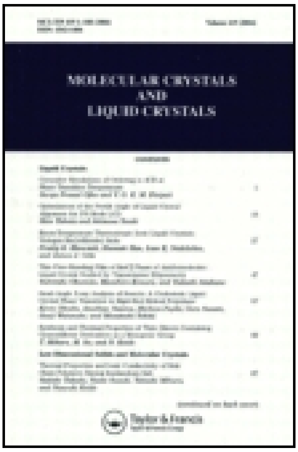

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TOF Mass Spectroscopy of Fullerenes-Identification of C_{58}-$C_{60}O$ Pair Fullerenes-

Chiemi Fujikawa [a], Katsuyuki Morii [a], Tadaoki Mitani [a], Hiroshi Kitagawa [b], Masaaki Nagata [b], Nobuo Mizutani [b] & Hiroo Inokuchi [b]

[a] Japan Advanced Institute of Science and Technology (JAIST), Tatsunokuchi, Ishikawa, 923-12, JAPAN

[b] Institute for Molecular Science, Okazaki, 444, JAPAN

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TOF MASS SPECTROSCOPY OF FULLERENES --IDENTIFICATION OF C_{58}-$C_{60}O$ PAIR FULLERENES--

CHIEMI FUJIKAWA, KATSUYUKI MORII, TADAOKI MITANI
Japan Advanced Institute of Science and Technology (JAIST), Tatsunokuchi
Ishikawa 923-12, JAPAN

HIROSHI KITAGAWA, MASAAKI NAGATA, NOBUO MIZUTANI,
HIROO INOKUCHI
Institute for Molecular Science, Okazaki 444, JAPAN

Abstract Higher fullerenes, including newly identified C_{86}, were purely isolated by HPLC (High Performance of Liquid Chromatography). The precise mass spectroscopy by LD-TOF (Laser Desorption - Time of Flight) method leads to an observation of a new oxidized product during the HPLC process, which can be assigned to C_{58}-$C_{60}O$ pair fullerenes by comparing with the LD-TOF mass spectrum of chemically oxidized C_{60}.

INTRODUCTION

The fullerenes has a large potentiality for design and construction of new molecular functions due to their flexible molecular structures.[1] To gain an insight into their substances, it is unquestionably required to establish isolation techniques of pure C_{60} and higher fullerenes. The HPLC (High Performance of Liquid Chromatography) method has a high efficiency for isolation of higher fullerenes from solutions.[2,3] Recent improvement of column used as an isolation material in HPLC makes it possible precisely to isolate pure higher fullerenes. In addition, the LD-TOF (Laser Desorption - Time of Flight) mass spectroscopy with a high sensitivity has been developed. The combination of the HPLC measurements and LD-TOF spectroscopy is expected to lead to a new identification of higher fullerenes.

In this letter, the experimental results of identification and characterization of higher fullerenes by LD-TOF mass spectroscopy are reported. As expected, new higher fullerene, C_{86} and C_{88}, are clearly identified. It should be noted that fullerenes are considerably influenced by oxidation during the HPLC process, as pointed out by Creegan et al.[4] and Diedrich et al.[2] Rather, at present, the reaction of C_{60} with air gives a severe problem to interpret the experimental data of the fullerenes particularly related with the transport phenomena. The LD-TOF measurement under a condition of a low level excitation of laser power provides an useful information of such an oxidation product. We will propose a new model for interpretation of a new product introduced in the HPLC process on the basis of the data of the LD-TOF measurements on fully oxidized C_{60} samples.

EXPERIMENT AND RESULTS

Preparation of Fullerenes

The black soot containing fullerenes was made by arc discharge of pure graphitic carbon in an atmosphere of ~100 torr of helium gas.[5] Soluble materials in toluene were obtained by the soxhlet extractor. The fullerenes were isolated by a HPLC (Waters™ 600E) system, in which the temperature of the column (Buckyclutcher I, Trident-Tri-DNP) was controlled within an accuracy of 0.2 ℃ and two variable eluants are mounted to change the proportion of solvents. It was required to use these technics for high resolution of isolation. At same time, it is important to monitor the UV spectrum of samples. Typical experimental conditions are as follows; toluene : n-hexane = 1 : 1, pressure 1000 psi, flow rate 15 ml/min., UV detection at 280 nm, and temperature of columns at 43 ℃.

The repetition of the cyclic HPLC operation provides higher quality of fullerenes. The first run gives two strong peaks of C_{60} and C_{70} and several other peaks. Removing the C_{60} and C_{70} components in the first run, the profile of the second run shown in Fig.1(a) has at least 10 bands (A-J). In the third run after the insolation of the E band twice, the band was clearly separated into two peaks. These structures directly correspond to peaks observed in the LD-TOF mass spectrum presented later.

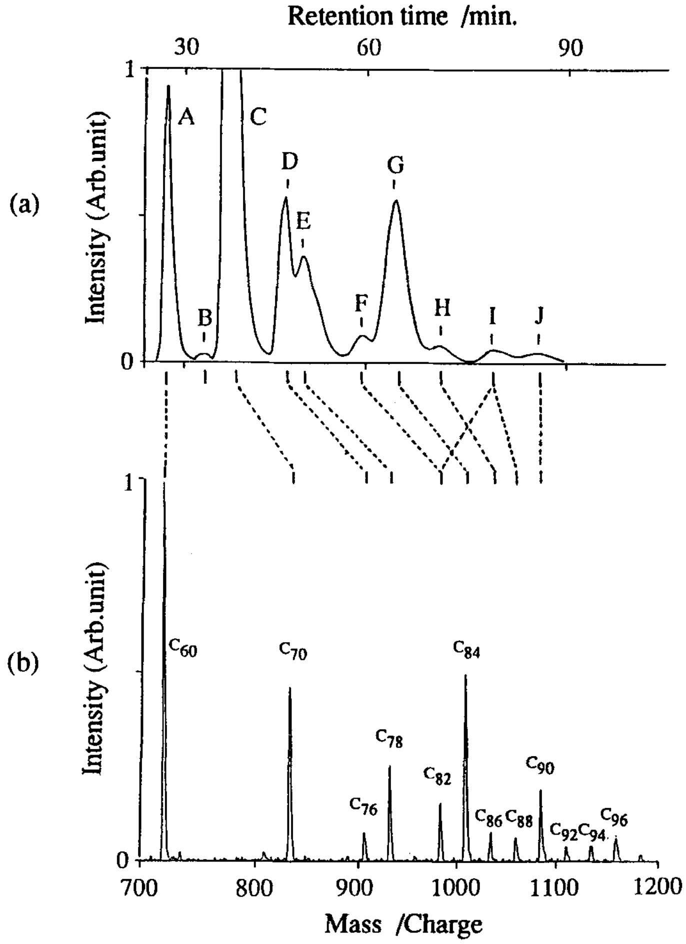

FIGURE 1 (a) the second run HPLC profile and (b) the LD-TOF negative ion mass spectrum of soluble materials in toluene after reduction of concentrations of A (C_{60}) and C (C_{70}) components. (see text.)

LD-TOF Mass Spectroscopy

Fig.1(b) shows the spectrum of soluble materials in toluene, in which the C_{60} and C_{70} components were almost separated out in the process of the soxhlet extraction. Thus, the concentrations of C_{60}, C_{70} and other higher fullerenes are almost of same order. This leads to a same order of intensities of the structures in a wide region of regulated time lag. In addition, this makes it possible to measure with no ghost lines usually observed in the LD-TOF measurements.[6] From this spectrum, it can be concluded that components of C_{60}, C_{70}, C_{76}, C_{78}, C_{82}, C_{84}, C_{86}, C_{88}, C_{90}, C_{92}, C_{94}, and C_{96} are well soluble in toluene, but C_{72}, C_{74} and C_{80} could not be separated. Comparing with the LD-TOF mass spectrum of samples directly sublimated from the soot, the component of C_{74} certainly was found in the soot and insoluble in toluene. Other members of C_{72} and C_{80} could not be clearly detected. This reason is not clear. More higher fullerenes, such as C_{98} and C_{100}, have been identified by the LD-TOF analysis, but their concentrations were considerably smaller than the fullerenes sited above.

The results of identification of the A-J bands are presented by the dashed lines in Fig.1. This indicates that the column of the Buckyclutcher I used provides a regular

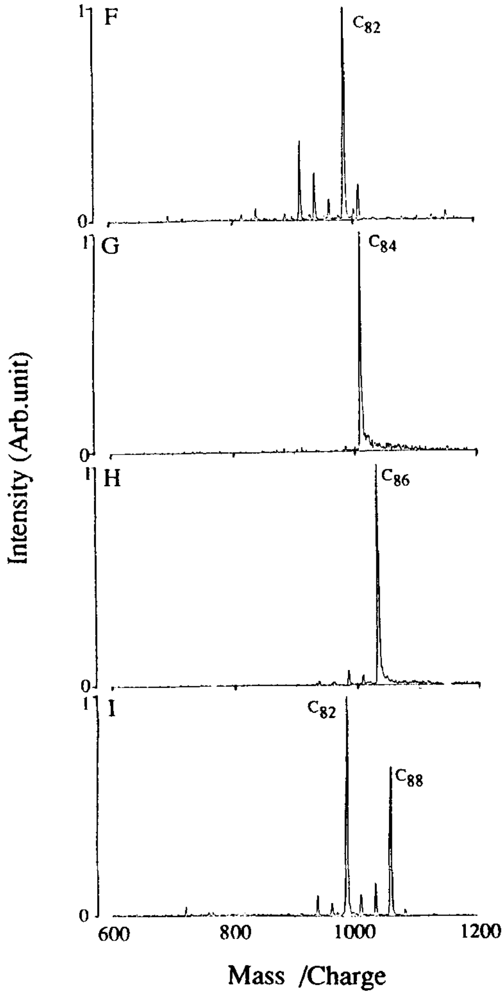

FIGURE 2 The LD-TOF mass spectra of the isolated F-I region.

ordering of mass numbers except for some fraction of the B, F, and I bands. In order to clarify the irregularity of the F and I band, the individual LD-TOF mass spectra of the isolated F-I bands are shown in Fig.2. The observation of mass number of C_{82} in the I band, which is assigned to the mass number of C_{88}, might be responsible for the presence of the structural isomer of C_{82} in the I band.[7]

The LD-TOF mass spectrum of the B band is shown in Fig. 3(a). Mass numbers of main peaks in this band are 696, 720, and 736, which might be corresponding to C_{58}, C_{60}, and $C_{60}O$. This assignment suggests an oxidation of C_{60} during the HPLC process as reported in previous papers.[2,3] In order to confirm such an oxidation of C_{60},

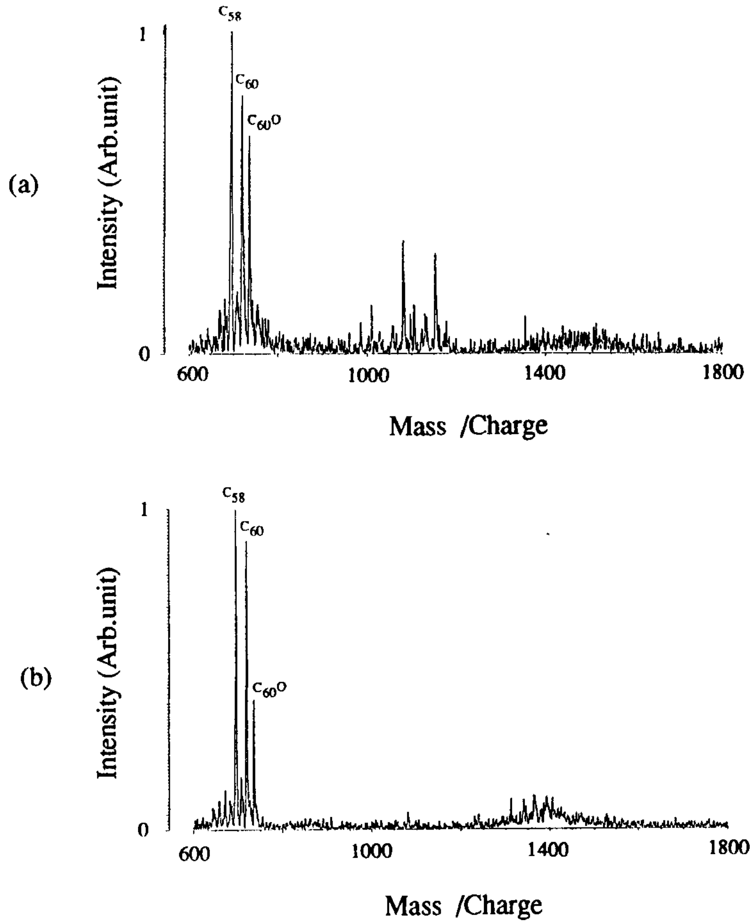

FIGURE 3 The LD-TOF mass spectra of (a) the isolated fraction from B band (see Fig.1(b)) and (b) the chemically oxidized sample.

the LD-TOF measurement has been made on oxidized samples obtained by light-induced method.[4] In Fig. 3 (b), the result is shown compared with the spectrum of the B band of Fig. 3 (a).

The profiles of both spectra are similar and have a structure corresponding to the C_{58} component, in common. Taking account of no observation of such signals in fresh samples before repeating the isolation process as show in Fig. 1(b), the C_{58} fragment might be produced by oxidation. This suggest a pair formation of the C_{58} and $C_{60}O$ fragments during a reaction in solution. The conformation of C_{58} previously reported[8] is considered to have a stable structure if C_{58} is bridged by $C_{60}O$ through an oxygen atom. Detailed experimental results of optical and vibrational properties of higher fullerenes including the pair fullerene will be shortly reported elsewhere.

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