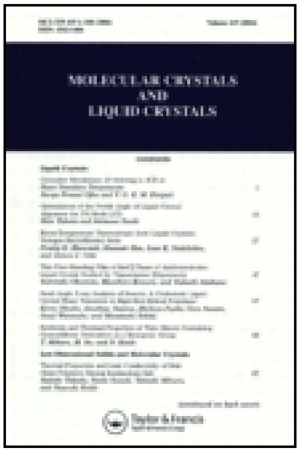

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Study of Structure of Colloidal Particles of Fullerenes in Water Solution

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The formation in water of highly stable cluster/crystallite structures from fullerene C_{60} is theoretically predicted and experimentally confirmed.

Keywords: fullerene water solution; molecular dynamics; Raman and absorption spectra

INTRODUCTION

Recently a method[1-2] has been offered for production of highly stable and finely dispersed colloidal solutions of fullerenes C_{60} in water (in the absence of any additives) and this resulted in the generation of solutions with fullerene aggregate sizes from several nanometers to 200. These aggregates consisted of more small spherical particles with diameter approximately (2-3) nm containing (4-13) molecules of C_{60}. The evaluation of the characteristics of this solution from the point of view of colloidal chemistry indicated high stability with no essential changes during (12-18) months on storage at normal conditions. It should be noted that the formation of similar structures in the solutions C_{60} in different organic solvents was not observed[3-6] showing the important influence of water on their formation and existence[7-8]. This needs additional theoretical and experimental studies of possible structure of fullerene aggregates in water.

Calculation of Structure of Fullerene Aggregates C_{60} in Water Solution

The spherical clusters were formed of fullerenes C_{60} (I_h symmetry group) by translation 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 molecule C_{60} situated in the centre. 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 simulation of solid C_{60} structure[9]. Minimizing the energy was carried out in the approximation of rigid molecules using the atom-atom potential method and the dense-packing principle[10] (the entropy factor did not consider 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 against a number of molecules C_{60} entering them is given in Fig. 1. It is obvious that the fullerene cluster of diameter 3.56 nm consisting of N=33 of C_{60} molecules has the most stable structure (the geometrical structure of this fullerene

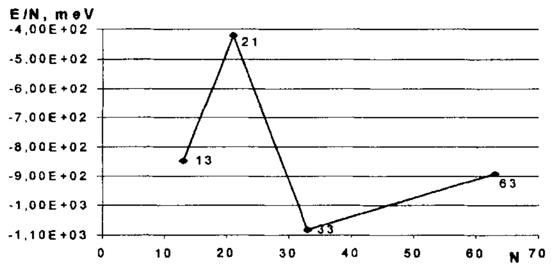

FIGURE 1 The calculated energies (normalized to one molecule) of possible clusters in dependence on the number of molecules C_{60} entering them.

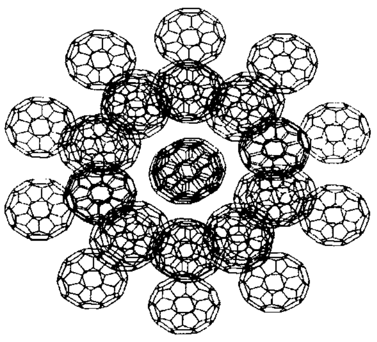

FIGURE 2 The calculated structure of fullerene cluster consisted of N=33 of C_{60} molecules.

aggregate is given in Fig. 2). The structure with a number of molecules C_{60} N=21 being unstable is transient between the structures with N=13 and N=33. It is to be noted that the obtained diameter 2.52 nm of cluster formed of N=13 of C_{60} molecules is in excellent agreement with the experimental results[1-2].

The above mentioned calculations were made disregarding the water effect on a geometry of the fullerene clusters. It is may be explained as follows. First, the authors[1-2] state that the formation of clathrate-like networks of water molecules[7-8] 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[7] that without stresses of valency angles (let us remind that in the molecule H_2O it is equal to 104.5^0) 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 are not contrary to this fact.

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 in comparison with the results for individual C_{60} molecules[11] by the magnitude of (2-6) per cents. This increase we associate with strengthening the intramolecular bonds on forming hydrated fulerene aggregates in water solution described above. In other words the effect of water comes to external hydrostatic compression of the molecules C_{60} in the aggregate leading to the negligible decrease of its geometrical sizes and increase of bond energy.

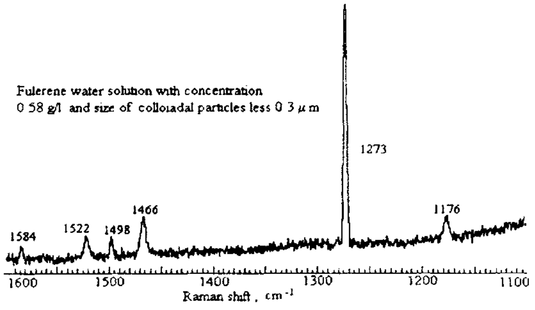

FIGURE 3 Raman spectrum of the fulerene water solution.

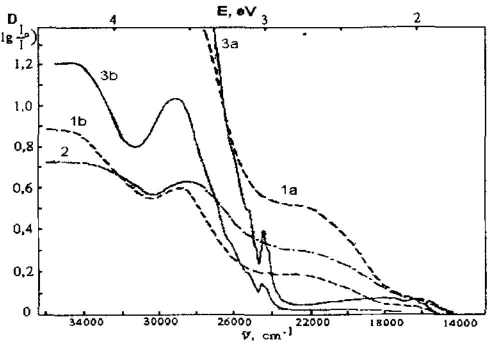

FIGURE 4 Optical absorption spectra:
the curves 1b and 3b are the fullerene C_{60} water solutions, the size of colloidal particles does not exceed 0.1 μm, the concentrations are 0.06×10^{-4} mol/l and 0.22×10^{-4} mol/l correspondingly; the curve 2 is the fullerene C_{60} water solution, the size of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

At last the problem of formation of stable hydrated microcrystals[7] in water solution of fullerenes C_{60} should not be out of our attention. 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 absorption of C_{60} solutions in CCl_4. On the contrary, the absorption spectra of fullerene aqueous solutions (the curves 1b, 2 and 3b) are near the absorption spectra of solid C_{60} (a hcp lattice with the parameters a=1.002 nm and c=1.636 nm)[12].

The performed numerical calculations indicate a possible existence in water of hydrated crystallites C_{60} with a minimum linear size of 2.86 nm. Let us remind that C_{60} molecules freely rotate in the solid at room temperature[12]. In our opinion, the effect of water on forming hydrated crystallites is connected with the fixation of C_{60} molecules orientation in the unit cell of the lattice, i.e. the transition from disordered structure to orientationally ordered crystalline phase takes place.

Conclusion

The main results obtained are as follows: 1) using the atom-atom potential method, the dense-packing and symmetry principles we calculated the structure of fullerene aggregates C_{60} in water solution. The spherical clusters with the diameter of 3.56 nm containing 33 molecules C_{60} were shown to be the most stable ones among possible hydrated aggregates; 2) a possible existence of stable hydrated crystallites C_{60} having a minimum linear size of 2.86 nm in water solution of fullerenes was stated; 3) the obtained theoretical results were found to be in a good agreement with the experimental ones.

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