CHEMISTRY LETTERS, pp. 1233-1236, 1991.

Visible, UV, and VUV Absorption Spectra of C_{60} Thin Films Grown by the Molecular-Beam Epitaxy (MBE) Technique

Yohji ACHIBA,* Takashi NAKAGAWA, Yoko MATSUI, Shinzo SUZUKI,
Haruo SHIROMARU, Kotaro YAMAUCHI, Kozaburo NISHIYAMA, Masatsune
KAINOSHO, Hajime HOSHI,† Yusei MARUYAMA,† and Tadaoki MITANI†
Department of Chemistry, Tokyo Metropolitan University,
Hachiohji, Tokyo 192-03
†Institute for Molecular Science, Myodaiji, Okazaki 444

On single-crystal alkali halide substrates, the C_{60} film shows a new band in visible wavelength region. The absorption spectrum of the C_{60} film has been extended to vacuum UV region, and several new bands and/or humps were found for the first time.

Very recently, Hebard et al.$^{1)}$ have first demonstrated that alkali-metal doped thin films of C_{60} shows superconductivity at 18 K. This finding has been supported by recent developments in the synthesis of macroscopic amounts of C_{60} and C_{70} carbon clusters.$^{2)}$ NMR measurements$^{3,4)}$ strongly confirmed the proposed "soccer ball" structure.$^{5)}$ Optical absorption properties of pure C_{60} molecule in solution have also been measured in the visible and UV region.$^{4)}$ Furthermore, absorption measurements in solution have been extended to C_{60} transient species of radical anion,$^{6)}$ cation$^{6)}$ and excited triplet state.$^{7)}$

However, so far, there have been no reports on absorption spectra of C_{60} in solid state for which a thin film is prepared on well defined substrates. Such measurements would provide information on properties of electronic structures in solid state, particularly those induced by ordered or disordered orientation. Furthermore, extension of absorption measurements up to vacuum UV region would result in further understanding the higher electronically excited states. Here we present absorption spectra from 2 to 11 eV of C_{60} deposited on alkali halide single crystals.

We prepared samples of C_{60} by arc heating graphite in 100 Torr of helium. These procedures are essentially the same as those reported so far.$^{2)}$ Chromatographic separation was performed with hexane for C_{60}. In order to prepare thin film of C_{60}, we used the MBE method previously described.8) The deposition was carried out, keeping the substrate temperature at 300 K. Synchrotron radiation light (0.75 GeV) of UVSOR combined with a Seya-Namioka monochromator (1.5 m) was used as a vacuum UV light source.9)

Figure 1 shows absorption spectra in the wavelength region from 200 to 700 nm for the film of C_{60} deposited on LiF (100) and NaCl (100) in 240 A thickness. The absorption spectrum of C_{60} in hexane is inserted in Fig. 1 for comparison. The band positions of three strong bands peaking at 211, 256, and 328 nm in hexane solution shift to the longer wavelengths in the films, with peaks at 221.2, 271.8, and 346.6 nm for NaCl, and 221.5, 270.2, and 347.3 nm for LiF, respectively. The band widths are slightly broadened as well. Such absorption properties in solid state have first been reported by Kraetschmer et al.2) In their experiments, the powder of C_{60}/C_{70} mixture was sublimed and deposited on quartz plate, and the resulting films showed that the positions of three strong peaks depend on the preparation conditions. It is interesting to note here that the degree of the peak shifts observed in the present work are larger than that observed even in the microcrystalline form.2)

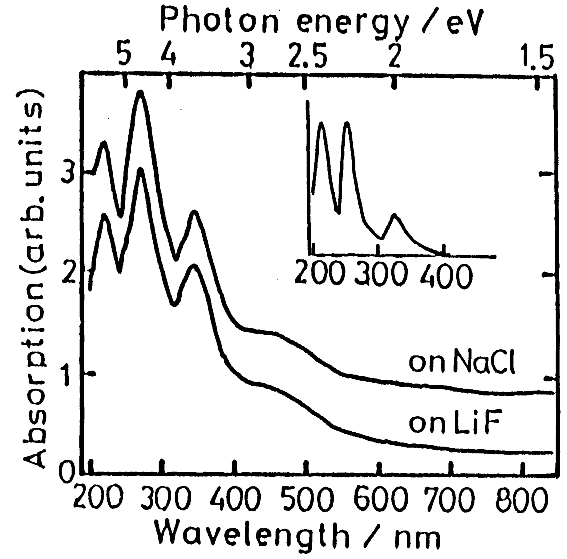

Fig.1. Absorption spectra of C_{60} films deposited on NaCl (100) and LiF (100) single crystals. Insertion is C_{60} in hexane solution.

In the longer wavelength region, there appeared a large difference between in solution and solid; the band at 445 nm with a shoulder around 495 nm is very much enhanced in intensity for the films. The appearance of this band has first been reported by Kraetschmer et al.,2) while the intensity observed in the present work is much more enhanced.

Taking into account of the results of one-electron energy band,10) the absorption in the visible wavelength is presumably assigned to transitions associated with a parity-forbidden HOMO-LUMO gap (h_u-t_{1u}). Actually, the intensity of the visible region in solution is one or two orders of magnitude weaker than that of the UV region. In films, however, the intensity of the 450 nm band is almost a half of the 350 nm band. This suggests that a symmetry breaking caused by imperfection of films or the charge transfer type of excitonic effect is induced by crystallization of C_{60} clusters. Anyhow, in order to confirm this, further experiments such as an electric field modulation spectroscopy are required.

So far there have been no reports on absorption of C_{60} in the vacuum UV region. Figure 2 shows absorption spectrum obtained for C_{60} on the LiF (100) at room temperature, using the synchrotron radiation light source. Three strong bands seen in Fig.1 are well reproduced by the a-c bands with a new band at 6.3 eV (d band) in Fig. 2. The absorption of the d band has not been reported so far.

Judging from these experimental results, the a-d bands are likely to be attributable to the relevant ($\pi - \pi$) transitions as suggested by the one-electron band calculation.[10] Definite assignments of these bands, however, might require more precise treatments of the optical transitions, particularly related to the excitonic effect.

More remarkable feature of the vacuum UV absorption spectra above the d band is that the absorption intensity changes steplikely, starting at 7.0 eV, with three humps at about 7.6 eV(e), 8.8 eV(f), and 10.5 eV (g).Such a behavior seems to be quite different from those observed for the a-d bands. Of particular interest, the energies of first two humps, e and f, are well coincident with the first and second ionization energies of solid C_{60}.[11]

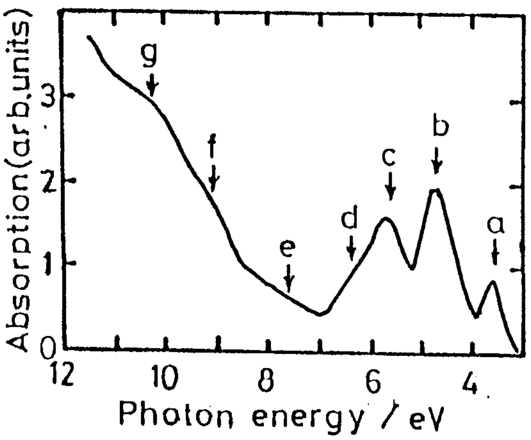

Fig.2. Absorption spectrum of C_{60} films deposited on LiF (100) at room temperature, using synchrotron radiation light source.

References

1) A.F.Hebard, M.J.Rosseisky, R.C.Haddon, D.W.Murphy, S.H.Glarum, T.T.M.Palstra, A.P.Ramirez, and A.R.Kortan, Nature, in press.
2) W.Kraetschmer, L.D.Lamb, K.Fostiropoulos, and D.R.Huffman, Nature, 347, 354(1990).
3) R.Taylor, J.P.Hare, A.K.Abdul-Sada, and H.W.Kroto, J. Chem. Soc., Chem. Commun., 1990, 1423.
4) H.Ajie, M.M.Alvarez, S.J.Anz, R.D.Beck, F.Diederich, K.Fostiropoulos, D.R.Huffman, W.Kraetschmer, Y.Rubin, K.E.Schriver, D.Sensharma, and R.L.Whetten, J. Phys. Chem., 94, 8630(1990).
5) H.W.Kroto, J.R.Heath. S.C.O'Brien, R.F.Curl, and R.E.Smalley, Nature, 318, 162(1985).

6) T.Kato, T.Kodama, T.Shida, T.Nakagawa, Y.Matsui, S.Suzuki, H.Shiromaru, K.Yamauchi, and Y. Achiba, Chem. Phys. Lett., in press.
7) Y.Kajii, T.Nakagawa, S.Suzuki, Y.Achiba, K.Obi, and K.Shibuya, submitted for publication.
8) A.J.Dann, H.Hoshi, and Y.Maruyama, J. Appl. Phys., 67, 1371(1990).
9) T.Mitani, T. Yamanaka, M. Suzui, T. Horigome, K. Hayakawa, and I. Yamazaki, J. Luminescence, 39, 313(1988).
10) S.Saito and A.Oshiyama, submitted for publication.
11) D.L.Lichtenberger, K.W.Nebesny, C.D.Ray, D.R.Huffman, and L.D.Lamb, Chem. Phys. Lett., 176, 203(1991); J. H. Weaver, J.L.Martins, T.Komeda, Y.Chen, T.R.Ohno, G.H.Kroll, N.Troullier, R.E.Haufler, and R.E.Smalley, Phys. Rev. Lett., 66, 1741(1991).

(Received April 20, 1991)