\begin{aligned}
\lambda_{1+} = & k_D + \frac{1}{4}r(r-1)k_S \\
& \pm \sqrt{k_D^2 + \frac{1}{2}(r-1)k_Dk_S + \frac{5}{8}(3-r)k_S^2}, \\
\lambda_{1-} = & 3(3+r)k_\beta.
\end{aligned} \tag{31}$$

Notice that  $\lambda_{1+}$  depends on  $k_S, k_D$  only, and  $\lambda_{1-}$  on  $k_\beta$  only. We also observe that  $\lambda_{3+}, \lambda_{3'}$  are independent of  $k_D$ , and all other frequencies depend on all four force constants.

(iii) All eigenfrequencies of vibration can be readily computed numerically from the characteristic equations  $Q_{\mu p} = 0$  if the force constants are given. Conversely, the four force constants can be determined by comparing the calculated spectrum with the experimentally measured frequencies. The work on the numerical fits as well as normal modes of vibration will be published later.

(iv) If  $k_\alpha, k_\beta = 0$  and  $k_S, k_D \neq 0$ , then one half of the 180 eigenfrequencies vanish. This is the consequence of the fact that in this case the constant potential energy surface for  $C_{60}$  is dependent only on the 90 bond lengths, not on all 180 degrees of freedom. The same reasoning explains the fact that there are 120 or 150 zero frequencies respectively for the cases of  $k_\alpha, k_\beta = 0$  together with  $k_D = 0$  or  $k_S = 0$ .

(v) For  $k_S, k_D = 0$  and  $k_\alpha, k_\beta \neq 0$ , there are only 35 (not 90) zero frequencies. This is because angular motion involves more displacements than bond-stretching does.

(vi) We have also studied special cases, such as  $k_S \neq 0, k_D = k_\alpha = k_\beta = 0$ ;  $k_D \neq 0, k_S = k_\alpha = k_\beta = 0$ ; and  $k_\alpha \neq 0, k_S = k_D = k_\beta = 0$ . In each of these three cases, all the eigenfrequencies can be obtained in closed form, and are in agreement with previous studies [1].

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