



Molecular vibrational modes of C_{60} and C_{70} via finite element method

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ABSTRACT

Molecular vibration spectra are of great significance in the study of molecular structures and characters. A widely-used analytical method of structural mechanics, finite element method, is imported into the domain of micro-scaled molecular spectra. The vibrational modes of fullerenes C_{60} and C_{70} are calculated depending on uniform carbon–carbon bonding elements, each of which has three force constants that are determined by fitting the C_{60} Raman spectra experimental data and one ratio factor which is the bond lengths ratio between the single and double bonds. The computational result shows reasonable agreement with both calculated and experimental results published before.

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1. Introduction

Since Kroto et al. discovered C_{60} by laser vaporizing graphite into a helium stream (Kroto et al., 1985); an impressive experimental and theoretical effort has been undertaken towards this highly symmetrical, large-cage carbon cluster which was named Buckminsterfullerene after the designer of geodesic domes. Through the following decades, the research aspect expanded to the whole fullerene series, especially C_{60} and C_{70} . Among those massive works, vibration spectra experiments (Bethune et al., 1991; Dennis et al., 1991; Gallagher et al., 1997; Krätschmer et al., 1991; Lynch et al., 1995; Meilunas et al., 1991) and vibrational motion calculations, which contribute to certify the molecular structure of C_{60} as “footballene” rather than “graphitene” (Negri et al., 1988; Stanton and Newton, 1988; Wu et al., 1987), are essential characters of fullerenes. Recently, experimentalists have reported “Surface Enhanced Raman Scattering” (SERS) spectra of C_{60} and C_{70} (Friedericks, 1996; Katayama et al., 1994; Luo and Yan, 2005) by depositing fullerenes on the electrode or metal surface in order to obtain more intensive and more distinguishable spectral signals.

The available approaches of C_{60} and C_{70} vibration calculation all belong to quantum mechanical method. They can mainly be classified as the Icosahedral symmetry analysis (Harter and Weeks, 1989; Weeks and Harter, 1989), force field model (Wu et al., 1987; Cyvin et al., 1988; Jishi et al., 1993), modified neglect of diatomic

overlap (MNDO) (Stanton and Newton, 1988), Quantum-mechanical Consistent Force Field Method for Pi-Electron Systems (QCFF/PI) (Negri et al., 1988), Austin Model 1 (AM1) (Slanina et al., 1989), density functional theory (Adams et al., 1991; Choi et al., 2000; Schettino et al., 2001; Sun and Kertesz, 2002; Schettino et al., 2002).

The Finite Element Method is broadly applied to the structure mechanics analysis and electromagnetic analysis. By constructing an atomic-scale element, the Finite Element Method can be applied to molecule analysis. However, so far, the molecular mechanics Finite Element Analysis has been restricted to strain-stress relationship (Chang and Gao, 2003; Liu et al., 2004) and structure vibration (Li and Chou, 2004), electromechanical analysis (Pantano et al., 2004) and none of them has involved molecular vibration spectra.

We have calculated the molecular vibrational modes of C_{60} via the Finite Element Method before (Zeng et al., 2006), and the results showed quantitative agreement with C_{60} Raman experimental values. In this work, we perform further analysis of C_{60} and a molecular mechanics Finite Element Analysis on the molecular vibrational modes of C_{70} . Two types of carbon–carbon bonding elements are constructed, by which the energy and motion of single and double carbon–carbon bond are characterized, respectively. By routine transformation and assembling procedures, the stiffness matrices of C_{60} and C_{70} at global coordinate are derived. The eigenfrequencies and vibrational vectors of C_{60} and C_{70} are obtained by calculating and normalizing the generalized eigenvalues and generalized eigenvectors of stiffness matrixes and mass matrixes. This method generates correct number of modes, the correct point group characters, and qualitatively correct frequencies. The vibrational movements of each atom and the derivative dipole moment due to molecular vibration are also discussed.

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2. Calculation theory

The geometry of ground state equilibrium C_{60} is a truncated isohedron with 60 vertices, 12 pentagons and 20 hexagons. The carbon atoms in C_{60} are in $sp^{2.28}$ bonding state (Titantah and Lamoen, 2004), while those in C_{70} can be expected to exhibit another bonding state. To avoid the error introduced by applying the same force constants on C_{60} and C_{70} which have carbon atoms in different states, the Kekulé structure was adopted. So an alternating arrangement of single and double bonds is shown in the calculation model, such that not only every carbon atom is in the full quantum state, but also the symmetries of the molecules are maintained. In the C_{60} calculation model, the bonds shared by a hexagon and a pentagon are treated as single bonds while others are treated as double bonds.

The structure of C_{70} is an elongated cage with D_{5h} symmetry, and has 12 pentagons and 25 hexagons on its surface. The calculation model of C_{70} is shown in Fig. 1, showing the distribution of single and double bonds. The carbon–carbon bonds constructing C_{70} are considered to be the same as that in C_{60} .

Summarizing the previous calculation and experimental works (Hirsch, 1999); the bond lengths of single and double bonds are 1.451 and 1.381 Å, respectively. However, carbon–carbon bonds in the real material structure of C_{60} and C_{70} should be uniform. So, in both models, those bonds are built with equal length of 1.433 Å. A ratio factor, which is the bond length ratio of single and double bonds, is introduced. By multiplying it with the force constants, the ratio between single-bond and double-bond force constants is made to be the inverse ratio of the bond lengths.

According to the Born–Oppenheimer hypothesis, the total energy of each covalent bond can be separated into several parts as (Chang and Gao, 2003)

$$U_{total} = U_x + U_\sigma + U_\pi + U_t + U_{vdw} + U_{es}. \quad (1)$$

Here, U_x is the bond stretching energy, U_σ is the bond bending energy in the σ -plane, U_π is the bond bending energy in the π -plane, U_t is the torsional energy, U_{vdw} is the energy induced by the Van der Waals force and U_{es} is the energy corresponding to static charge. The effect generated by the last three terms is negligible so that formula (1) can be simplified to

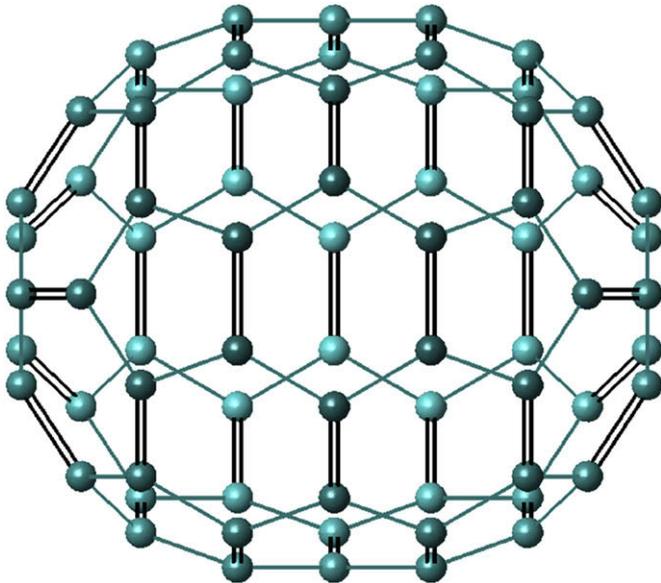


Fig. 1. Calculation model of C_{70} .

$$U_{total} = U_x + U_\sigma + U_\pi. \quad (2)$$

To simplify the problem, and in contrast to the conventional way, the minimum energy at the equilibrium point is chosen to be to the zero-energy point. Also, the potential energy of each bond in the neighborhood of the equilibrium point is approximated by a quadratic equation. We describe the energy of each bond by a three-force-constant element with a local Cartesian coordinate of which the x -axis is along the bonding direction, the y -axis and z -axis are in the σ -plane and π -plane, respectively. Let a_{C-C} be the bond length. Assuming that two atoms of a bond are located in positions (x_i, y_i, z_i) and (x_j, y_j, z_j) , respectively, we express the stretching energy of bond as

$$U_x = \frac{1}{2}k_x\delta_x^2 = \frac{1}{2}k_x(x_j - x_i - a_{C-C})^2, \quad (3)$$

where δ_x is the bond elongation and k_x is the bond-stretching force constant. The bond rotation energy is divided into two parts as

$$U_\sigma = \frac{1}{2}k_y(y_j - y_i)^2, \quad (4)$$

$$U_\pi = \frac{1}{2}k_z(z_j - z_i)^2, \quad (5)$$

where k_y and k_z are the bond-bending force constants in the σ -plane and the π -plane, respectively.

We consider each molecule as a structure, treating each carbon atom as a node and each carbon–carbon bond as an element. According to the bond potential energy, the stiffness matrix \bar{K}_{C-C}^e of a carbon–carbon bonding element in local coordinates can be deduced as

$$\bar{K}_{C-C}^e = \begin{bmatrix} k_x & 0 & 0 & -k_x & 0 & 0 \\ 0 & k_y & 0 & 0 & -k_y & 0 \\ 0 & 0 & k_z & 0 & 0 & -k_z \\ -k_x & 0 & 0 & k_x & 0 & 0 \\ 0 & -k_y & 0 & 0 & k_y & 0 \\ 0 & 0 & -k_z & 0 & 0 & k_z \end{bmatrix} \quad (6)$$

When multiplied by the coordinate transformation matrix \mathbf{R}^e , \bar{K}_{C-C}^e is transformed into the stiffness matrix of carbon–carbon bonding element in global coordinates, \mathbf{K}_{C-C}^e . According to the atomic numbering, we assemble every \mathbf{K}_{C-C}^e to obtain the stiffness matrix \mathbf{K}_{C-C} in global coordinates, with a size of $3n \times 3n$, n being the number of atoms in the molecule. Because the absolute majority of the mass of an atom is located on the atomic nucleus rather than the electron cloud, the mass matrix \mathbf{M}_{C-C} is a $3n \times 3n$ diagonal matrix of which each diagonal element is the mass of a single carbon atom. The eigen frequencies and vibrational vectors are obtained by calculating and normalizing the generalized eigenvalues and generalized eigenvectors of \mathbf{K}_{C-C} and \mathbf{M}_{C-C} .

Although the full vibrational modes can be obtained from the above calculation scheme, group theory is introduced to help classify and analyze the results. Considering C_{60} and C_{70} , which have I_h and D_{5h} symmetries, respectively, we find the following distributions of the normal vibrations among the different irreducible representations:

$$I_{C60} = 2A_g + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u, \quad (7)$$

$$I_{C70} = 12A'_1 + 9A'_2 + 21E'_1 + 22E'_2 + 9A''_1 + 10A''_2 + 19E''_1 + 20E''_2, \quad (8)$$

where A , E , T , G and H represent one-dimensional to five-dimensional modes, respectively; primes and double primes indicate

Table 1
Calculated and experimental Raman vibrational frequencies for C₆₀ (cm⁻¹).

Symmetry	Raman spectra			SERS		Calculation				
	Meilunas et al. (1991)	Lynch et al. (1995)	Luo and Yan (2005)	Luo and Yan (2005)	Stanton and Newton (1988)	Negri et al. (1988)	Choi et al. (2000)	Schettino et al. (2001)	Adams et al. (1991)	This work
A _g (1)	496	496	497	491	610	513	495	496	537	443
A _g (2)	1470	1467	1467	1462	1667	1442	1470	1468	1680	1599
H _g (1)	273	272	273	254	263	258	267	264	249	232
H _g (2)	434	485	433	399	447	440	431	430	413	465
H _g (3)	710	709	709	659	771	691	711	709	681	701
H _g (4)	774	772	772	766	924	801	775	773	845	751
H _g (5)	1100	1100	1100	1099	1261	1154	1101	1101	1209	1111
H _g (6)	1250	1250	1249	1246	1407	1265	1251	1251	1453	1384
H _g (7)	1426	1424	1422	1421	1596	1465	1427	1425	1624	1624
H _g (8)	1576	1574	1574	1565	1722	1644	1576	1576	1726	1671

those modes that are, respectively, symmetric and antisymmetric with respect to reflection operation σ_h ; subscripts *g* and *u* are attached to symbols for representations which are, respectively, symmetric and antisymmetric with respect to inversion; subscripts 1 and 2, attached to *A_s*, designate those modes which are, respectively, symmetric and antisymmetric with respect to mirror symmetry plane perpendicular to the 5-fold rotation symmetry axis; subscripts 1 and 2, attached to *E_s* and *T_s*, are regarded as arbitrary labels (Cotton, 1990).

Although each molecule has $3n - 6$ vibrational modes, not all of them can be measured in experiments. The modes that can be observed in infrared spectra are called IR-active modes, those that inducing peaks in the Raman spectra are called Raman-active modes. According to group theory (Cotton, 1990), the high symmetry of C₆₀ gives rise to only 14 IR-active and Raman-active modes ($4T_{1u}$ and $2A_g + 8H_g$). The lower symmetry of C₇₀ leads to much more complicated vibrational spectra with 31 IR-active and 53 Raman-active modes ($21E'_1 + 10A''_2$ and $12A'_1 + 22E'_2 + 19E''_1$). The calculation results have the same order of magnitude as the experimental results (Bethune et al., 1991; Dennis et al., 1991; Gallagher et al., 1997; Lynch et al., 1995; Meilunas et al., 1991).

3. Calculation and analysis of C₆₀

Our calculated frequencies of C₆₀ are fitted with Raman spectra data in order to determine the 3 force constants. In the process of matching, we find that the two *A_g* modes only depend on bond stretching force-constant k_x . Those radial breathing and tangential stretching modes only involve bond length stretching or shrinking, and the C=C or C-C bond angles play no role. The bond stretching force-constant k_x is determined by matching the two *A_g* modes. By fitting the other eight Raman-active modes ($8H_g$), we determine the σ -plane and π -plane bond-bending force constants k_y and k_z . The values obtained are

$$k_x = 560 \text{ nN/nm}, \quad k_y = 130 \text{ nN/nm}, \quad k_z = 90 \text{ nN/nm}.$$

The force constant k_z was expected to be substantially smaller than k_y . However, the fitting showed that these are the best parameters. The reason is because that k_z has very tiny effects on the vibration, i.e. even if k_z was set to be substantially smaller than k_y , the vibration frequencies will not change a lot and will still be very close to the experiment results.

Table 2
Quantitative analysis of the calculated vibrational vectors of C₆₀.

Symmetry	Frequencies (cm ⁻¹)		Atomic motion						Dot products					
			% radial		%tangential		% radial		%tangential		C-C		C=C	
			C=C		perp		C=C		perp		C-C		C=C	
	Stanton and Newton (1988)	This work	Stanton and Newton (1988)		This work		Stanton and Newton (1988)		This work		Stanton and Newton (1988)		This work	
rot*	0	0	0.0	50.0	50.0	0.0	50.0	50.0	0.92	0.92	0.89	0.85		
trans*	0	0	33.3	33.3	33.3	33.3	33.3	33.3	1.00	1.00	1.00	1.00		
A _g	A _g (1)	610	442.86	100.0	0.0	0.0	100.0	0.0	0.91	0.94	0.92	0.91		
	A _g (2)	1667	1599.2	0.0	100.0	0.0	100.0	0.0	0.40	-0.94	0.39	-0.91		
H _g	H _g (1)	263	231.97	69.3	15.2	15.5	48.2	26.6	25.1	0.88	0.88	0.87	0.87	
	H _g (2)	447	464.78	90.0	5.7	4.3	59.9	20.4	19.7	0.54	0.27	0.49	0.39	
	H _g (3)	771	701.33	96.5	2.1	1.4	76.4	11.8	11.7	0.52	0.19	-0.12	0.12	
	H _g (4)	924	751.14	30.5	27.1	42.4	37.1	32.8	30.0	0.49	0.67	0.48	0.63	
	H _g (5)	1261	1110.6	9.6	48.5	41.8	21.9	46.8	31.3	-0.16	0.09	-0.01	-0.03	
	H _g (6)	1407	1383.6	2.1	21.7	76.2	9.9	45.3	44.7	-0.32	-0.21	-0.01	-0.43	
	H _g (7)	1596	1623.5	0.8	87.2	12.0	1.3	59.4	39.3	0.01	-0.92	-0.44	-0.45	
	H _g (8)	1722	1671.1	1.2	92.5	6.3	1.7	57.4	40.9	-0.41	-0.97	-0.63	-0.75	
T _{1u}	T _{1u} (1)	577	567.66	93.5	3.2	3.3	55.7	15.1	29.2	0.46	-0.62	0.91	0.30	
	T _{1u} (2)	719	597.49	66.6	15.3	18.1	76.3	21.0	2.7	0.73	0.83	0.23	0.25	
	T _{1u} (3)	1353	1283.2	6.0	48.7	45.3	12.2	46.9	40.8	0.72	0.70	-0.40	0.43	
	T _{1u} (4)	1628	1621.8	0.5	99.5	0.0	0.1	80.3	19.6	0.34	-0.91	-0.19	-0.48	

* The pure rotations and translations have been included for the purpose of comparison.

Table 3
Analysis of the infrared-active modes of C₆₀.

Symmetry	Infrared spectra						Calculation					
	Krätschmer et al. (1991)		Meilunas et al. (1991)		Luo and Yan (2005)	Stanton and Newton (1988)		Choi et al. (2000)	Schettino et al. (2001)	Adams et al. (1991)	This work	
	freq	I	freq	I	freq	freq	dip	freq	freq	freq	freq	dip
T _{1u} (1)	528	100	527	100	513	577	100	526	525	494	568	100
T _{1u} (2)	577	32	577	37	550	719	57	577	578	643	597	67
T _{1u} (3)	1183	24	1183	23	1194	1353	137	1180	1182	1358	1283	44
T _{1u} (4)	1429	31	1428	24	1421	1628	211	1433	1433	1641	1622	29

* The infrared spectra frequencies (freq) and intensity (I) are compared with calculated frequencies (freq) and derivative dipole moment (dip). The frequencies are expressed in cm⁻¹. The intensity of spectra lines and the dipole moment are presented as relative values.

Our calculated frequencies of C₆₀ are compared with those experimental and calculation frequencies, as shown in Table 1. Meilunas et al. (1991), Lynch et al. (1995) and Luo and Yan (2005) provided Raman spectra experiment data of C₆₀, which are almost identical to each other. Luo and Yan (2005) also provides Surface Enhanced Raman Scattering spectra data of C₆₀, which include some offset of the spectra peaks. Calculation in Stanton and Newton (1988), Negri et al. (1988), Choi et al. (2000), Schettino et al. (2002), and Adams et al. (1991) are based on quantum mechanics, some of which have noticeable disparity. The results from this work have correct number of modes, the correct point group characters, and qualitatively correct frequencies.

The assignment of Raman-active modes is based on both the accuracy of frequencies and the depolarization ratios. The assignment of IR-active modes is related to the dipole moment deviation. Stanton published quantitative analysis of C₆₀ atomic motion (Stanton and Newton, 1988), which is considered of great contribution to the assignment of C₆₀ vibration modes. We have performed a similar quantitative analysis of the calculated vibrational

vectors of C₆₀, and the results of the major modes of C₆₀ are shown in Table 2. Taking into account that the frequencies provided by Stanton have a noticeable error compared to the Raman experiment data, the analysis of atomic motion provided by Stanton and Newton (1988) might also lack quantitative accuracy.

Using the Finite Element structural vibration analysis, the atomic motion of each atom is represented by the vibrational vectors of on each node. These vectors are normalized results which have arbitrary unit. The vibrational vectors are projected into a local Cartesian coordinate system which is defined by Stanton and Newton (1988) as “the radial direction outward from the center of the molecule, the direction perpendicular to the radius and in the plane formed by the radius and the double bond, and the tangential direction perpendicular to the first two” in order to obtain the fractional contributions of each direction. The dot products of the adjacent-atom displacements are calculated in order to determine whether they are moving in phase with each other. Adjacent atoms connected by single bonds and double bonds are treated separately. Our work shows qualitative agreement with Stanton especially for the pure rotation, translation

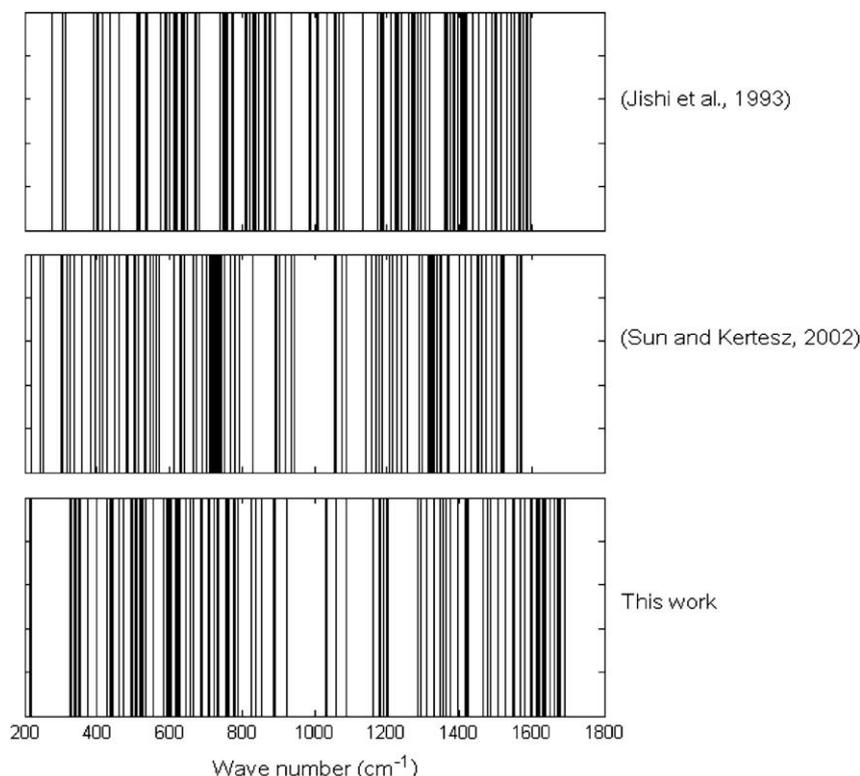


Fig. 2. Raman vibrational frequencies for C₇₀.

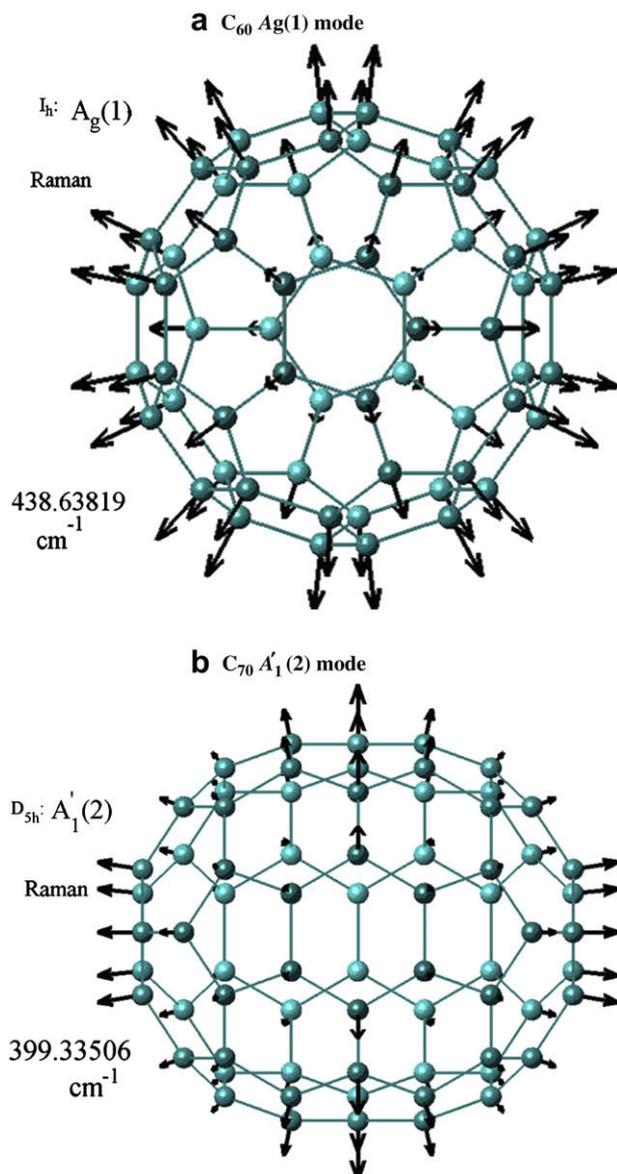


Fig. 3. Comparison between $C_{60} A_g(1)$ mode and $C_{70} A'_1(2)$ mode.

and low order modes. In both methods, the atoms move towards the radial direction at low frequencies, and gradually turn into tangential direction when the frequency is increased.

The infrared spectra intensity is determined by the dipole moment, which can be derived from the molecular vibrational motion. We calculated the derivative dipole moments of C_{60} and compared them with experimental peaks (Krätschmer et al., 1991; Luo and Yan, 2005; Meilunas et al., 1991) and calculation results (Adams et al., 1991; Stanton and Newton, 1988). The scaled quantum mechanical method (Choi et al., 2000) and density functional perturbation theory (Schettino et al., 2001) have predicted more accurate frequencies than the others, but our results given in Table 3 show better correspondence with the intensity than the references.

4. Calculation and analysis of C_{70}

As far as we know, no complete Raman spectrum or IR spectrum peaks of C_{70} have been published, and a thorough assessment of them is still under discussion. Accordingly, we present our calculation results and compare them with those of other calculations.

As shown in Fig. 2, the vibrational frequencies of in total 174 modes calculated by this work, are compared to those of two references (Jishi et al., 1993; Sun and Kertesz, 2002). Our computations produce the correct point group symmetry and qualitative agreement with other works. Most of the low-frequency part of the results fall in the middle of that of the force field model (Jishi et al., 1993) and density functional theory (Sun and Kertesz, 2002). The high-frequency part of the calculation results is a little higher than both references. This may be caused by the fact that part of the bond energy (1) has been neglected, and the results may be revised by further improvement of the calculation model.

Similar quantitative analysis of the calculated C_{70} vibrational vectors is performed. The low-frequency modes tend to move towards the radial direction while the high-frequency modes tend to move towards the tangential way. This tendency accords with that of C_{60} . The $C_{70} A'_1(2)$ mode exhibits similar characters to those of $C_{60} A_g(1)$ breathing mode. The vibrational vectors of it are almost all composed with radial movement, while $C_{60} A_g$ mode moves completely along the radial direction. Moreover, both modes are Raman-active modes. These two modes are compared in Fig. 3. The $A'_1(12)$ mode of C_{70} exhibits similar characters to the $A_g(2)$ mode of C_{60} , in which the carbon atoms vibrate along the bonding direction, as shown in Fig. 4. Those similarities indicate the peculiar nature of those two modes of C_{70} , which will hopefully prove helpful in the assignment of C_{70} Raman spectra.

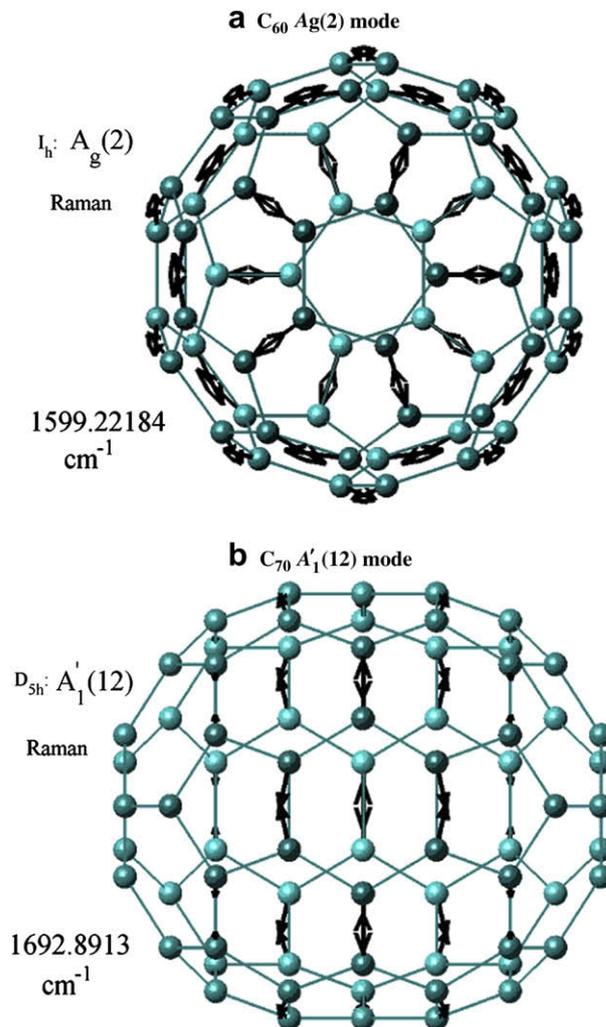


Fig. 4. Comparison between $C_{60} A_g(2)$ mode and $C_{70} A'_1(12)$ mode.

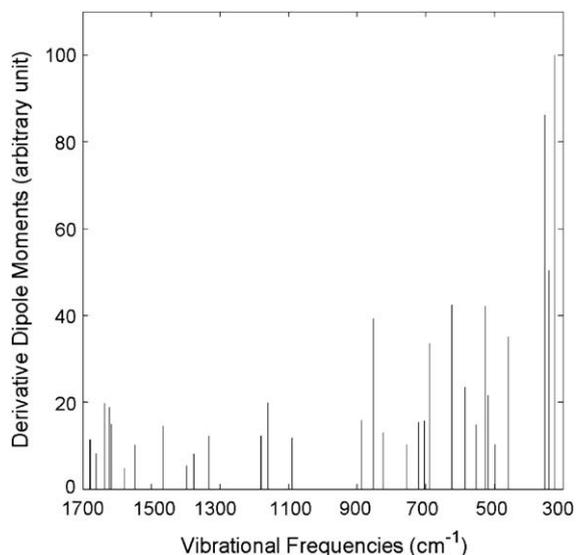


Fig. 5. Derivative dipole moment of C_{70} .

The computed derivative dipole moments of IR-active modes of C_{70} are shown in Fig. 5. We hope that the calculated frequencies and dipole moments will help to the assignment of experimental IR spectra data.

5. Discussion

In this work, we introduce a widely used structural mechanics analysis method, Finite Element Method, into micro-scale molecular mechanics. The calculation of vibrational modes of fullerenes C_{60} and C_{70} is presented using on a molecular mechanics Finite Element Analysis via uniform carbon–carbon bonding element, which has uniform geometric and mechanical parameters. The mechanics models are based on three force constants which are determined by fitting the C_{60} Raman spectra experimental data and a ratio of bond lengths. The computational result shows reasonable agreement with both calculated (Adams et al., 1991; Choi et al., 2000; Jishi et al., 1993; Negri et al., 1988; Schettino et al., 2001; Schettino et al., 2002; Slanina et al., 1989; Stanton and Newton, 1988; Sun and Kertesz, 2002) and experimental results (Dennis et al., 1991; Gallagher et al., 1997; Krättschmer et al., 1991; Lynch et al., 1995; Luo and Yan, 2005; Meilunas et al., 1991). We have calculated and analyzed the vibrational modes of C_{70} in the hope of promoting the assessment of the vibrational modes of C_{70} .

The chief ingredient of the procedure is the calculation of the generalized eigenvalues and eigenvectors of \mathbf{K}_{C-C} and \mathbf{M}_{C-C} . The construction of \mathbf{K}_{C-C} and \mathbf{M}_{C-C} is a routine procedure in the Finite Element Method, especially the transformation of local element stiffness matrix to global element stiffness matrix and the assembling of the full stiffness matrix. As in most molecular mechanics methods, diagonalization of a matrix with size equal to \mathbf{K}_{C-C} and \mathbf{M}_{C-C} is the major calculation approach. Hence, our computational model can express the bond energy in a simple and standard way, and accomplish the calculation in a standard procedure with both good accuracy and high speed.

This method generates exactly the same the number of modes and the point group characters as group theory does. However, the frequencies of most modes still have noticeable disparities compared to experimental results. Besides experimental inaccuracies, the calculation model and calculation process of this method can still be improved. The disparities may be induced by the

inaccuracies of the model: (a) the neglect of the bond energy U_t , U_{vdw} and U_{es} ; (b) the neglect of high-order part of the bond energy U_x , U_σ , U_π . This can be amended by taking those parts of energy into account.

Considering the results of C_{60} , the frequencies according to traditional quantum mechanics methods (Stanton and Newton, 1988; Negri et al., 1988) also lacked quantitative accuracy. However, the modified quantum mechanics methods (Choi et al., 2000; Schettino et al., 2001) with a scale-factor or the other algorithm improvement exported highly accurate frequencies with no more than 5 cm^{-1} error compared to Raman spectra experiment. These quantum mechanics methods used different geometric and mechanical parameters of each bond. The calculation results were multiplied by scale factors in order to approach to the experimental results. It is possible that the present molecular mechanics Finite Element Method can be improved by similar revisions. Further work in this field will be performed in the future.

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