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

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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 icosehedral 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 icosehedral 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 icosehedral group, I_h, and the generators which generate 120 symmetry operations of the icosehedral group are given by the matrices

$$C_5 = \frac{1}{2}\begin{pmatrix} -\tau & -\sigma & 1 \\ \sigma & 1 & \tau \\ -1 & \tau & -\sigma \end{pmatrix} \quad C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad I = -\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad (1)$$

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 3×3 irreducible generators have been obtained by breaking the symmetries of SO(3) group [10]. Character table which characterize C_{60} of full icosehedral 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, 60×60 reducible matrix generators, which transforms the radial vectors r_i to each other $(i = 1, 2, \ldots, 60)$, are carried out yielding characters χ_{site} as given in Table 1. The symmetries of the

electronic levels of the molecule can be found by taking the direct product of χ_{site} with A_g, F_{1u} and H_g for s, p and d functions, respectively.

Table 1. Character table for the full icosehedral group I_h. The last two rows demonstrates the characters of site symmetry matrices and the characters of 180×180 matrices

I_h	E	12C	12C	20C	15C	I	12S	12S	20S	15σ	
A_g	1	1	1	1	1	1	1	1	1	1	
F_{1g}	3	τ	$-\sigma$	0	-1	3	$-\sigma$	τ	0	-1	R_x, R_y, R_z
F_{2g}	3	$-\sigma$	τ	0	-1	3	τ	$-\sigma$	0	-1	
G_g	4	-1	-1	1	0	4	-1	-1	1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
F_{1u}	3	τ	$-\sigma$	0	-1	-3	σ	$-\tau$	0	1	x, y, z
F_{2u}	3	$-\sigma$	τ	0	-1	-3	$-\tau$	σ	0	1	
G_u	4	-1	-1	1	0	-4	1	1	-1	0	
H_u	5	0	0	-1	1	-5	0	0	1	-1	
χ_{site}	60	0	0	0	0	0	0	0	0	4	
Γ_{180}	180	0	0	0	0	0	0	0	0	4	

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

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

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

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

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 neighbours 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

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

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 α_{ij} is the force constant between the ith and jth atoms in a C_{60} molecule. β 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 α_{ij}, excluding angle bending force constant β. Since the potential energy and kinetic energy of the C_{60} are separately invariant under symmetry operation, then we can write

$$R_{ij} V = V, \quad (5)$$

where R_{ij} are the 180×180 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 $\Phi(\kappa\kappa')$ is obtained from the potential energy given in Eqn. (4), such as

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

Throughout this paper, κ and κ' 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 180×180 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 ith 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.

Table 2. Symmetry vectors associated to the irreducible representations A_2 and A_u

Γ	Symmetry Vector $(x_1, y_1, z_1; x_2, y_2, z_2 \quad \ldots \quad x_{60}, y_{60}, z_{60})$
	$\{0,0,4;\tau,-\sigma,-2;0,0,-4;\tau,-\sigma,2;-\tau,-\sigma,2;2,-\tau,\sigma;-\tau,-\sigma,-2;-\tau,\sigma,2;$
	$-2,-\tau,-\sigma;-\tau,\sigma,-2;\tau,\sigma,-2;2,-\tau,-\sigma;\tau,-\sigma,2;-2,\tau,-\sigma;-2,-\tau,\sigma;-\sigma,-2,\tau;$
	$2,\tau,\sigma;-\sigma,-2,-\tau;\sigma,-2,-\tau;-2,\tau,\sigma;\sigma,-2,\tau;-\sigma,2,-\tau;2,\tau,-\sigma;0,-4,0;$
	$-\sigma,2,\tau;\sigma,2,\tau;0,-4,0;-4,0,0;-\sigma,2,-\tau;$
	$-4,0,0;\sigma,-2,-\tau;4,0,0;0,4,0;-\sigma,-2,\tau;\sigma,-2,-\tau;0,4,0;-2,-\tau,-\sigma;$
	$-\sigma,-2,-\tau;-\sigma,2,\tau;2,-\tau,\sigma;-\sigma,2\tau;\sigma,2,-\tau;-2,-\tau,\sigma;\sigma,2,\tau;2,\tau,\sigma;$
	$2,-\tau,-\sigma;-\tau,-\sigma,2;-2,\tau,-\sigma;-\tau,-\sigma,-2;\tau,-\sigma,-2;2,\tau,-\sigma;2,\tau,-\sigma;\tau,-\sigma,2;$
	$\tau,\sigma,-2;-2,\tau,\sigma;\tau,\sigma,2;0,0,-4;-\tau,\sigma,-2;0,0,4\}/8\sqrt{15}$
A_J	$\{0,-4,0;-2,-\tau,-\sigma;0,-4,0;-2,-\tau,\sigma;2,-\tau,\sigma;-\sigma,-2,-\tau;2,-\tau,-\sigma;-2,-\tau,-\sigma;$
	$\sigma-2,\tau;-2,-\tau,\sigma;2,-\tau,\sigma;-\sigma,2\tau;2,-\tau,\sigma;-\sigma,-2,-\tau;\sigma-2,-\tau;-\tau,-\sigma,-2;$
	$\sigma,-2,\tau;-\tau,-\sigma,2;\tau,-\sigma,2;-\sigma,-2,\tau;\tau,-\sigma,-2;-\tau,-\sigma,-2;\sigma,-2,-\tau;-4,0,0;\tau,-\sigma,2;$
	$-\tau,-\sigma,2;4,0,0;0,0,-4;\tau,-\sigma,2;0,0,4;0,0,4;-\tau,\sigma,-2;$
	$0,0,-4;-4,0,0;\tau,\sigma,2;-\tau,\sigma,2;4,0,0;-\sigma,2,-\tau;\tau,\sigma,-2;-\tau,\sigma,-2;\sigma,2,\tau;-\tau,\sigma,2;\tau,\sigma,2;$
	$-\sigma,2,\tau;\tau,\sigma,-2;-\sigma,2,-\tau;\sigma,2,-\tau;-2,\tau,-\sigma;\sigma,2,\tau;-2,\tau,\sigma;-\sigma,2,\tau;$
	$2,\tau,-\sigma;-2,\tau,-\sigma;\sigma,2,-\tau;-2,-\tau,\sigma;0,4,0;2,\tau,-\sigma;0,4,0\}/8\sqrt{15}$
A_u	$\{4,0,0;-\sigma,2,-\tau;-4,0,0;\sigma,-2,-\tau;\sigma,2,\tau;\tau,\sigma,-2;-\sigma,-2,\tau;\sigma,-2,\tau;-\tau,\sigma,2;$
	$-\sigma,2,\tau;-\sigma,-2,-\tau;-\tau,-\sigma,-2;\sigma,2,-\tau;-\tau,-\sigma,2;\tau,-\sigma,2;2,-\tau,-\sigma;\tau,-\sigma;-2;$
	$-2,-\tau,\sigma;\tau,\sigma,2;2,\tau;\sigma;-2,\tau,\sigma;-\tau,\sigma,-2;0,0,-4;2,\tau,-\sigma;2,-\tau,\sigma;$
	$0,0,4;0,-4,0;-2,-\tau,-\sigma;0,4,0;0,-4,0;2,\tau,-\sigma;$
	$0,4,0;0,0,4;-2,\tau,\sigma;-2,-\tau,-\sigma;0,0,-4;\tau,-\sigma,-2;2,-\tau,\sigma;$
	$-2,-\tau,\sigma;-\tau,-\sigma,2;2,\tau,\sigma;2,-\tau,-\sigma;-\tau,\sigma,-2;-2,\tau,-\sigma;-\tau,\sigma,2;\tau,\sigma,2;-\sigma,$
	$-2,-\tau;\tau,\sigma,-2;\sigma,-2,\tau;\tau,-\sigma,2;-\sigma,2,\tau;-\tau,-\sigma,-2;$
	$-\sigma,-2,\tau;\sigma,2,-\tau;4,0,0;\sigma,-2,-\tau,\sigma;-4,0,0\}/8\sqrt{15}$

Table 3. Force constants α and distances d between atoms in mdyn/cm and angstrom, respectively

$\alpha_1 = 4.56$	$d_1 = 1.40$	$\alpha_2 = 2.48$	$d_2 = 1.47$	$\alpha_3 = 1.28$	$d_3 = 2.38$	$\alpha_4 = 1.06$	$d_4 = 2.49$
$\alpha_5 = -0.98$	$d_5 = 2.83$	$\alpha_6 = 0.032$	$d_6 = 3.62$	$\alpha_7 = 0$	$d_7 = 3.74$	$\alpha_8 = 0.39$	$d_8 = 4.16$
$\alpha_9 = 0.012$	$d_9 = 4.57$	$\alpha_{10} = 0$	$d_{10} = 4.66$	$\beta = 0.196$			

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}.

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]

Rep.	Expt.	Present	Feldman	Jishi	Quong	Rep.	Expt.	Present	Feldman	Jishi	Quong
A_g	496	493	496	492	478	A_u		883	1012	1142	850
	1470	1501	1470	1468	1499						
						F_{1u}	527	541	527	505	547
F_{1g}		558	584	501	580		577	565	578	589	570
	970*	959	879	981	788		1183	1025	1208	1208	1176
	1369*	1303	1297	1346	1252		1428	1447	1445	1450	1461
F_{2g}	560*	507	573	541	547	F_{2u}	355*	335	377	367	342
		731	888	847	610		680*	779	705	677	738
	870*	785	957	931	770			995	1014	1025	962
	1360*	1346	1433	1351	1316			1167	1274	1212	1185
								1548	1564	1575	1539
G_g		439	449	498	486						
		633	612	626	571	G_u	403*	341	346	385	356
		775	840	805	759		760*	669	829	789	683
	1065*	987	1153	1056	1087			739	931	929	742
	1360*	1173	1396	1375	1296		1065*	937	994	961	957
		1408	1534	1521	1505		1310*	1286	1425	1327	1298
							1440*	1378	1451	1413	1440
H_g	273	258	268	269	258						
	437	428	438	439	439	H_u	355*	358	387	361	404
	710	769	692	708	727		560*	523	521	543	539
	774	806	782	788	767			583	667	700	657
	1099	1075	1094	1102	1093			625	814	801	737
	1250	1234	1226	1217	1244			1159	1141	1129	1205
	1428	1372	1431	1401	1443			1361	1358	1385	1320
	1575	1579	1568	1575	1576		1555*	1541	1558	1552	1565

* The experimental datas 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, α_1, α_2 and α_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 α_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 α_1, α_2 and α_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 α_3 and α_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.

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