

Electronic and Optical Properties of Fullerene Nanostructures

© Yu.I. Prilutski, S.S. Durov

Kiev Shevchenko University,
252033 Kiev, Ukraine

E-mail: prilut@office.ups.kiev.ua

Two new types of molecular/electronic fullerene nanostructures are considered: 1) highly stable hydrated clusters (I_h symmetry group) and microcrystals (T_h symmetry group) of fullerene C_{60} in water solution and 2) the single-walled carbon nanotube from C_{60} fullerenes. The vibrational spectra of these fullerene nanostructures are calculated using the molecular dynamics approach. The electronic properties of a single-walled fullerene nanotube are investigated using the tight-binding method. The obtained theoretical results were compared with available experimental data.

Fullerenes are widely investigated currently and have potential for various technical applications [1]. In particular, for biomedical testing, water-soluble forms of fullerenes are undoubtedly of great interest. Poor solubility in water of fullerenes and their derivatives limits biological and medical studies, even though there were reports on successfully prepared micro- and macro-colloidal particle solutions in organic solvents or in water [2–7]. In particular, G.V. Andrievsky with collaborators [5–7] has recently proposed a method for obtaining molecular-colloidal dispersions of fullerenes in water without any stabilizers and this resulted in the generation of solutions with fullerene aggregate sizes from several nanometers to 200 nm. These aggregates have been consisted of more small spherical particles with diameter approximately 2–3 nm containing 4–13 molecules of C_{60} [6]. The fullerene water solutions (FWS), being molecular-colloidal systems, were found to be stable for more than 12 months at ambient conditions. At present time, the highest concentration of C_{60} achieved in the FWS is ~ 1.4 g/l [5–7]. It should be noted that the formation of similar fullerene C_{60} structures in different organic solvents was not observed [2–4] showing an important influence of water on their formation and existence [5–7].

The discovery of single-walled carbon nanotubes [8,9] have provided the opportunity to study their mechanical, optical and electronic properties [10,11]. Specifically, their electronic characteristics are predicted to vary depending upon the nanotube symmetry and diameter, thus giving either metallic or semiconducting behaviour [1]. It is very important for the creation of novel materials for nanoengineering.

The geometric structure of possible fullerene aggregates in water was studied in detail in paper [12]. The present paper is devoted to the calculation of the vibrational spectrum of fullerene aggregates in water solution and the structure of a single-walled fullerene nanotube (SWFN), as well as its electronic and optical properties. The obtained theoretical results were compared with available experimental data [13–15].

1. Study of Vibrational Spectrum of Fullerene Aggregates C_{60} in Water

Using the atom-atom potential method, the dense-packing and symmetry principles we have calculated the structure of fullerene aggregates C_{60} in water solution [12]. The main results obtained were as follows: a) the spherical clusters (I_h symmetry group) with the diameter of 3.56 nm containing 33 molecules of C_{60} (see Fig. 1) were shown to be the most stable ones among possible hydrated aggregates; b) possible existence of stable hydrated microcrystals C_{60} (the space group is T_h , the lattice parameters are $a = 1.002$ nm and $c = 1.636$ nm [16]) having a linear size of (2.51–5.84) nm in water solution of fullerenes was stated; c) the water effect on a geometry of the fullerene aggregates was discussed; d) the obtained theoretical results were experimentally confirmed.

The calculated vibrational frequencies of the most stable hydrated fullerene cluster consisted of 33 of C_{60} molecules ($\omega = (14–152)$ cm^{-1}) lie significantly lower the fundamental intramolecular modes for the individual C_{60} fullerene ($\omega = (296–1590)$ cm^{-1}) [17]. The Raman spectrum of this cluster is represented in table 1.

Table 1. The calculated Raman frequencies (cm^{-1}) of hydrated fullerene cluster consisted of 33 of C_{60} molecules

Symmetry	Theory (cluster C_{60})	Theory [17] (molecule C_{60})
H_g	14	296
H_g	28	437
A_g	33	476
H_g	58	721
H_g	63	780
H_g	82	1142
H_g	85	1288
H_g	94	1406
A_g	101	1485
H_g	103	1550

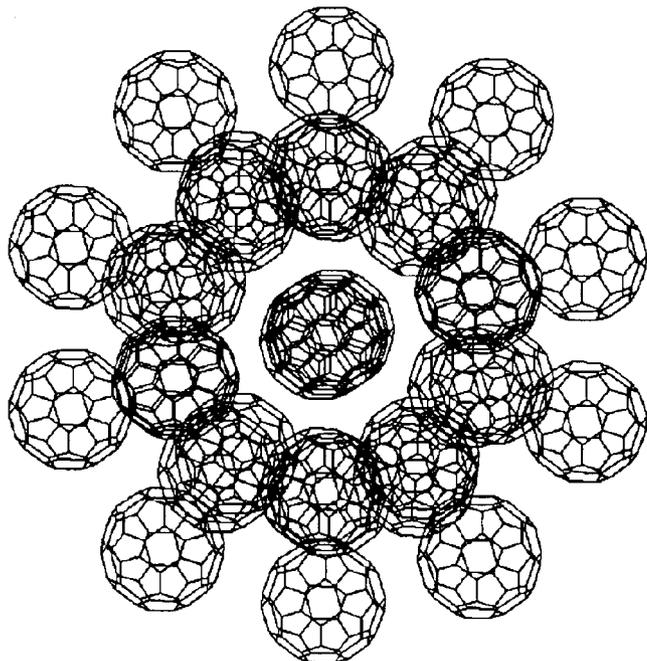


Figure 1. The calculated structure of a fullerene cluster consisted of 33 of C_{60} molecules.

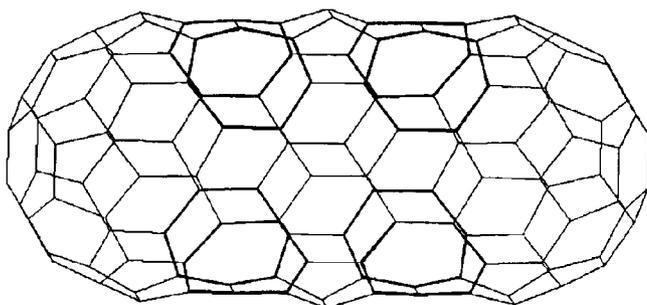


Figure 2. The calculated structure of a single-walled fullerene nanotube.

The limiting intermolecular spectrum of hydrated microcrystal C_{60} is represented in table 2. As we can see the calculated vibrational frequencies lie lower the fundamental modes for solid C_{60} [18].

It should be noted that low vibrational frequencies of fullerene cluster C_{60} ($2H_g$ and A_g modes, see table 1) can coincide with some intermolecular frequencies of microcrystal C_{60} (E_g , E_u and F_u modes, see table 2).

The numerical calculations were carried out in the approximation of a Lennard-Jones (12–6) atom-atom potential only (the entropy factor did not consider because an assumption was made that the formation of orientationally ordered structures in water takes place [12]) using the proposed molecular dynamics model for a fullerene crystal C_{60} [18].

2. Study of Electronic and Vibrational Properties of the SWFN

The simulated structure of the SWFN is presented in Fig. 2. The radius and the length of ideal part of a nanotube are equal to 0.35 nm [19] and 0.43 nm, correspondingly.

As is known [1,11], the dependence of the gap on the radius R of a single-walled carbon nanotube may be approximately described by the formula

$$\varepsilon_g = \varepsilon_{\pi\pi} \frac{d_0}{R}.$$

In our case, $\varepsilon_{\pi\pi}$ is the average energy of interaction between two π -electrons located on the single and double bonds in the C_{60} molecule; d_0 is the average distance between the neighbouring carbon atoms in the C_{60} molecule. The numerical calculations carried out by using the tight-binding method [20] has shown that $\varepsilon_{\pi\pi} = 2.35$ eV and $d_0 = 0.14$ nm. The presence of a heptagon-heptagon pair as a defect in the structure of the SWFN leads to the change of its radius from 0.35 to 0.38 nm (the average distance between the neighbouring carbon atoms in the heptagon is equal to d_0 too). As a result, the decrease of the gap from 0.94 to 0.87 eV takes place. Thus, the semiconductor-semiconductor heterojunction with different values of the gap is formed. It should be noted that the similar hetero-

Table 2. The calculated limiting ($k = 0$) intermolecular frequencies (cm^{-1}) of hydrated microcrystal C_{60}

Symmetry	Theory (microcrystal C_{60})	Theory [18] (solid C_{60})
A_u	21	35
E_u	27	48
F_u	23	43
F_u	30	53
A_g	13	19
E_g	14	20
F_g	9	17
F_g	11	18
F_g	18	23

Table 3. The calculated and experimental Raman-active vibrational frequencies (cm^{-1}) for the single-walled nanotube

Symmetry	Theory	Experiment [15]
H_g	119	116
H_g	190	186
A_g	396	377
H_g	770	755
H_g	885	855
H_g	1356	1347
H_g	1525	1526
H_g	1549	1550
A_g	1583	1567
H_g	1606	1593

junction was really observed in the experiment [13,14] for the single-walled carbon nanotube with a pentagon-heptagon defect.

The calculated vibrational frequencies of the SWFN (in the framework of the proposed molecular dynamics model [17]) lie in the range of $\omega = (49-1744) \text{ cm}^{-1}$. The Raman spectrum of this nanotube is represented in table 3. As we can see, they are in a satisfactory agreement with the available experimental results [15] for the single-walled carbon nanotube of "armchair" configuration.

3. Conclusion

The main results obtained are as follows.

1) The vibrational spectra of possible fullerene aggregates C_{60} in water (clusters (I_h symmetry group) and microcrystals (T_h symmetry group)) are calculated using the molecular dynamics approach [18]. The obtained theoretical results can be useful for the further optical experiments;

2) As a model for the calculation of electronic and optical of a single-walled carbon nanotube, the nanotube formed of the C_{60} molecules was proposed. The presence of a heptagon-heptagon pair as a defect in the structure of this nanotube leads to the formation of the semiconductor-semiconductor heterojunction with the different value of gap. The electronic characteristics and vibrational spectrum of a single-walled fullerene nanotube are investigated using the molecular dynamics model [17] and the tight-binding method [20]. The obtained theoretical results are in a good agreement with the available experimental data [13-15].

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