



Vibration spectra of fullerene family

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ABSTRACT

This Letter considers a molecular mechanics approach for the vibration spectra analysis of fullerenes. Sixteen different fullerenes starting from C_{20} to C_{720} are considered. The universal force field potential is used for the molecular mechanics approach. An analytical expression based on the elastic shell theory is suggested to explain the variation of the natural frequencies across the whole family. It is shown that any given frequency across the fullerene family varies proportional to the inverse square root of their mass.

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1. Introduction

Fullerene C_{60} is one of the earliest man-made nano-structure and its discovery [1] started the revolution of nanotechnology, marked by key discoveries such as carbon nanotube [2] and graphene [3]. Extensive experimental [4–13] and theoretical studies [14–21] have been conducted on different types of fullerenes to develop further understanding of these cage-like structures containing carbon atoms. The fullerene family contains several molecules ranging from C_{20} to C_{720} . Among various properties of these molecules, the natural free vibration of received significant interest and is the primary topic of this Letter. From the point of view of structural shape, fullerenes can be broadly divided into two categories. They include spherical or near-spherical fullerenes such as C_{60} and C_{70} and ellipsoidal/non-spherical type fullerenes such as C_{90} and C_{100} . Among these two types, the vibrational analysis of spherical fullerenes has received considerable attention. Several theoretical studies (for example [22,23]) have been attempted to explain the pattern of the vibration modes and variability of the natural frequencies. Assuming the fullerenes as thin spherical elastic shells [24,25], it has been shown that the natural frequencies of spherical fullerenes can be given by

$$\omega_{n1,2}^2 = \frac{E}{R^2 \rho} \Omega_{n1,2}^2 \quad (1)$$

where n is the mode number, E is the elastic modulus, R is the radius and ρ is the density. Subscripts 1 and 2 denote higher and

lower branches of the frequency spectrum. The dimensionless frequency parameter $\Omega_{n1,2}$ can be expressed as

$$\Omega_{n1,2}^2 = \frac{1}{2(1-\mu^2)} \{n(n+1) + 1 + 3\mu \pm \sqrt{[n(n+1) + 1 + 3\mu]^2 - 4(1-\mu^2)[n(n+1) - 2]}\} \quad (2)$$

The upper branch of the frequency spectrum is denoted by a_0, a_1, a_2, \dots for different values of n . The lower branch is denoted by b and also numbered in a similar way. It can be seen from Eq. (2) that b_0 is negative and b_1 has a null frequency (i.e., a rigid body mode). Therefore, only the modes from b_2 are positive and therefore physically realistic. All b modes are lower than even the smallest a mode which is denoted by a_0 . The a_0 mode is also known as the breathing mode and is of particular significance. Substituting $n = 0$ and $n = 1$ in Eq. (2) for the upper branch we obtain $\Omega_{a_0} = 2/(1-\mu)$ and $\Omega_{a_1} = 3/(1-\mu)$. Similarly expressions for other modes can also be obtained [24,22].

Majority of the existing theoretical works are based on specific types of fullerenes and use the continuum theory to predict the vibration spectrum. In this Letter the complete range of fullerenes is considered to develop an understanding of the overall vibrational behavior. The molecular mechanics approach is used to calculate the frequencies across the complete range C_{20} – C_{720} . The details of the adopted methodologies can be found in [26–28]. Molecular mechanics is an empirical technique to optimize structures with high accuracy and comparably little computational expense. Simulations were performed with Gaussian [29], using the general purpose Universal Force Field (UFF). The UFF is parameterized for the full periodic table and investigated for structures of main group,

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organic, transition metal inorganic, and organometallic compounds. All the force field parameters include a set of hybridization, effective nuclear charges, and connectivity. The UFF is well suited for dynamics simulations because it allows more accurate vibration measurements than many other force fields, which do not distinguish bond strengths.

2. Methodology

Different structural configurations can be considered in an unified manner within the scope of molecular mechanics. The general expression of total energy is a sum of energies due to valence or bonded interactions and non-bonded interactions [30]

$$E = \sum_0^{N_B} \frac{1}{2} k_{IJ} (r - r_{IJ})^2 + \sum_0^{N_A} k_{IJK} (C_0 + C_1 \cos \theta + C_2 \cos 2\theta) + \sum_0^{N_T} \frac{1}{2} V_\phi (1 - \cos(n\phi_0) \cos(n\phi)) + \sum_0^{N_I} V_\omega (C_0^I + C_1^I \cos \omega + C_2^I \cos 2\omega) + \sum_0^{N_{nb}} R_{IJ} \left[-2 \left(\frac{x_{IJ}}{x} \right)^6 + \left(\frac{x_{IJ}}{x} \right)^{12} \right] + \sum_0^{N_{nb}} \frac{q_I \cdot q_J}{\epsilon \cdot x} \quad (3)$$

N_B , N_A , N_T , N_I and N_{nb} are the numbers of the bond-, angle-, torsion-, inversion- and the non-bonded-terms, respectively. k_{IJ} and k_{IJK} are the force constants of the bond- and angle-terms, respectively. r and r_{IJ} are the bond distance and natural bond distance of the two atoms I and J , respectively. θ and θ_0 are the angle and natural angle for three atoms I - J - K , respectively. ϕ and ϕ_0 are the torsion angle and torsion natural angle for three atoms I - J - K - L , respectively. V_ϕ , n , V_ω , ω are the height of the torsion barrier, periodicity of the torsion potential, height of the inversion barrier and inversion- or out-of-plane-angle at atom I , respectively. C_0^I , C_1^I and C_2^I are the Fourier coefficients of the inversions terms. x and x_{IJ} are the distance and natural distance of two non-bonded atoms I and J . R_{IJ} is the depth of the Lennard-Jones potential. q_I and ϵ are the partial charge of atoms I and dielectric constant. For the general non-linear case, the bend function should have a minimum $\theta = \theta_0$, with the second derivative at θ_0 equal to the force constant (k_{IJK}). The Fourier coefficients of the general angle terms C_0 , C_1 and C_2 are evaluated as a function of the natural angle θ_0 :

$$C_2 = \frac{1}{4 \sin^2 \theta_0} \\ C_1 = -4C_2 \cos \theta_0 \\ C_0 = C_2 (2 \cos^2 \theta_0 + 1) \quad (4)$$

The bond stretching force constants (k_{IJ}) are atom based and are obtained from generalization of Badger's rules. The assumption is that the bonding is dominated by attractive ionic terms plus short-range Pauli repulsions [30]. The force constant (in units of (kcal/mol)/Å²) then becomes

$$k_{IJ} = 644.12 \frac{Z_I^* Z_J^*}{r_{IJ}^3} \quad (5)$$

The Z_I^* is the effective atomic charges, in electron units. Similarly, the angle bend force constants (k_{IJK}) are generated using the angular generalization of Badger's rule. The force constant (in units of kcal/mol rad²) then becomes [29]:

$$k_{IJK} = 644.12 \frac{Z_I^* Z_J^*}{r_{IJ}^5} [3r_{IJ} r_{JK} (1 - \cos^2 \theta_0) - r_{IK}^2 \cos \theta_0] \quad (6)$$

The torsional constant (kcal/mol) is defined as

$$V_\phi = 5 \sqrt{U_I U_J} [1 + 4.18 \ln(BO_{JK})] \quad (7)$$

where, BO_{JK} is the bond order for Atom- J and Atom- K . U_I and U_J are the atomic constants defined with UFF sp^2 . Regarding the inversion term, the coefficients are $C_0^I = 1$, $C_1^I = -1$ and $C_2^I = 0$ for sp^2 atom type. In this study, we used the UFF model [30], wherein the force field parameters are estimated using general rules based only on the element, its hybridization and its connectivity. The force field functional forms and parameters used in this study are in accordance with [30]. The calculation of frequency and their validation for CNTs and ZnO NTs were detailed in [27,28,31]. In the next section, we apply this frequency calculation approach across the fullerenes family.

3. Results and discussions

The first natural frequency of the 16 fullerenes considered here is shown in Fig. 1. Each of the 16 molecules was individually modeled using the molecular mechanics method and the eigenvalue analysis was performed to extract the vibration modes. The first natural frequency decreases with the increasing mass of the fullerenes as expected. The first natural frequency is simply the smallest non-zero natural frequency. In the context of spherical fullerenes this mode is the b_2 mode. Substituting $n = 2$ in Eq. (2) for the lower branch we obtain $\Omega_{b_2} = [7 + 3\mu - \sqrt{33 + 25\mu^2 + 42\mu}]/2(1 - \mu^2)$.

If we assume that the thickness h of a fullerene is much smaller compared to its diameter, then for spherical fullerenes the total mass can be approximately expressed as

$$M \approx 4\pi R^2 \rho h \quad (8)$$

Substituting this in Eq. (1) one obtains

$$\omega_{n1,2} = \frac{2\sqrt{\pi E h}}{M^{1/2}} \Omega_{n1,2} \quad (9)$$

Therefore, we generally expect natural frequencies of fullerenes to decrease as $M^{-1/2}$. Note that this decrease is independent of the choice of n , which in turn implies that the relative decrease across the fullerene is independent of the mode of vibration. For the breathing mode, this relationship was experimentally established in [8]. Here we will verify its validity for higher modes and over the entire range of fullerenes. Continuum model has been widely used for the vibration analysis of carbon nanotubes [32–37]. Here we use this approach to the fullerene family. The widely used expression of the frequency given in Eq. (2) neglect the thickness of the fullerenes. If the thickness is taken into account, then following [25] we have

$$\Omega_{n1,2}^2 = \frac{1}{2(1 - \mu^2)} \{A \pm \sqrt{A^2 - 4mB}\} \quad (10)$$

where

$$m = n(n + 1) - 2, \quad \alpha^2 = \frac{1}{12} \left(\frac{h}{R} \right)^2 \quad (11)$$

$$A = 3(1 + \mu) + m + \alpha^2(m + 3)(m + 1 + \mu) \quad (12)$$

$$B = 1 - \mu^2 + \alpha^2[(m + 1)^2 - \mu^2] \quad (13)$$

When the thickness is neglected, by substituting $h = 0$, Eq. (10) reduces to Eq. (2) which has been used widely in the literature. Substituting $n = 0$ and $n = 1$ in Eq. (10) for the upper branch we

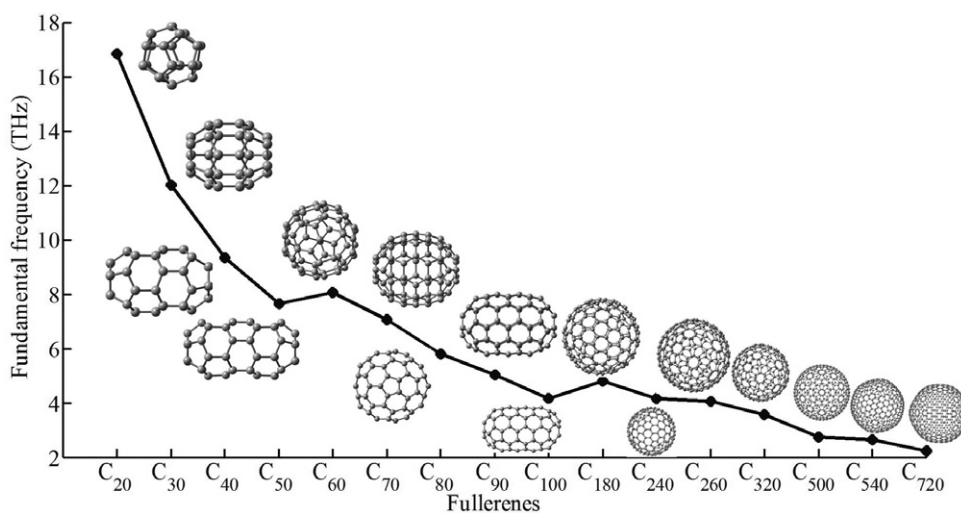


Fig. 1. The variation of the first natural frequency across the complete range of fullerenes calculated using the molecular mechanics method [26–28]. Both spherical and ellipsoidal types of fullerenes are considered. The 8 spherical type of fullerenes include C_{60} , C_{80} , C_{180} , C_{240} , C_{260} , C_{320} , C_{500} , C_{720} and the 8 ellipsoidal (or non-spherical) type of fullerenes include C_{20} , C_{30} , C_{40} , C_{50} , C_{70} , C_{90} , C_{100} and C_{540} (fullerenes are not drawn in scale). The frequencies (f) decrease approximately with the increase of the fullerene mass (M) as $f \propto M^{-1/2}$.

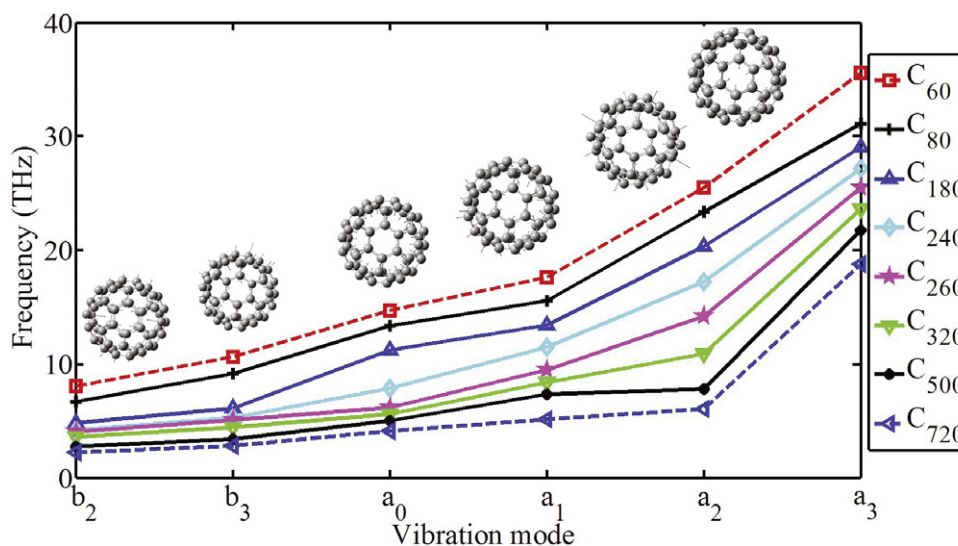


Fig. 2. Six natural frequencies and vibration mode shape of spherical type fullerenes. The modes include four a modes a_0 – a_3 and two b modes b_2 and b_3 .

obtain $\Omega_{a_0} = 2/(1 - \mu)$ and $\Omega_{a_1} = 3[1 + \alpha^2]/(1 - \mu)$. For the b_2 mode, which is numerically the smallest mode as shown in Fig. 1, one has $\Omega_{b_2} = [7 + 3\mu + \alpha^2(35 + 7\mu) - \{(490\mu + 49\mu^2 + 1225)\alpha^4 + (58\mu^2 + 308\mu + 90)\alpha^2 + (33 + 25\mu^2 + 42\mu)\}^{1/2}]/2(1 - \mu^2)$. This implies that the breathing mode frequency is not effected by the consideration of the shell thickness. However, frequency of b_2 , a_1 and indeed all the higher modes increase slightly if one uses Eq. (10) as opposed to Eq. (2).

Because C_{60} is the most widely investigated molecule, we use this to validate the numerical results arising from our molecular mechanics method. In Table 1 Raman vibrational frequencies of C_{60} (cm^{-1}) are compared with some existing theoretical and experimental results. Molecular mechanics results and analytical results obtained using the proposed frequency equation (10) are shown in Table 1. For the continuum theory based approach we use the properties of graphene sheet [39,40] as considered in [23]. The following values are taken in the numerical calculations: elastic modulus $E = 1.020$ TPa, Poisson's ratio $\nu = 0.145$, density $\rho = 2.27$ g/cm^3 , radius $R = 0.35$ nm and thickness $h = 0.06$ nm. There are differences in the values of equivalent continuum properties of graphene sheets in literature. The exact values of the frequency ob-

Table 1

Comparison of Raman vibrational frequencies of C_{60} (cm^{-1}) between this work and existing theoretical and experimental results.

Mode number	Present work	Eq. (10)	Theory [23]	Theory [22]	Experiment [38]
a_0	490	492	503	496	496
a_1	587	603	594	607	576
a_2	850	855	894	833	774
a_3	1187	1162	1218	1109	1183
b_2	269	252	259	273	273
b_3	355	324	303	324	526

tained using the continuum theory will change depending on the parameter values. However, we observed that the overall trend do not change significantly. If the shell thickness was neglected, the values of the six frequencies obtained using Eq. (2) become 492, 602, 851, 1156, 245 and 286 cm^{-1} . As mentioned before, except a_0 , the frequencies of all the other modes decrease slightly if Eq. (2) is employed. Table 1 demonstrates that the results for C_{60} using the proposed molecular mechanics and continuum theory are at par with published works. Having validated the methodology, we now use this across the fullerene family.

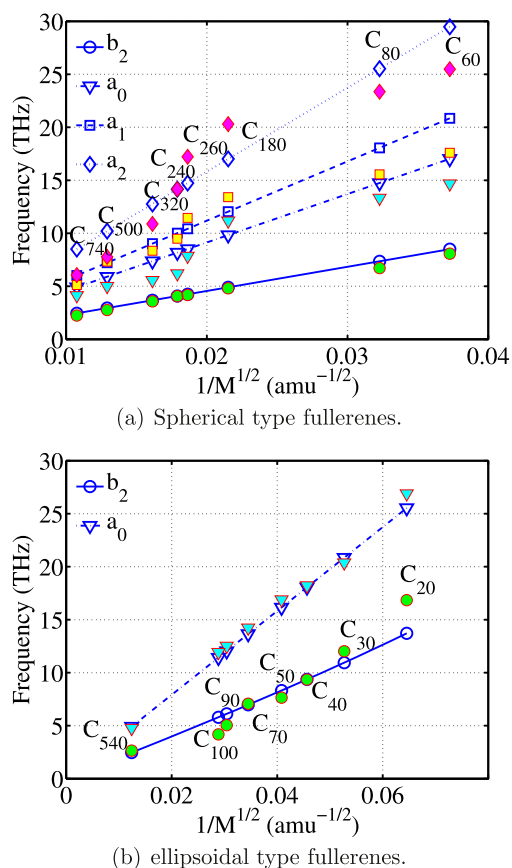


Fig. 3. Comparison of natural frequencies of spherical and ellipsoidal fullerenes calculated using the molecular mechanics simulation and analytical expression obtained using the continuum shell theory (Eq. (10)). Modes b_2 , a_0 , a_1 and a_2 are considered for spherical fullerenes, while only modes b_2 and a_0 are considered for ellipsoidal fullerenes.

In Fig. 2 we show six natural frequencies and vibration mode shape of spherical fullerenes C_{60} , C_{80} , C_{180} , C_{240} , C_{260} , C_{320} , C_{500} and C_{720} . The distinction between spherical and ellipsoidal (non-spherical) type of fullerenes adopted here is not always very strict and done purely for the simplification of discussion of the results. This categorization does not influence the main conclusions. The six modes in Fig. 2 are four a modes – a_0 – a_3 , and two – b modes b_2 and b_3 . It can be seen that the rate of increase of the frequencies are not the same for all fullerenes as lines are not perfectly parallel to each other. This is due to the fact that not all of the molecules are perfectly spherical. It is in general difficult to identify b_3 , a_1 , a_2 and a_3 modes for non-spherical type fullerenes. Therefore, a categorization of vibration modes similar to Fig. 2 becomes less meaningful for the other 8 fullerenes considered in the family. Only the fundamental frequency b_1 (shown in Fig. 1) and the breathing mode a_0 can be identified in a consistent manner across the complete range.

We examine the validity of the proposed analytical expression of the natural frequencies across the fullerene family. We calculate natural frequencies by substituting $\Omega_{n,2}^2$ from Eq. (10) into Eq. (9). The values of R to be used in Eqs. (12) and (13) are obtained using Eq. (8) for two different fullerenes. Since the values of M and R for C_{60} are well documented in literature ($M_{[C_{60}]} = 720$ amu, $R_{[C_{60}]} = 3.5$ Å), we use these as reference values and obtain the value of R for other members of the family. Note that the radius R obtain in this way is the equivalent radius to be used in expressions (12) and (13) and may not exactly coincide with the true radius of the molecules. In Fig. 3 natural frequencies calculated using the molecular mechanics simulation and analytical expression

are compared. Eight spherical fullerenes as shown in Fig. 2 and 8 ellipsoidal fullerenes such as C_{20} , C_{30} , C_{40} , C_{50} , C_{70} , C_{90} , C_{100} and C_{540} are considered. The x -axis of the figure is $M^{-1/2}$ so that following Eq. (9), the variation of all natural frequencies would be linear. Fig. 3 shows remarkably good agreement with molecular mechanics results. Even b_2 and a_0 modes for ellipsoidal fullerenes show fairly good agreement with the proposed analytical expression. In Fig. 3(a), higher order modes a_1 and a_2 for C_{240} , C_{260} and C_{180} show some discrepancies. This is due to the fact that higher modes are comparatively more sensitive to the mode shape and for these molecules they differ slightly from the classical spherical mode shapes. The overall variation of the frequencies across the complete fullerene family is generally explained well by the proposed analytical expression.

4. Conclusions

Molecular mechanics simulation has been used to investigate the natural frequency and vibration modes of molecules across the fullerene family. We used the UFF model, wherein the force field parameters are estimated using general rules based only on the element, its hybridization, and its connectivity. In total 16 molecules ranging from C_{20} to C_{720} have been considered. An analytical expression based on the continuum spherical shell theory has been proposed to explain the variability of the natural frequencies across the family. Results for C_{60} obtained using the molecular mechanics and the analytical expression have been validated against existing numerical and experiential results. The simple analytical expression explains our molecular mechanics results well across various frequencies for both spherical and non-spherical fullerenes. It is shown that any given frequency across the fullerene family varies proportional to the inverse square root of their mass. An explicit expression of the proportionality constant is derived as a function of mode number, equivalent radius, thickness, elastic modulus and Poisson's ratio. The results obtained in this Letter offer a simple and unified way of understanding the frequency variation across the whole fullerene family.

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