Symmetry of $C_{60}$ and a Force Constant Model for Vibrational Modes

Ramazan KOÇ, Hayriye TÜTÜNCÜLER
University of Gaziantep,
Department of Physics Engineering,
27310 Gaziantep - TURKEY

Received 19.12.1996

Abstract
A force-constant model for the vibrational modes in $C_{60}$ is presented. The Keating type potential is adopted for calculating the dynamical matrix. Using symmetries of the molecule, the dynamical matrix which yields the vibrational modes is block-diagonalized. We summarize the role of group theory in specifying the vibrational modes. The results are in excellent agreement with experiments. The effect of bond-stretching force constants on the vibrational modes will be presented.

1. Introduction
$C_{60}$ has been the focus of attention of many fields of science, after its preparation in solid form [1, 2]. From the physical point of view, relatively high $T_c$ superconductivity (43 K) and the fivefold symmetry of the icosahedral $C_{60}$ are of great importance. A detailed calculation of phonon density of state is necessary to understand the superconductivity mechanism in compounds of $C_{60}$. On the basis of the force constant model one can calculate phonon density of state [3].

The $C_{60}$ cages consists of 20 hexagons and 12 pentagons arranged in a polyhedron known as ‘truncated icosahedron’. In this case the total number of atoms is sixty and the symmetry group is icosahedral, $I_h$. Group theoretical analysis gives 46 distinct vibrational modes, of which only 10 are raman active and 4 are infrared active. Both experimental and theoretical information on vibrational frequencies have been provided from inelastic neutron-scattering measurement [4-9]. The existence of all 46 frequencies have also been provided from inelastic neutron-scattering measurements [1]. Several calculations of vibrational frequencies for $C_{60}$ were reported by a number of authors. In many force constant models, only bond stretching force constants between nearest
neighbour atoms have been considered, in addition to angle bending force constants. In such models many of the frequencies could not be reproduced with any reasonable accuracy, and different models which fit the same data give widely different values for interatomic force constants.

In the present work, we propose a model that includes Keating parameters and force constants that connect further than nearest neighbour atoms for vibrational frequencies of isolated $C_{60}$. We discuss the effect of bonded and unbonded atoms to analyse the normal frequencies of $C_{60}$. One of the motivations for this work is to investigate the effect of the force constants between unbonded atoms in $C_{60}$. In many models those were not taken into consideration, and consequently many normal frequencies did not appear.

This paper is organized as follows. In Section 2, we present a group theoretical analyses to determine the types of the normal frequencies of $C_{60}$. The site symmetry of icosahedral $C_{60}$ and symmetry vector are also obtained in this section. In Section 3, normal mode frequencies of $C_{60}$ are calculated and listed by constructing a simple model. Finally, we discuss the effect of force constants between bonded and unbonded atoms and we compare our results with the experimental and some theoretical results.

2. Symmetry of $C_{60}$

$C_{60}$ is the most prominent molecule which has icosahedral symmetry, with 120 symmetry operations. We begin with the standard analysis of molecular vibrations of $C_{60}$ molecule. It is known that normal mode frequencies of $C_{60}$ are qualitatively analysed by using symmetries associated with the corresponding irreducible representation. The group for $C_{60}$ is the icosahedral group, $I_h$, and the generators which generate 120 symmetry operations of the icosahedral group are given by the matrices

\[
C_5 = \frac{1}{2} \begin{pmatrix}
-\tau & -\sigma & 1 \\
\sigma & 1 & \tau \\
1 & \tau & -\sigma
\end{pmatrix},
C_2 = \begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix},
I = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix},
\]

where $\tau = \frac{1}{2}(1 + \sqrt{5})$ and $\sigma = \frac{1}{2}(-1 + \sqrt{5})$. The first matrix $C_5$ represents a rotation by $2\pi/5$ about a fivefold axis. The second matrix $C_2$ is a cyclic permutation of the axes and the third matrix is the inversion. Generation relation of the generators are $(C_5)^5 = (C_2)^2 = (C_5C_2)^3 = I$. The $3 \times 3$ irreducible generators have been obtained by breaking the symmetries of SO(3) group [10]. Character table which characterize $C_{60}$ of full icosahedral group $I_h$ is given in Table 1.

The site symmetry for an isolated $C_{60}$ molecule can be found in the following simple way. We consider a radial vector $r_i$ from the center of $C_{60}$ molecule to ith atom in a site. The vectors associated with other atoms in a site are obtained by applying generators given in Eqn. (1), on the vector $r_i$. After a few attempts, $60 \times 60$ reducible matrix generators, which transforms the radial vectors $r_i$ to each other ($i = 1, 2, \ldots, 60$), are carried out yielding characters $\chi_{\text{site}}$ as given in Table 1. The symmetries of the
electronic levels of the molecule can be found by taking the direct product of \( \chi_{\text{site}} \) with \( A_g, F_{1u} \) and \( H_g \) for \( s, p \) and \( d \) functions, respectively.

**Table 1.** Character table for the full icosahedral group \( I_h \). The last two rows demonstrates the characters of site symmetry matrices and the characters of \( 180 \times 180 \) matrices

<table>
<thead>
<tr>
<th>( I_h )</th>
<th>E</th>
<th>12C</th>
<th>12C</th>
<th>20C</th>
<th>15C</th>
<th>I</th>
<th>12S</th>
<th>12S</th>
<th>20S</th>
<th>15( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>3</td>
<td>( \tau )</td>
<td>( -\sigma )</td>
<td>0</td>
<td>-1</td>
<td>3</td>
<td>( -\sigma )</td>
<td>( \tau )</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>( F_{1g} )</td>
<td>3</td>
<td>( -\sigma )</td>
<td>( \tau )</td>
<td>0</td>
<td>-1</td>
<td>3</td>
<td>( \tau )</td>
<td>( -\sigma )</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>( H_g )</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>( A_u )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( F_{1u} )</td>
<td>3</td>
<td>( \tau )</td>
<td>( -\sigma )</td>
<td>0</td>
<td>-1</td>
<td>-3</td>
<td>( \sigma )</td>
<td>( -\tau )</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( F_{2u} )</td>
<td>3</td>
<td>( -\sigma )</td>
<td>( \tau )</td>
<td>0</td>
<td>-1</td>
<td>-3</td>
<td>( -\tau )</td>
<td>( \sigma )</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( G_u )</td>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>-4</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>( H_u )</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-5</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

\[ \chi_{\text{site}} = 60 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 4 \]

\[ \Gamma_{180} = 180 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 4 \]

This subject will be discussed elsewhere [11]. The vibrational modes are qualitatively classified in a usual way such that direct product of \( 60 \times 60 \) matrices, which are obtained from site symmetry with the generators given in Eqn. (1), gives \( 180 \times 180 \) matrix generators of the group \( I_h \). Conjugacy classes \( \Gamma_{180} \) of \( 180 \times 180 \) reducible representations is given in the Table 1. Decomposition of reducible representation \( \Gamma_{180} \) in terms of irreducible representation specifies the vibrational modes such that

\[ \Gamma_{180} = 2A_g + 4F_{1g} + 4F_{2g} + 6G_g + 8H_g + A_u + 5F_{1u} + 5F_{2u} + 6G_u + 7H_u. \quad (2) \]

The six degrees of freedom associated with the translations \( F_{1u} \) and rotations \( F_{1g} \) must be subtracted from \( \Gamma_{180} \) to classify the vibrational modes:

\[ \Gamma_{\text{vib}} = 2A_g + 3F_{1g} + 4F_{2g} + 6G_g + 8H_g + A_u + 4F_{1u} + 5F_{2u} + 6G_u + 7H_u. \quad (3) \]

It is shown that there are 174 degrees of freedom for isolated \( C_{60} \) molecule; a number of them are degenerate due to high symmetry. As such, 46 distinct mode frequencies are appearing for the \( C_{60} \) molecule in Eqn. (3). Four fundamentals \( F_{1u} \) can appear in the infrared spectrum and ten \( 8H_g + 2A_g \) in the Raman spectrum.
3. Vibrational Modes

As we mentioned in Section 1, some force constant models include only bond-stretching force constants between two bonded atoms and bending force constants. But it is apparent that the interaction beyond nearest neighbors should be included to obtain the normal mode frequencies with a reasonable accuracy. In our approach, each atom in $C_{60}$ is assumed to be a point mass, and they are connected with springs. The Keating type potential as employed for the $C_{60}$ molecule can be written in the form

$$V = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{\alpha_{ij}}{2} |(u_i - u_j) \cdot \hat{r}_{ij}|^2 + \frac{\beta}{2} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \sum_{k=j+1}^{N} |(u_i - u_j) \cdot \hat{r}_{ik} + (u_k - u_i) \cdot \hat{r}_{jk}|^2,$$  \hspace{1cm} (4)

where $u_i$ is the small displacement of ith carbon atom about its equilibrium position, $r_{ij}$ is the unit vector of $r_i - r_j$ and $\alpha_{ij}$ is the force constant between the ith and jth atoms in a $C_{60}$ molecule. $\beta$ can be considered as the angle bending force constant. In Eqn. (4) the summations are taken over all neighbour pairs, so that the value of N is 60. It is obvious that the potential equation include 1770 different force constants excluding angle bending force constant $\beta$. Since the potential energy and kinetic energy of the $C_{60}$ are separately invariant under symmetry operation, then we can write

$$R_{ij}V = V,$$ \hspace{1cm} (5)

where $R_{ij}$ are the 180 $\times$ 180 reducible matrix generators of the $I_h$ group. The potential energy can be simplified and number of force constants can be determined from the symmetry operation in Eqn. (5). After performing a few calculations, we obtain only 23 different radial force constants of which two of unbonded and the remaining 21 are unbonded force constants. Dynamical matrix $(\Phi)$ is obtained from the potential energy given in Eqn. (4), such as

$$\Phi(\kappa \kappa') = \frac{\partial^2 V}{\partial u_i \partial u_j} \hspace{1cm} (i = 1, 2, \ldots 180) \hspace{0.5cm} \text{and} \hspace{0.5cm} (j = 1, 2, \ldots 180).$$  \hspace{1cm} (6)

Throughout this paper, $\kappa$ and $\kappa'$ indicate the atom index and take on values for the number of atoms in a site. Eigenvalues of the dynamical matrix $\Phi(\kappa \kappa')$ of size 180 $\times$ 180 corresponds to the vibrational frequencies $m\omega^2$ of the $C_{60}$. The matrix $\Phi(\kappa \kappa')$ is block-diagonalized by using symmetry vectors. Eigenvalues of each block matrix gives vibrational eigenvalues for corresponding irreducible representation. The symmetry vectors belonging to the $i$th irreducible representation can be obtained by the projection method. In this work calculation of the symmetry vectors was carried out symbolically by mathematica, developing a simple method. The symmetry vectors for $A_g$ and $A_u$ representations are listed in Table 2.

We have carried out a calculation for eigenvalues of block diagonalized matrix $\Phi(\kappa \kappa')$, by considering interaction up to ten-neighbours. The values of the bond-stretching and angle bending force constants that we have used to obtain the results are given in Table 3.
determination of the electron-phonon coupling strength and vibrational frequencies in interpretation of experimental data. This model should serve as the starting point for results. These comparisons give us confidence modes are in agreement with experimental observations are listed. For comparison, we have also listed the 14 optically observed Raman and infrared active modes, each atom and its ten neighbouring atoms. In Table 4, the 46 distinct vibrational frequencies were computed.

Table 3. Force constants $\alpha$ and distances $d$ between atoms in mdyne/cm and angstrom, respectively

| $\alpha_1$ | 4.56 | $d_1$ | 1.40 | $\alpha_2$ | 2.48 | $d_2$ | 1.40 | $\alpha_3$ | 1.28 | $d_3$ | 2.38 | $\alpha_4$ | 1.00 | $d_4$ | 2.49 |
| $\alpha_5$ | 0.98 | $d_5$ | 2.83 | $\alpha_0$ | 0.98 | $d_6$ | 3.63 | $\alpha_7$ | 1.74 | $d_7$ | 0.39 | $\alpha_8$ | 0.98 | $d_8$ | 1.19 |

The calculated 46 distinct vibrational frequencies are listed in Table 4.

4. Concluding Remarks

So far, we have obtained dynamical matrix $\Phi(\kappa\kappa')$ that involves interactions among each atom and its ten neighbouring atoms. In Table 4, the 46 distinct vibrational frequencies are listed. For comparison, we have also listed the 14 optically observed Raman and infrared active modes, the modes measured by neutron inelastic scattering and high resolution electron-energy-loss spectroscopy, and some recent calculations. It can be shown that, with a few exceptions, all computed modes are in agreement with experimental results. These comparisons give us confidence modes are in agreement with experimental results. These comparisons give us confidence that our model should be useful for interpretation of experimental data. This model should serve as the starting point for determination of the electron-phonon coupling strength and vibrational frequencies in doped $C_{60}$. 

127
Table 4. Calculated, experimental and other theoretical values for the vibrational modes of the C$_{60}$ in cm$^{-1}$. Experimental data is taken from Refs. [5, 6] and theoretical results are from [4, 5, 7].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_{g}$</td>
<td>1470</td>
<td>1501</td>
<td>1470</td>
<td>1468</td>
<td>1499</td>
<td>1418</td>
<td>1512</td>
<td>1414</td>
<td>1548</td>
<td>1564</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$_{1u}$</td>
<td>558</td>
<td>584</td>
<td>501</td>
<td>580</td>
<td>577</td>
<td>565</td>
<td>578</td>
<td>569</td>
<td>570</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G$_{g}$</td>
<td>439</td>
<td>449</td>
<td>498</td>
<td>486</td>
<td>403$^*$</td>
<td>341</td>
<td>346</td>
<td>385</td>
<td>356</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_{u}$</td>
<td>273</td>
<td>258</td>
<td>268</td>
<td>258</td>
<td>355$^*$</td>
<td>358</td>
<td>387</td>
<td>361</td>
<td>404</td>
<td></td>
</tr>
</tbody>
</table>

* The experimental data indicated by symbol (*) were measured by neutron inelastic scattering and high resolution electron-energy-loss spectroscopy [7].

The choice of bond stretching force constants, which is given in Table 3, $\alpha_1$, $\alpha_2$ and $\alpha_3$ were in agreement with the corresponding values in graphite and the other similar models [4, 5, 6]. We also investigated the effect of the bond-stretching force constants $\alpha_1$, $\alpha_2$, $\alpha_3$ and $\alpha_4$ on the vibrational modes. It turns out that the $A_u$ mode, the lowest $A_g$ mode, the first lowest $F_{1g}$, $F_{2g}$, $F_{1u}$ and $F_{2u}$ modes and the first three lowest $G_g$ and $G_u$, $H_g$ and $H_u$ modes not dependent on the values of $\alpha_1$, $\alpha_2$ and $\alpha_3$. Therefore any force constant model should includes force between four or five shells of atoms. For the model of Ref. [6], at least a large radial forth and fifth nearest neighbour force constant was needed whereas the model did not include a radial force constant between further than nearest neighbours. For Ref. [7], although the distances between reference atom and third nearest neighbour atom is approximately equal to the distance between reference atom and fourth nearest atom, their force constants are found much differently from each other. In fact, the force constants $\alpha_3$ and $\alpha_4$ should be nearly equal to each other.

The present results demonstrate that our method is a useful to study electron-phonon interactions between vibrational levels.
Acknowledgements

We thank the Research Fund of the University of Gaziantep for partial financial support.

References