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Ultraviolet photoelectron spectroscopy of C_{60}^- produced by three different generation methods

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Abstract. The photoelectron spectra of C_{60}^- produced with three different generation methods were recorded with 6.4 eV photon energy using a magnetic-bottle-type time-of-flight photoelectron spectrometer. From these spectra, it was suggested that the laser vaporization of a graphite rod mainly produces C_{60}^- of ring-like structure. On the other hand, C_{60}^- produced by the fragmentation process of the fullerene C_{70} through C_2 or C_{2n} elimination give different photoelectron features from those of C_{60}^- having an icosahedral (I_h) symmetry or a ring-like structure.

PACS. 33.60.-q Photoelectron spectra – 36.40.-c Atomic and molecular cluster

1 Introduction

Since the discovery of the icosahedral fullerene C_{60} and other higher fullerenes as stable and solvent extractable species [1], their formation mechanism has been one of the most intriguing issues for researchers, and has been extensively investigated and discussed. Several formation mechanisms, e.g., the pentagon road [2], the fullerene road [3], and the ring-stacking model [4], have been proposed in these experiments. Recent rapid progress in ion chromatography investigation suggests that the fullerene-like structure may be formed through the annealing of other nonfullerene forms of carbon clusters [5–7]. It has also been proposed that C_{60} could be generated as a result of a "shrink-wrapping" process from larger carbon clusters, where a C_2 unit is ejected from larger carbon clusters than C_{60}. Molecular dynamics simulations have also been extensively performed in order that light may be shed on these formation processes [8].

The photoelectron spectroscopy technique is a powerful tool when it is applied to the carbon cluster anions, since it can give information about molecular, electronic, and vibrational structures for size-selected neutral carbon clusters [9–14]. Yang *et al.* applied this technique to C_n^- (up to $n = 84$) generated using the laser vaporization of the graphite rod for the first time [9, 10]. They determined the vertical electron affinity of C_n ($n = 2 - 29$), and deduced that carbon clusters of C_2 to C_9 have a linear form and that those of C_{10} to C_{29} have a planar monocyclic ring form based on the vEA. Wang *et al.* reported that the photoelectron spectra of C_{60}^- having I_h symmetry [13]. Recently, it has been found that the relative ratio of linear and ring forms of carbon cluster anions changes when the laser vaporization condition is carefully varied for C_n^- ($10 \le n \le 16$) [14, 20].

We aim in this paper to compare the photoelectron features of the icosahedral fullerene C_{60}^- (I_h-C_{60}^-) with those of C_{60}^- generated by laser vaporization of the graphite rod and by the fragmentation process of the fullerene C_{70}. We hope to show that C_{60}^- of different molecular and electronic structures will have different photoelectron features.

2 Experimental

The details of the apparatus are described elsewhere [15]. Briefly, the apparatus consists of a cluster ion source, a time-of-flight mass spectrometer and a magnetic-bottle-type photoelectron spectrometer. Three different kinds of C_{60}^- were produced, by (1) laser desorption of the icosahedral fullerene C_{60}, (2) laser vaporization of the graphite rod, and (3) fragmentation of the chromatographically separated fullerene C_{70}, respectively. The fullerenes C_{60} and C_{70} were sublimed on a copper rod of 6 mm in diameter, and these copper rods were used for laser desorption. The desorbed C_{60}^- and other species were swept through an extender with pulsed helium carrier gas supplied from an injector, operated at backing pressure of 4 atm, and then accelerated to 2.0 keV with a Wiley–Mclaren–type time-of-flight mass spectrometer [16]. After the cluster anions traveled a field-free drift tube, we selected them by size with a mass gate to ensure that only a certain size-selected carbon cluster anions enter the photodetachment region.

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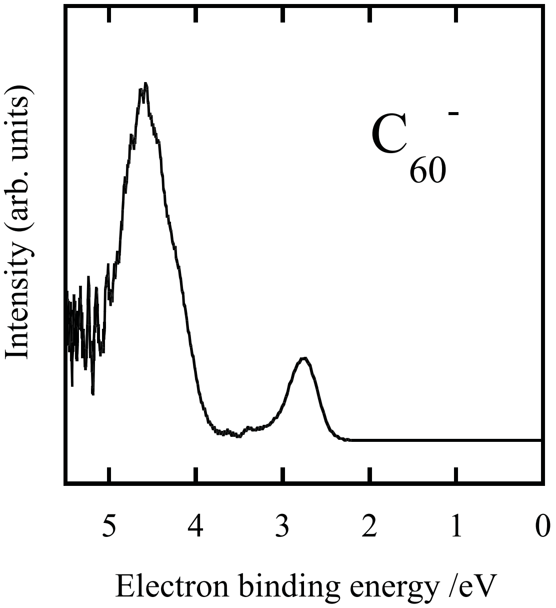

Fig. 1. Photoelectron spectra of C_{60}^- generated by the desorption of the isolated fullerene C_{60}.

After decelerating to a few hundred eV of kinetic energy, the ions were irradiated by an ArF excimer laser (193 nm, 6.4 eV) a few centimeters downstream of the decelerator. The photoelectron spectra presented in this study were typically obtained by the accumulation of 2000 laser shots. The kinetic energy of the photoelectron was calibrated against the known data of C_n^- $(5 \leq n \leq 9)$. The resolution of the spectrometer is generally $\Delta E/E = 0.1$ on average. The background electron signals generated by the scattered light interacting with the photodetachment chamber were subtracted from the data.

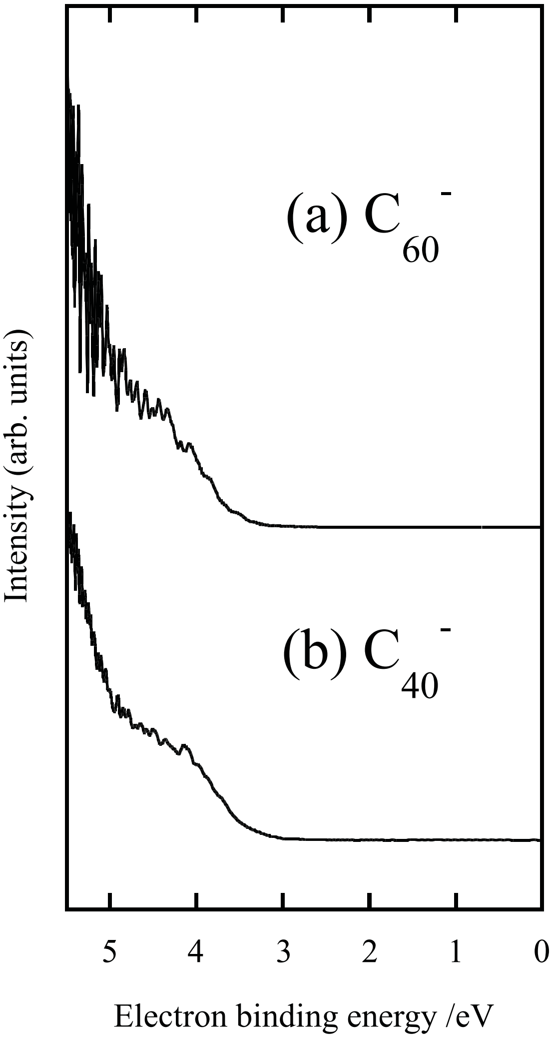

Fig. 2. Photoelectron spectra of C_{60}^- (a) and C_{40}^- (b) generated by laser vaporization of a graphite rod.

3 Results and discussion

Figure 1 shows the photoelectron spectrum of C_{60}^- produced by laser desorption of C_{60} having an icosahedral (I_h) symmetry. The observed photoelectron feature is essentially the same as that reported by Wang *et al.*, exhibiting two distinct peaks at 2.7 and 4.5 eV electron binding energy [13]. This photoelectron feature is well recognized when the electronic structure of C_{60} has an I_h symmetry [17,18]; therefore, it is rationalized that the photoelectron spectrum seen in Fig. 1 originates from C_{60}^- having a "soccer ball" structure.

On the other hand, Fig. 2a shows a quite different photoelectron feature of C_{60}^-, in the case where C_{60}^- was produced by laser vaporization of the graphite rod. The photoelectron spectrum of C_{40}^- produced under the same laser vaporization condition is shown in Fig. 2b as a reference. It can be clearly seen that the photoelectron features of C_{60}^- and C_{40}^- generated by laser vaporization of a graphite rod resemble each other very much, while the photoelectron spectrum obtained for C_{60}^- of I_h symmetry (shown in Fig. 1) is quite different from the other two spectra.

According to the ion chromatography investigation, most of the nonfullerene isomers containing $30-50$ carbon atoms can be annealed into two dominant isomers, i.e., the fullerene isomer and the large monocyclic ring isomer, associated with fragmentation by loss of C_2 [5–7]. Additionally, Gotts *et al.* demonstrated in their ion chromatography experiment of C_n^- produced by laser vaporization of a graphite rod that the amount of ring-like structure is very high (80%–90%) in C_n^- of larger size [5]. It is of interest that Yang *et al.* observed the photoelectron spectrum of a C_{60}^- of I_h symmetry (I_h-C_{60}^-) when two laser beam were irradiated to a graphite rod. The first laser was used to generate carbon vapor by the irradiation of a graphite disc, while the second laser (ArF excimer) was used to generate a shower of electrons for attachment to the neutral clusters as they emerged into a downstream cooling tube prior to free expansion [10]. As a result, C_{60}^- was seen as a magic number in the mass

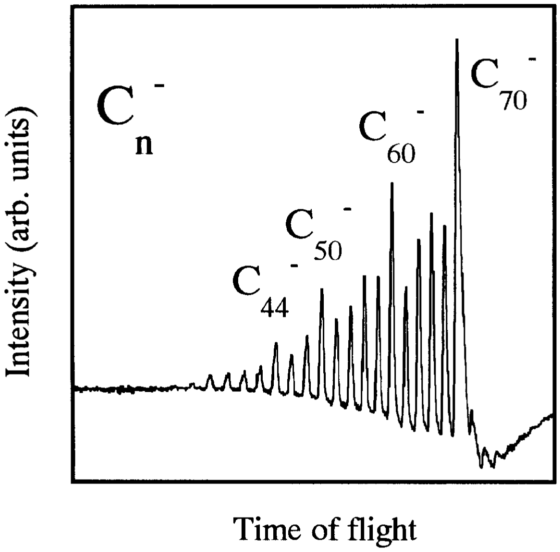

Fig. 3. Mass spectra obtained by a fragmentation process of fullerene C_{70}.

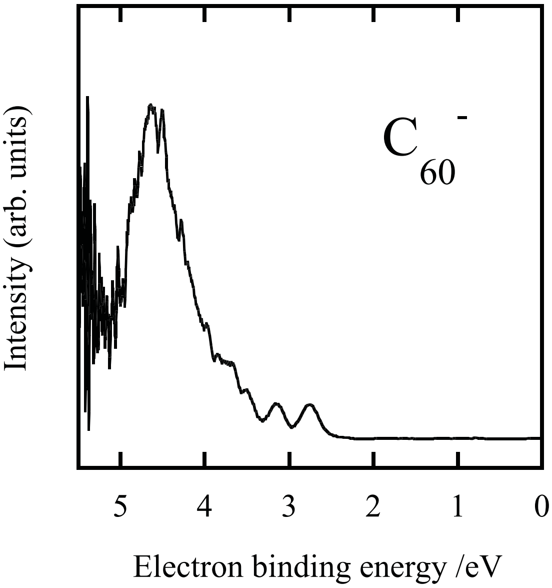

Fig. 4. Photoelectron spectra of C_{60}^- generated by the fragmentation of the isolated fullerene C_{70}.

spectrum. On the other hand, when only one laser for the vaporization of a graphite rod was used, only a smooth mass distribution around C_{60}^- could be seen in the mass spectrum. Under these circumstances, a different spectral feature from that of I_h-C_{60} was obtained; thus the existence of another conformational isomer should be considered. Since our laser vaporization condition is considered to be similar to the latter case (using only one laser for the vaporization), we may conclude that the photoelectron feature seen in Fig. 2a originates from C_{60}^- having a ring-like structure. This suggestion is consistent with the results of the ion chromatography experiment demonstrated by Gotts *et al.* A similar observation has been made by Handschuh *et al.*, who make (I_h-C_{60}^-) only when using their novel annealing technique [19]. That means the number of the conformational isomers can be changed with different cluster ion source conditions. This is further confirmed by a systematic investigation of the photoelectron spectra of C_n^- ($5 \leq n \leq 41$) produced by laser vaporization with a careful control of laser fluence; this will be presented in an upcoming paper [15].

Figure 3 shows the mass spectrum obtained by a fragmentation process of fullerene C_{70} with high laser fluence. The mass spectrum shown in Fig. 3 indicates that the fragmentation pattern of C_{70} shows a characteristic mass distribution for the fullerene species, i.e., C_{2n}^- ($32 \leq 2n < 70$) appears as fragment ions, and C_{44}^-, C_{50}^-, and C_{60}^- can be recognized as magic numbers in the spectrum. The photoelectron spectrum of C_{60}^-, generated by the fragmentation of the isolated fullerene C_{70}, is shown in Fig. 4. It can be clearly seen that the obtained photoelectron feature does not resemble that of the C_{60}^- having either an icosahedral symmetry or a ring-like structure. This photoelectron feature has a peak at 4.6 eV, but does not show any characteristic feature of I_h-C_{60} around 2.7 eV. The large HOMO-LUMO gap that well characterizes the spectrum of I_h-C_{60} was not seen for the case shown in Fig. 4. So it is very likely that there exists another conformational isomer formed in the C_{2n}^- loss process.

According to the study of the photoexcitation and subsequent fragmentation process of C_{60}, it is strongly suggested that the fullerene molecule can easily be internally excited [21–23]. Also, the molecular dynamics study clearly demonstrates that there is a certain internal temperature where the phase of the fullerene molecule turns to a “floppy” or “pretzel” phase from a solid phase [24]. According to the molecular dynamics simulation of I_h-C_{60}, the fragmentation process seems to require high internally excited states. Thus it is rationalized that the form of C_{60}^- produced by the fragmentation of the fullerene C_{70} is not exactly the same as that having I_h symmetry, even if the ball-like structure could be preserved after C_2 or C_{2n} elimination. A preliminary investigation of the photoelectron spectra of C_{58}^- and C_{62}^- generated by the fragmentation process of C_{70}^- in a laser vaporization ion source was also suggestive. The results show that each photoelectron spectrum is all similar to each other indicating that there are rather common forms which are not responsible for a particular isomer such as I_h-C_{60}.

In conclusion, a C_{60}^- which is produced by laser desorption of the icosahedral fullerene C_{60} preserves its form (I_h-C_{60}^-), that produced by laser vaporization of the graphite rod mainly has ring-like structure, and that produced by fragmentation of the chromatographically separated fullerene C_{70} has non (I_h-C_{60}^-) form, but probably ball-like C_{60}^- structure.

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References

1. W. Kraetschmer, K. Fostiropoulos, D.R. Huffman: Chem. Phys. Lett. **170**, 167 (1990)
2. R.E. Smalley: Acc. Chem. Res. **25**, 98 (1992)
3. D.E. Manolopoulos, P.W. Fowler: *The Chemical Physics of Fullerene 10 (and 5) Years Later*, NATO ASI Series **316**, 51 (1992)
4. T. Wakabayashi, Y. Achiba: Chem. Phys. Lett. **190**, 465 (1992)
5. N.G. Gotts, G. von Helden, M.T. Bowers: Int. J. Mass. Spectrom. Ion Processes **149/150**, 217 (1995)
6. G. von Helden, M.T. Hsu, N. Gotts, M.T. Bowers: J. Chem. Phys. **97**, 8182 (1993)
7. J.M. Hunter, J.L. Fye, M.F. Jarrold: J. Chem. Phys. **99**, 1785 (1993)
8. Y. Yamaguchi, S. Maruyama: Chem. Phys. Lett. **286**, 343 (1998)
9. S.H. Yang, K.J. Taylor, M.J. Craycraft, J. Conceicao, C.L. Pettiette, O. Cheshnovsky, R.E. Smalley: Chem. Phys. Lett. **144**, 431 (1988)
10. S.H. Yang, C.L. Pettieete, J. Conceicao, O. Cheshnovsky, R.E. Smalley: Chem. Phys. Lett. **139**, 233 (1987)
11. D.W. Arnold, S.E. Bradforth, T.N. Kitsopoulos, D.M. Neumark: J. Chem. Phys. **95**, 8753 (1991)
12. C. Xu, G.R. Burton, T.R. Taylor, D.M. Neumark: J. Chem. Phys. **107**, 3428 (1997)
13. L.-S. Wang: Surf. Rev. Lett. **3**, 423 (1996)
14. M. Kohno, T. Moriwaki, S. Suzuki, H. Shiromaru, Y. Achiba: Chem. Phys. Lett. **282**, 330 (1998)
15. M. Kohno *et al.*: (to be submitted)
16. W.C. Wiley, I.H. McLaren: Rev. Sci. Instrum. **26**, 1150 (1955)
17. R.C. Haddon, L.E. Brus, K. Ragavachari: Chem. Phys. Lett. **125**, 459 (1986)
18. M.D. Newton, R.E. Stanton: J. Am. Chem. Soc. **108**, 2469 (1986)
19. H. Handschuh, G. Gantefoer, B. Kessler, P.S. Bechthold, W. Eberhardt: Phys. Rev. Lett. **74**, 1095 (1995)
20. M. Kohno, S. Suzuki, H. Shiromaru, Y. Achiba: J. Chem. Phys. **110**, 3781 (1999)
21. E.E.B. Campbell, T. Raz, R.D. Levine: Chem. Phys. Lett. **253**, 261 (1996)
22. H. Hohmann, R. Ehlich, S. Furrer, D. Grosenick, E.E.B. Campbell: Z. Phys. D **33**, 143 (1995)
23. K.R. Lykke, P. Wurtz: J. Phys. Chem. **95**, 3191 (1992)
24. S.G. Kim, D. Tomanek: Phys. Rev. Lett. **72**, 2418 (1994)