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Theoretical predictions and experimental studies of self-organized C_{60} nanoparticles in water solution and on the support

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Abstract. The formation in water of highly stable hydrated clusters (I_h symmetry group) and microcrystals (T_h symmetry group) from C_{60} fullerenes is theoretically predicted using a molecular dynamics calculation. The proposed models are confirmed by the experiments on the Raman and absorption spectra of the fullerene aqueous solution. The additional study of the structure of C_{60} fullerene aggregates in the dry layer on the support (dielectric/semiconductor) is also performed.

PACS. 02.70.Ns Molecular dynamics and particle methods – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 78.20.-e Optical properties of bulk materials and thin films

1 Introduction

The experimental studies of different physical and chemical properties of fullerenes that have been performed indicate unique perspectives as regards their future practical use [1]. Recently a method [2,3] has been offered for production of highly stable and finely dispersed colloidal solutions of C_{60} fullerenes in water (in the absence of any additives) and this has resulted in the generation of solutions with fullerene aggregate sizes from several to 200 nanometers. These aggregates consist of more small spherical particles with diameters of approximately 2–3 nm that contain 4–13 molecules of C_{60}. The evaluation of the characteristics of this solution from the point of view of colloidal chemistry [4] indicates high stability with no essential changes during 12–18 months in storage at normal conditions. It should be noted that the formation of similar structures in the C_{60} solutions in different organic solvents was not observed [5–8]; this shows the important influence of water on their formation and existence [9,10]. Additional theoretical and experimental studies of the possible structure of C_{60} fullerene aggregates in water and in the dry layer on the support (dielectric/semiconductor) are needed.

2 Theoretical study of the structure of C_{60} fullerene aggregates in water solution

Spherical clusters were formed from C_{60} fullerenes (I_h symmetry group) by the translation of the molecules on the same length along the symmetry axes C_5 (the first coordination sphere consists of 12 molecules), C_3 (the second coordination sphere consists of 20 molecules), and C_2 (the third coordination sphere consists of 30 molecules) of the single C_{60} molecule situated in the center. We assume that the intermolecular interactions are described by a Lennard–Jones (12–6) potential with the values of parameters taken from our previous paper on the simulation of solid C_{60} structure ($\varepsilon = 2.935\,\text{meV}$ and $\sigma = 0.347\,\text{nm}$) [11]. Energy minimization was carried out in the approximation of rigid molecules using the atom–atom potential method and the dense packing principle [12] (the entropy factor was not considered because an assumption was made that the formation of orientationally ordered structures in water takes place).

The energy (normalized to one molecule) of possible clusters is plotted against the number of C_{60} molecules entering into them in Fig. 1. It is obvious that the fullerene cluster of diameter 3.56 nm consisting of $N = 33$ C_{60} molecules has the most stable structure (the geometrical

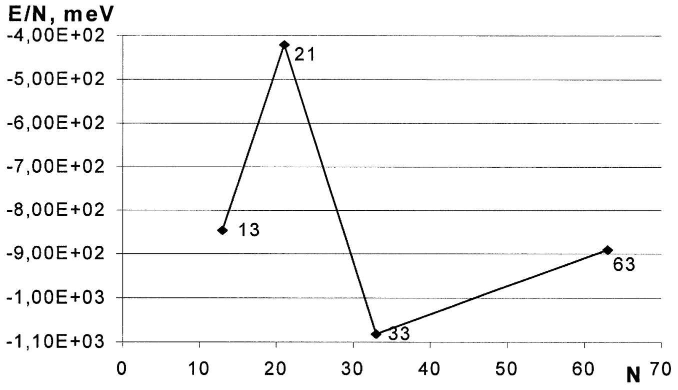

Fig. 1. The calculated energies (normalized to one molecule) of possible clusters plotted against the number of C_{60} molecules entering into them.

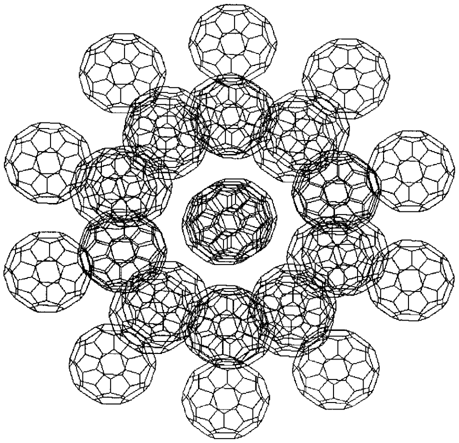

Fig. 2. The calculated structure of a fullerene cluster consisting of $N = 33$ C_{60} molecules.

structure of this fullerene aggregate is given in Fig. 2). The structure with a number of C_{60} molecules $N = 21$, being unstable, is transient between the structures with $N = 13$ and $N = 33$. Note that the obtained diameter 2.52 nm of clusters formed of $N = 13$ C_{60} molecules is in excellent agreement with the experimental results [2, 3].

The above-mentioned calculations disregard the water effect on the geometry of fullerene clusters. This effect may be explained as follows. First, the authors [2, 3] state that the formation of clathrate-like networks of water molecules [9, 10] around fullerene C_{60} aggregates, stabilized due to the low conformational mobility of fullerenes and geometrical matching between the structures, which may be formed by hydrogen bonding of water molecules in the clathrate and covalent bonds of the fullerene carbon atoms, takes place. On the other hand, it is known [9] that without the stresses of valency angles, the diameter of the shell formed of the water molecules around the dissolved aggregate can be increased to 2 nm, and within the admissible stresses of hydrogen bonds, it can be increased even to 6 nm. The obtained results for the fullerene clusters with a number of C_{60} molecules $N = 13$, 33, and 63 do not contradict this.

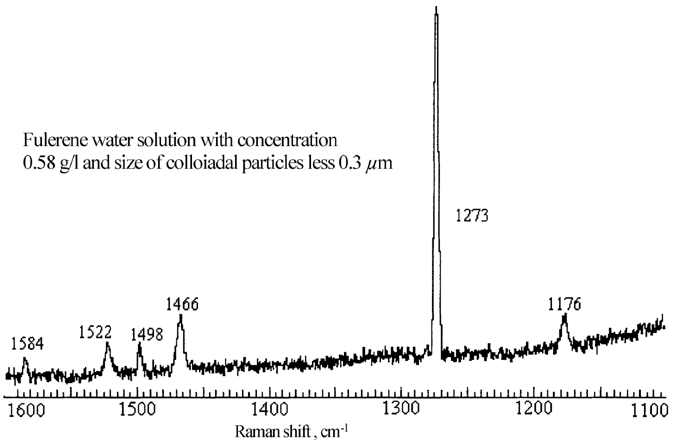

Fig. 3. Raman spectrum of the fullerene water solution.

Finally, the problem of the formation of stable hydrated microcrystals [9] in water solution of C_{60} fullerenes should be considered. The performed numerical evaluations indicate a possible existence in water of hydrated C_{60} microcrystals with a minimum linear size of 2.86 nm (an hcp lattice with the parameters $a = 1.002$ nm and $c = 1.636$ nm [13]). Let us remember that C_{60} molecules freely rotate in a solid at room temperature [14]. In our opinion, the effect of water on the formation of hydrated microcrystals is connected with the fixation of C_{60} molecules oriented in the unit cell of the lattice; i.e., a transition from disordered structure (O_h symmetry group [14]) to orientationally ordered (T_h symmetry group [15]) crystalline phase takes place.

3 Experimental study of the structure of C_{60} fullerene aggregates in water solution

The high-frequency Raman spectrum of the fullerene water solution is given in Fig. 3. In this spectrum, we can see an increase of the frequencies of the vibrational fundamental bands for all the observed modes, as compared with the results for individual C_{60} molecules [16] by the magnitude of 2%–6%. We associate this increase with the strengthening of the intramolecular bonds that occurs when hydrated fullerene aggregates in water solution are formed, as described above. In other words, water affects external hydrostatic compression of the C_{60} molecules in the aggregate, and this leads to a negligible decrease of its geometrical size and an increase of bond energy.

The optical absorption spectra of fullerene water solutions in comparison with C_{60} solutions in CCl_4 are given in Fig. 4. The absorption spectra of fullerene solution in CCl_4 (the curves 1a and 3a) testify to the mainly molecular character of the absorption of C_{60} solutions in CCl_4. On the other hand, the absorption spectra of fullerene aqueous solutions (curves 1b, 2, and 3b) are near the absorption spectra of solid C_{60} [13].

A study of the structure of C_{60} fullerene aggregates in the dry layer on the support (dielectric/semiconductor)

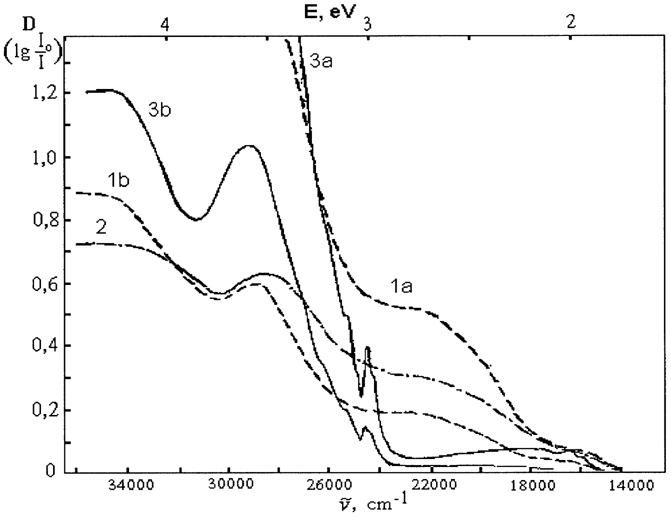

Fig. 4. Optical absorption spectra: the curves 1b and 3b are the C_{60} fullerene water solutions; the size of colloidal particles does not exceed $0.1\,\mu$m; and the concentrations are 0.06×10^{-4} mol/l and 0.22×10^{-4} mol/l, correspondingly. The curve 2 is the C_{60} fullerene water solution; the size of colloidal particles does not exceed $0.3\,\mu$m; and the concentration is 0.08×10^{-4} mol/l. The curves 1a and 3a are the C_{60} fullerene solutions in CCl_4.

was also performed. As mentioned above, water, a stabilizer, keeps the fullerenes in the clathrate-like structures. After the aqueous solution dries, the fullerene clusters are disintegrated, and the single C_{60} molecules, along with the C_{60} microcrystals described above, are presented on the support. As a result, the vibrational fundamental modes for C_{60} fullerenes [16] and the absorption spectra of solid C_{60} [13] are observed in the experiments.

4 Conclusion

The main results obtained are as follows. Using the atom–atom potential method and the dense packing and symmetry principles, we calculated the structure of C_{60} fullerene aggregates in water solution:

(a) the spherical clusters (I_h symmetry group) with a diameter of 3.56 nm containing $N = 33$ C_{60} molecules were shown to be the most stable ones among possible hydrated aggregates; and
(b) there is a possible existence of stable hydrated C_{60} microcrystals (T_h symmetry group) having a minimum linear size of 2.86 nm in a water solution of fullerenes.

The obtained theoretical results were found to be in a good agreement with the experimental ones.

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