

## Electronic Absorption Spectra of the Fullerene C<sub>60</sub>: From a Molecule to Crystals

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### Fullerene C<sub>60</sub>의 전자흡수 스펙트럼 : 분자에서 결정까지

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초록 분자들이 용액 내에서의 cluster나 박막 내에서의 cluster와 같이 다른 cluster로 뭉쳐졌을 때, 가시광선과 자외선부근의 영역에서 fullerene C<sub>60</sub>의 전자흡수 스펙트럼 변화가 관찰되었다. 2.73eV에서 흡수 피크들이 관찰되었는데, 이러한 피크들은 독립된 분자들로 부터 온 것이 아니라 분자들의 직접적인 상호작용으로 부터 온 것으로 생각된다. Grained fullerene 박막에서는 흡수 피크들이 3.35eV에서도 관찰되었는데 이러한 피크들은 grain의 계면에서 분자들의 상호작용으로 부터 온 것으로 생각된다. 이러한 흡수의 Dichroism은 비등방성 macrostructure를 갖는 시료에서도 관찰되었다.

**Abstract** The change of electronic absorption spectra of the fullerene C<sub>60</sub> in the visible-near UV range was examined when the molecules aggregated into different clusters such as clusters in solution and clusters in thin films. Absorption peaks were observed at 2.73 eV. These peaks did probably not come from the feature of the isolated molecules but from the direct interaction of the molecules. Absorption peaks were also observed at 3.35 eV from grained fullerene films. We think these peaks came from the interaction of the molecules at interfaces of grains. Dichroism of this absorption was also found from samples with anisotropic macrostructures.

### 1. Introduction

Growing interest is being attracted to the condensed systems of fullerenes due to their photoconducting and superconducting properties.<sup>1,2)</sup> Full understanding of these properties requires knowing how electronic levels of the molecule transform when the molecule forms a crystal.

Electronic absorption spectra provide information about the energy levels and the electronic density of states. It is known that the absorption by C<sub>60</sub> starts at the visible energy region near 1.6 eV and followed by a series of strong bands in the UV energy region above 3 eV. The strong bands are usually observed at the absorption spectra of both the isolated fullerene molecules and condensed fullerene systems which are single crystals or polycrystalline thin films.<sup>3)</sup> Main differences between the two cases appear at the energy region which is lower than 3.5 eV. Unlike isolated molecules,

condensed species show strong absorption at the visible energy region. Such a discrepancy has a great importance to understand how electronic excitations of C<sub>60</sub> transform. However, no unique explanation about the phenomenon has been provided yet. Some authors refer the changes in spectra to the breakdown of the initial Ih symmetry of the molecule.<sup>3,4)</sup> Others have attributed those to solid state effects.<sup>5)</sup> This means that the formation of the bands in the electronic structure of the C<sub>60</sub> crystal should be attended with additional substructures with allowed transitions.<sup>6,7)</sup>

To clarify this problem in more details we have compared electronic absorption spectra of the material in molecular form to those in various condensed states. The molecular form was prepared as monomers in diluted solution, while the condensed form was prepared as small aggregates in binary solution or as sublimed and cast films of different thickness.

## 2. Experimental

In this work, we used the fullerene which was synthesized by Ioffe Physico-Technical Institute (St. Petersburg). Benzene and butyl alcohol were used as solvents. The fullerene powder was dissolved in benzene to prepare its solution.

To obtain aggregated species, binary solution and solid films were prepared. The binary solutions were prepared by gradually adding butyl alcohol to the solution of  $C_{60}$ . After mixing, the mixture was kept in the air for spontaneous evaporation of the solvents. The volume of the solution was kept constant ( $10^{-6}$  M) by adding necessary amount of butyl alcohol. Thus the benzene component in the mixture was reduced. However, during this process a little amount of the fullerene diffused upwards over the wall of the cuvette and the final concentration of the fullerene slightly decreased ( $\sim 10^{-5}$  M). Thin films with different thickness were prepared by sublimation of the material onto glass plates. Details of the preparing method were given elsewhere.<sup>8)</sup>

The dual-beam spectrometer SPECORD M-40 was used for optical measurements in the visible-near UV range. Here the absorption of transmitted light was recorded. Diffusion reflection spectra were also obtained from films, which have relatively large grains.

## 3. Results

The absorption spectra from diluted solutions and cast films of the fullerene are shown in Fig. 1. It shows that the absorption of isolated fullerene molecules is significantly different from that of aggregated ones. In this figure we have obtained the absorbance of equimolar amount of the material in the solution and in the cast film using extinction coefficient at 3.7 eV.<sup>16)</sup>

The spectra can be separated into the three energy ranges: (1) near UV range at 4.0–3.2 eV, where strong absorbance is observed from both isolated and aggregated molecules; (2) 3.2–2.3 eV region, where significant absorbance from only aggregated species is observed; (3) 2.3–1.6 eV region, where the absorption from both isolated and aggregated species is weak.

The binary mixture of benzene/butyl alcohol provides weak aggregation of  $C_{60}$  molecules. Since the fullerene is subjected to complete dissolution only with the benzene component, the greater the content of butyl alcohol, the greater the fraction of aggregates should be expected in the solution. This process gives rise to a marked absorption band centered at 2.73 eV (Fig. 2).

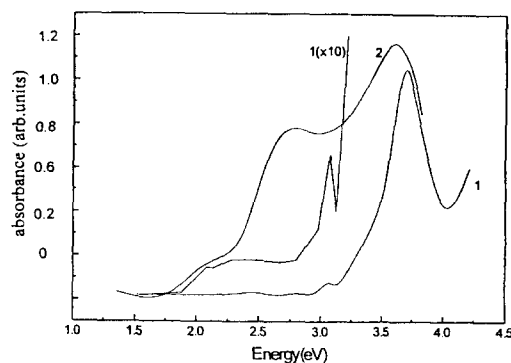


Fig. 1. Optical absorption spectra of equimolar amounts of  $C_{60}$  calculated from the data (1) in solution and (2) in cast film.

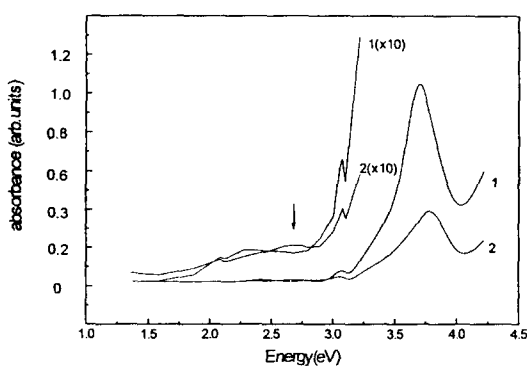


Fig. 2. Optical absorption spectra of  $C_{60}$  solutions (1) in benzene and (2) in a binary mixture of (10%) benzene/(90%) butyl alcohol with a high fraction of butyl alcohol. Concentration of  $C_{60}$  in the latter case is  $10^{-7}$  M. Arrow indicates the appearance of a new peak.

The further development of this band was observed from films. In Fig. 3, the 2.73 eV absorption band from the thick sublimed film is greater compared to that from the thin submonolayer film. The cast film demonstrates the further increase of this band.

As shown in Fig. 1, the absorption spectrum of isolated species is different from that of aggregated species. A single peak with a maximum at 3.72 eV was observed from the isolated molecules in solutions. For the case of aggregated species this peak was shifted to 3.60 eV. Furthermore it depends on the way of preparation method and thickness of films. The spectra from thick films show broadening of the low energy side of the band. From the second derivative of the spectrum with respect to the energy, this broadening can be identified as a new peak at 3.35 eV. The dichroism of absorption spectra was found in the cast films with anisotropic structure (Fig. 4). This dichroism should be assigned just to the 3.35 eV band. The preferable direction of the dipole transition moment corresponding to this band was observed to be perpendicular to the direction of strips in the film.

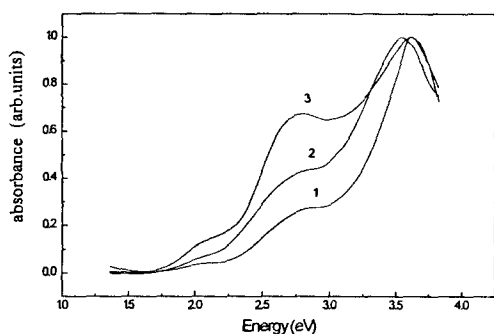


Fig. 3. Optical absorption spectra of (1) submonolayer sublimed, (2) thick sublimed 50nm and (3) cast film of  $C_{60}$  500nm. The spectra were normalized to the same absorption maximum.

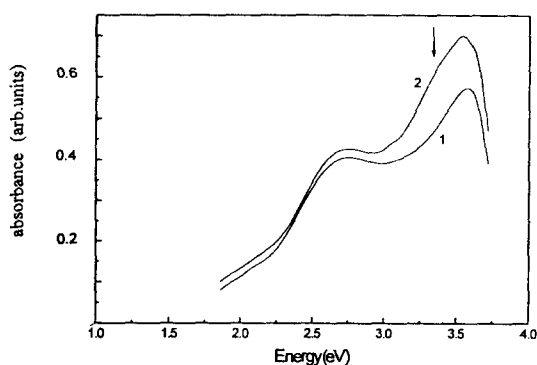


Fig. 4. Dichroism of optical absorption spectra of cast fullerene films. (1) Electric vector is parallel and (2) perpendicular to the direction of strips in the film. Arrow indicates the 3.35 eV band marked by the 3.7 eV peak.

The features of the submonolayer, thick sublimed and cast films were qualitatively reproducible from different series of samples.

#### 4. Discussion

It has been reported that the comparison of the absorption spectra of isolated and aggregated molecules of  $C_{60}$  shows two groups of absorption bands. The first group includes bands attributed to the both isolated and aggregated species. These bands are at 3.7 eV and 2.0 eV and should be assigned to intramolecular transitions which were discussed in details elsewhere.<sup>7,9-13</sup> The second group shows bands at 3.35 and 2.73 eV, which are observable only from aggregated species.

The 2.73 eV band comes from the aggregates in the solution (Fig. 2). The features of monomers are present together at the spectrum. The small peak suggests that aggregation is weak. Here only a few molecules may be involved to form an aggregate. Evidently, true crystals are not formed yet in this process. Therefore the small peak is not associated with characteristics of the band structure in solid  $C_{60}$ .

The nature of this band seems to be still open question. Several authors attribute the band to the intramolecular transition where electrons are strongly screened by the isolated molecules due to collective excitations of  $\pi$ -electrons. Indeed, theoretical calculation predicts the lowest energy transition allowed by molecular symmetry,  $h_u-t_{1g}$ , at about 3.0 eV.<sup>6,7</sup> This transition can be identified with the small peak at 3.04 eV of the spectra of the diluted solution (Fig. 1). The higher peak from solid films might be due to the decrease of the screening effect (Fig. 1).

Moreover, we could not find any intermediate form between the 3.04 eV band of the molecule and the 2.73 eV band of the aggregate (Fig. 2). We therefore conclude that this band is due to intermolecular excitations. This is consistent with the previous work in which it is predicted that the intermolecular charge-transfer exciton appears in the visible range of solid  $C_{60}$ .<sup>14</sup> Ross and his coworkers have reported that pronounced photoconductivity was observed from thick  $C_{60}$  films in the region of 2.5 to 3.1 eV.<sup>15</sup> This fact also supports our conclusion.

The band at 2.73 eV in the Fig. 3 may be related to the increase of the film crystallinity. The sublimed films have large amorphous area. This area decreases as the film thickness increases.<sup>9,17-20</sup> However, the cast films mainly consist of crystals. Therefore, the strong correlation between the molecules within a crystal leads to the increase of the 2.73 eV peak as shown in Fig. 3.

As mentioned about, The thick sublimed and cast films display marked absorption at 3.35 eV. This absorption, however, is not observed in small aggregated species in solution and in submonolayer sublimed films. In the case of solution true crystals are not formed. In sublimed films large amount of the material is in the amorphous state. Therefore, interaction of crystals or grains should be taken into account to explain the band at 3.35 eV. The molecules at the surface of grains are in asymmetrical position compared with the molecules inside the grains. Therefore the 3.35 eV band seems due to the breakdown of the  $I_h$  symmetry of the surface molecules. The interface between two grains gives the preferable direction to the molecular dipoles of adjacent grains, which interact with. Since there are more grains in the direction of the strip than across it, such an interaction leads to macroscopic optical anisotropy explaining the dichroism at the 3.35 eV band.

## 5. Conclusion

$\pi - \pi^*$  excitations are dominant in absorption spectra of the molecule. The interaction probably leads to overlap with the  $\pi$ -electron density of neighbouring molecules.<sup>6)</sup> On the other hand, the  $\pi - \pi^*$  excitations may contribute to intermolecular interaction, forming the C<sub>60</sub> crystal.

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