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The Origin of the ESR Signal of C_{60} Seen in the Powder and in Benzene Solution. The Indication of the Reaction of C_{60} with Oxygen Induced by Photoexcitation

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ESR signals were obtained for the C_{60} sample in powder and in benzene solution, by irradiation with Xe lamp in an atmosphere of oxygen. It was shown that the ESR signal with g-value of 2.0026 and a derivative peak-to-peak width of about 0.175 mT was clearly enhanced by the irradiation. This fact indicates that C_{60} is reactive with oxygen by irradiation of light and produces the radical which gives the ESR signal.

Since the discovery of the method of generating macroscopic quantities of the C_{60} cluster and other cage molecules made of carbon (called fullerenes),$^{1,2)}$ a variety of spectroscopic studies have been made to clarify the physical properties of these clusters. Among these investigations, ^{13}C-NMR measurements have been performed these few years,$^{3-6)}$ because they can give the informations about the molecular structures for fullerenes of various sizes in solution$^{5-6)}$ and the dynamics such as the temperature dependence of molecular rotation of C_{60} in powders$^{3,4)}$ and in the single crystal.

The previous work on the ^{13}C-NMR measurements,$^{3,4)}$ has shown that the C_{60} powder gives a weak ESR signal, with g-value of 2.0 and a derivative peak-to-peak line width of 0.15 - 0.19 mT. However, the electronic ground state of C_{60} is known as a singlet state, and then C_{60} is ESR silent. This discrepancy is left unresolved up to now, though it is important to clarify the origin of the spectrum in order to investigate the magnetic properties of fullerenes and metal encapsulated fullerenes such as Fe@$C_{60}$$^{7)}$ or M@C_{82} (M = Sc, Y, and La).$^{8-14)}$

On the other hand, the effect of light for the stability of C_{60} has been demonstrated by R. Taylor et al.$^{15)}$ According to their observation, the deep magenta color from C_{60} in benzene solution is lost and a small amount of brown deposit is produced, if the solution is exposed to light and oxygen. They suggested that some kind of photochemical reaction occurred in this system. Here we report the first observation of ESR signals due to the photoexcitation of C_{60} in powder and even in benzene solution and discuss the origin of these signals.

We prepared samples of C_{60} by the arc heating of graphite rod in 100 Torr helium atmosphere, which is essentially the same as those reported by Kraetschmer et al.[1)] After an extraction procedure with CS_2 as a solvent,a preparative chromatographic separation was performed with CS_2 as an elute.[16)] First, the obtained fresh powder of C_{60} itself, was investigated using an ESR spectrometer (JEOL RE-3X) at room temperature. Only a small amount of ESR signal was seen when the sample was treated under a

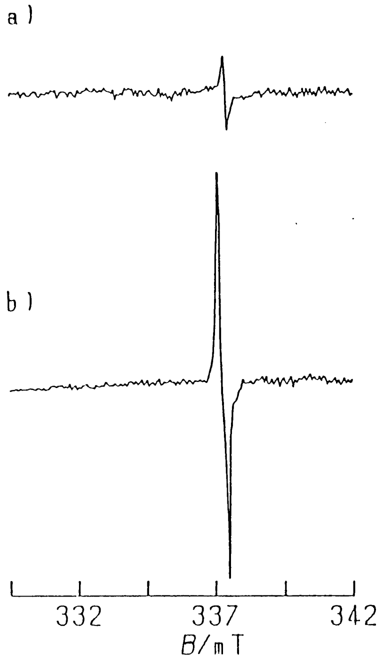

Fig. 1. The change of the ESR spectrum of C_{60} powder, purged with oxygen: (a) before and (b) after irradiation of Xe lamp for 1 h at room temperature. The frequency of the resonant microwave was 9.446 GHz.

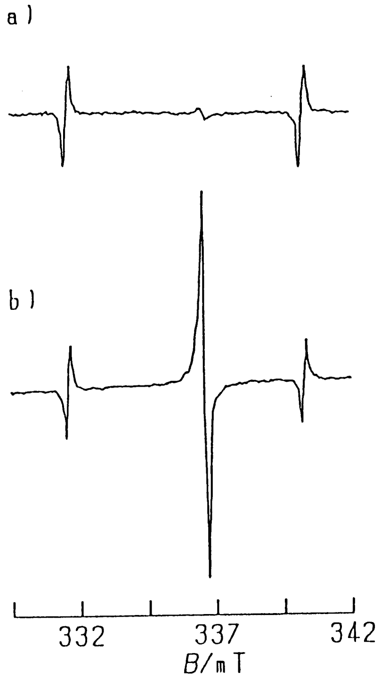

Fig. 2. The change of the ESR spectrum of C_{60} in benzene solution, purged with oxygen: (a) before and (b) after irradiation of Xe lamp for 1 h at room temperature. The side bands are due to the manganese ions used as the internal reference. The frequency of the resonant microwave was 9.425 GHz.

nitrogen atmosphere. This signal did not change even after the irradiation with 500 W Xe short arc lamp (USHIO UXL=500D-0) for 1 hour. However, when the sample was purged with oxygen and irradiated by Xe lamp for 1 hour, the intensity of the ESR spectrum greatly increased (see Fig.1). The g-value and a derivative peak-to-peak line width of the spectrum were estimated to be 2.0026 and 0.175 mT, respectively. These values are similar to those obtained by the previous ESR investigation of C_{60} powder,[3,4] indicating that this signal was attributed to the products made by the exposure to light and oxygen. Similar ESR spectra were obtained for C_{70} and other higher fullerenes.

Second, the C_{60} in benzene solution (2 mM) was purged with oxygen and irradiated by Xe lamp for 1 hour (Fig.2) at room temperature. After 1 hour irradiation, the color of the solution changed from deep magenta to light orange, but the brown deposit was not observed. Surprisingly, the change in the ESR spectral intensity was clearly seen even in benzene solution: the ESR signal intensity became large as about ten times as the one before the irradiation of light. This signal remains stable after irradiation, which means the radical produced by this photoexcitation process is stable in benzene solution. The estimated g-value and a derivative peak-to-peak line width were 2.0026 and 0.175 mT, respectively. These values are the same as those estimated from the ESR signal observed in C_{60} powder under photoexcitation in oxygen atmosphere, and the spectral line shape is simulated using Gaussian type function, which suggests that the radical may be trapped in the micro crystal in benzene solution.

Judging from these experimental findings, the process of the production of these radical was assumed in the following. First, the photon emitted from Xe lamp was mainly absorbed by C_{60} itself in solid and in benzene solution, since the radical was also produced under irradiation of visible light which neither benzene nor oxygen absorbs.[17] It is well known that C_{60} is easily photoexcited to the triplet state in benzene solution,[18,19] then it is likely that C_{60} of this triplet state may react with oxygen to yield the radical observed in the ESR spectrum. The structure of this radical is unknown at the moment, but the obtained g-value resembles to that of carbon-centered radicals, which suggests that the spin density mainly populates on carbon atoms of C_{60}. In conclusion, one has to take great care in treating C_{60} and other fullerenes under exposure to oxygen and light, especially when one does the experiment for obtaining the information about the magnetic properties of these fullerenes.

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