Selforganization of the fullerene complexes on solution

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It is shown that the van-der-Waals energy of the cluster-cluster interaction in the fullerene systems is described well via the change of the plasmon energy. The energetical reason gives a guess that the solution of the single C_{60} cluster is not favorable. Contrary, the dimer solution energy is negative, which results in the supposition that the dissolving occurs via the dimerization. The possible experiment to proof the result is discussed.

After last six year efforts which are manifested by hundreds of papers on the physics, chemistry of the fullerenes and the fullerene based materials it is known a lot about the electronic structure of the single macromolecule which is the base of the different materials like the doped solids and the chemical adducts. A variety of the computational methods was used, from the *ab initio* calculation to the empirical approach to compute the energy of the inter-cluster interaction in the fullerene solid. One interesting in a review of the calculation and experiment can look at the references in [1,2].

This paper introduces the simple theoretical approach allowing to evaluate the energy of the van-der-Waals interaction in the fullerene condensed phase. The main part of this interaction is determined by the plasma modes of the solid. The same approach was used for the evaluation of the interaction of the single cluster with the different solids in [3]. The interaction of the cluster and the organic (non-polar) liquid solvent will be likewise considered below.

The optical and electrical properties of the fullerene materials allows to talk about C_{60} as the new artificial atomic unit for the nano-engineering. However the level of the fullerene technology is not high enough to be competitive with the standard electronic materials. The single cluster gives the classical example of the semiconducting quantum size dot. Relating to that it occurs interesting to know more about the stability of different fullerene complexes, namely, the dimer and other possible oligomers. As it has been declared in the abstract this theoretical paper predicts the formation of the fullerene dimer during the dissolving of the solid fullerene. The consideration, probably, correlates with the recent experiment [4], where the dimerized structures were observed in the water mixture. Even the polar liquid solvent stills beyond this theory.

I. THE ENERGY OF THE VAN-DER-WAALS INTERACTION

As usual the van-der-Waals energy is given by the shift of the plasmon zero-oscillation energy in the solid comparing with the single cluster. This shift is due to the Coulomb interaction between clusters which can be reduced to the elementary cell in the translational invariant system. The origin of the van-der-Waals forces is the same as the depolarization shift of the plasma mode frequency in the dielectric medium.

In the case of the cubic crystal and for the rotationally invariant system (liquid, for example) one can easily calculate this depolarization shift following the method of the mean field. Then the Lorentz-Lorenz approximation gives the shift including the local field effects. This is valid for the solid fullerene, which forms fortunately face-centered cubic lattice.

We calculate the mode frequencies for the face centered cubic cell with four clusters in the approximation of the dipole-dipole interaction. It was shown that the higher miltipolar interaction terms can be neglected [5]. However, it is not important because of our model allows to include any multipole correction if anybody needs more accuracy.

The dipole excitation of the single cluster is elementary unit in all our consideration. It was shown that C_{60} electron density has the collective mode with the frequency about 25 eV. This is the surface plasmon on the fullerene sphere. It can be described phenomenologically [6] as well as within more sophisticated approach (see [7] and references [10-14] in Ref.[7]). So far the dipole plasmon we will use as the elementary excitation of the fullerene "super-atom" unit.

In other terms, the van-der-Waals interaction can be written using the fluctuation-dissipation theorem as the integral over the frequency of the combination of the C_{60} cluster dynamic polarizability and the dielectric function of the medium. Of coarse, in the case of the pure crystal C_{60} it is the same function. Then this integral can be evaluated in the complex plane of the frequency. The main contribution comes from the excitation having the maximal oscillator strength. It is the collective plasma mode of the cluster.

Let us remind that the frequency of the dipole plasmon can be found as the hollow metal sphere plasmon frequency:

$$\omega_1 = \omega_p \sqrt{\frac{2}{3}} \sim 22 \text{ eV} \quad \omega_p = \sqrt{\frac{240\, e^2}{mR^3}} \sim 26.9 \text{ eV}, \tag{1}$$

here ω_p is the bare plasma frequency, 240 is the number of valence electrons of the cluster, with the electron mass m and the charge e. The sphere radius R is taken ~ 3.3 Å to describe the fullerene plasmon properly. The details of the calculation can be found in [7].

Considering the fullerene solid we use the Lorentz-Lorenz approximation due to the high polarizability of the single cluster, α. A packing factor coming into the dielectric function along with the dynamic polarizability reads as:

$$\alpha(\omega) = R^3 \frac{1}{1 - \omega^2/\omega_1^2}, \quad \eta = 4\pi\nu\alpha(0) = 4\pi\frac{4}{d^3}R^3 \tag{2}$$

where $\nu = 4/d^3$ is the density of the clusters, $d \sim 14.2$ Å is the lattice constant. This is very common parameter in such a calculation, we take it as 0.79.

It will be very convenient to use the square of dimensionless plasma frequency $x = \omega^2/\omega_1^2$. This Lorentz-Lorenz formula gives us the plasma longitudinal frequency $\omega_L = \omega_1\sqrt{x_L} \sim 26.2$ eV along with the transverse excitation frequency $\omega_T = \omega_1\sqrt{x_T} \sim 19.6$ eV as the zero and the pole of the ϵ, the dielectric function. Then the van-der-Waals energy is the simple difference between the plasma frequency of the cluster and the modes in the solid. It reads as:

$$W = \hbar\omega_1\left(\sqrt{x_L} + 2\sqrt{x_T} - 3\right) \sim -\hbar\omega_1\frac{\eta^2}{24} \tag{3}$$

The only two parameters determining the van-der-Waals energy are the plasmon energy and the packing factor. In the expression above we used the expansion on the small η. The interplay between these parameters gives us, for example, the plasma frequency on the boundary between some mediums, in the liquid, in the medium with polarizable dopant and so on. We will discuss it at length elsewhere. Substituting the numbers into Eq.(3) one gets the van-der-Waals energy about -0.36 eV per cluster in the solid. The one of the first papers containing similar consideration to be mentioned is [8]. In the next section we will compare the result with the energy in solution.

II. FULLERENE IN SOLUTION

The plasma frequency in the solution is different from the solid phase because of the depolarization shift is much weaker in any typical organic solvent than in the solid. The reason is that the fullerene cluster has the very high frequency of this bare plasmon due to the large number of the highly polarizable electrons. The standard medium is nearly transparent at this frequency. More precisely the dielectric function of the medium is slightly less than the unity at the frequency of C_{60} plasmon. Such a behavior of the dielectric function is not common. Probably, it was the reason that in earlier papers the depolarization shift of the plasmon of the C_{60} cluster in the dielectric liquid has been calculated improperly.

In [9] the dielectric function has not been considered, in contrary, the static permittivity has been used for the liquid surrounding the cluster. Then the boundary conditions change so that the plasma frequency depends on the permittivity of the solvent. Then the difference in the plasma frequency reads as follows:

$$\delta\sqrt{x} \simeq \frac{1}{3}(1 - \epsilon), \tag{4}$$

here we expand the expression Eq.(4) on the small positive parameter $1 \gg 1 - \epsilon > 0$. This is the logical way to solve the Barton model, we note that $\epsilon = \epsilon(x)$ is the function of the frequency by itself that was omitted in [9]. Then it is seen from Eq.(4) that the plasmon frequency shifts upward, that does not consist with the solubility of the fullerene.

According [7], the surface plasmon in C_{60} is the spherical oscillation of electron density σ_{LM}. For central symmetry of the cluster we use expansion of all quantities in complete spherical harmonics $P_L(r)Y_{L,M}(\Omega)$ those form a complete set on a sphere. In spherical geometry a radial jump in electric field is given by:

$$\frac{2L+1}{R}\varphi_{LM} = 4\pi\sigma_{LM} \tag{5}$$

where $\varphi^{act} = \varphi^{ext} + \varphi^{ind} = \varphi_{LM}^{ext} + 4\pi R\sigma_{LM}/(2L+1) + \varphi_{LM}^{sol}$ is acting potential, L, M are multipole power indexes (or angular momentum and its projection onto z-axis). The selfconsistency of the calculation is proved by this acting potential including the induced potential of the C_{60} plasmon as well as the potential due to charge density induced in the solvent. We close the equation system by writing the response function for the fullerene as:

$$\frac{4\pi R}{2L+1}\sigma_{LM} = -\frac{4\pi R}{2L+1}\chi_L\varphi_{LM}^{act} = \simeq -\frac{\omega_L^2}{\omega^2}, \tag{6}$$

where χ is a response function of single sphere. This expression is easily obtained from classic charge liquid equations [6,7]. This consideration is more general than our $L = 1$ case of the dipole plasmon mode. However for the spherical symmetry the expression Eq.(6) holds for all multipoles.

When the induced in the solvent potential $\varphi^{sol}_{LM} = 0$ is absent, we return to the bare plasmon frequency. The corresponding bare dispersion equation reads as:

$$-\frac{4\pi R}{3}\chi_1 = \frac{\omega_1^2}{\omega^2}\frac{1}{x} = 1, \tag{7}$$

while we simply change the unity to the dielectric function including the solvent potential. It is easily seen substituting the Eq.(6) into Eq.(5) and taking the standard RPA sum. As a result the plasma frequency in the solution is:

$$\Omega(\varepsilon) = \omega_1\sqrt{\varepsilon(\Omega)} \tag{8}$$

The frequency is smaller than for the bare C_{60} that is better than the result Eq.(4).

So far we obtain the plasmon in the fullerene solid and in the solution. We will use for the dielectric function of the liquid solvent the common formula:

$$\epsilon(\Omega) = \frac{\Omega^2 - \omega_L^2}{\Omega^2 - \omega_T^2} \tag{9}$$

where ω_L is the typical longitudinal frequency of the $\epsilon(\Omega)$, and ω_T is the transverse frequency. With this definition the van-der-Waals energy can be written as:

$$W \sim -3/2\hbar\omega_1\frac{\omega_L^2 - \omega_T^2}{\omega_T^2}\frac{\omega_T^2}{\omega_1^2} = -3/2\hbar\omega_1\left(\epsilon_0 - 1\right)\left(\frac{\omega_T}{\omega_1}\right)^2 \tag{10}$$

here ϵ_0 is the static permittivity which is related to the transverse and longitudinal frequencies. The typical values for ϵ_0 is 2.3 for the benzene, 2.4 for the toluene. The van-der-Waals energy is about -0.2 eV for these solvents. So we have to conclude that by this energetical reason the solid fullerene should be more stable.

Let us consider the fullerene dimer, the similar problem was done in the [5] for the C_{119} molecule. The plasmon frequency is splitted in the axial field. Therefore the new modes bring the energy of the interaction between clusters in the dimer as the difference between the frequency of the bare plasmon and new one. Then the van-der-Waals energy of the dimer coupling reads as:

$$W \sim -3/2\hbar\omega_1\left(\frac{R}{H}\right)^3\left(1 + \frac{3}{2}\frac{\omega_L^2 - \omega_T^2}{\omega_T^2}\frac{\omega_T^2}{\omega_1^2} + \ldots\right) \tag{11}$$

where $R \simeq 3.6$ Å and $H \simeq 8$ Å are the cluster radius and the inter-cluster distance; here the last term comes from the solvent depolarization, it is a small correction (about a percent) which will be neglected. The typical value of the van-der-Waals energy of such a dimer is about -0.7 eV.

We suppose that solvent softens the van-der-Waals forces between C_{60} clusters near the surface. Then the fullerenes form dimers near the surface. Certainly, the process has to be recalculated more accurately, including the conditions on the boundary between the fullerene solid and the solvent. We believe that these selforganized structures, probably, can be found in the solution. The Raman and IR-active phonon modes of the single cluster are splitted in the dimer like the plasmon frequency shown above. Besides that the UV irradiation of the solution can shift the equilibrium in the selforganization process because of the excitation of the single cluster plasmons. **Acknowledgments.** Author thanks M.V. Korobov for the . . .

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