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Electron ion Coincidence spectroscopy of C₆₀ by Using Synchrotron Radiation Photoionization

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Introduction

The dissociation dynamics of C₆₀ has been studied by many experimental methods, such as photoionization mass spectrometry^[1-3], electron impact ionization^[4], slow highly-charged-ion collision^[5] and heavy-ion excitation^[6] since the discovery of the fullerene molecule in 1985. Today it is commonly accepted that the dominant fragmentation mechanism involves the sequential loss of C₂ units from energized C₆₀⁺. Moreover, a huge kinetic shift has been found when a C₂ unit is removed from the parent ion. The larger kinetic shift is caused by many degrees of freedom and a very tight and symmetric structure of C₆₀.

However, the dissociation and fragmentation of C₆₀ after single-photon excitation has been studied in very few papers. Yoo *et al.* have observed C₆₀⁺ → C₅₈⁺ + C₂ fragmentation at $h\nu$ of 41eV^[1]. Reinkoster *et al.*^[2] and Juranic *et al.*^[3] have reported experimental results for the ionization and fragmentation of C₆₀ by using synchrotron radiation in the $h\nu$ range 26-130eV and 18-280eV, respectively. Since 2003, our group has studied the photoionization and photodissociation of fullerene molecules combining extreme vacuum violet synchrotron radiation from the beamline BL2B at the UVSOR in Okazaki. We have measured the yield curves of the fragments produced from photoionization of C₆₀ and C₇₀ by time-of-flight (TOF) mass spectrometry to study the dissociative mechanisms and kinetics. Namely, the yield curves for C_K_{2n}^{z+} (K=60 and 70, n≥1, z=1-3) produced from parent species are plotted as a function of the internal energy E_{int} of the parent C_K^{z+} (K=60 and 70) ions.^[7-9]

It is well-known that threshold photoelectron-photoion coincidence spectroscopy (TPEPICO) is one of the most precise methods for studying the kinetics and dynamics of molecular photoionization. The unimolecular decomposition of fullerene molecules can be investigated in more detail by the coincidence experiment. Drewello *et al.* have tried to investigate the gaseous C₆₀ by TPEPICO with the use of synchrotron radiation as the light source. But they have not observed any threshold electrons. In this report, we investigate PEPICO spectroscopy of C₆₀ with synchrotron radiation of $h\nu=25-120$ eV to further clarify the dynamics of dissociative photoionization of C₆₀.

Experiment

All of the experiments have been carried out at the bending magnet beamline BL2B equipped with an 18m spherical grating monochromator of Dragon-type. A molecular beam of C₆₀ was produced by heating the sample powder to approximated 680K. Monochromatized synchrotron radiation was focused onto the C₆₀ beam. The ionized recoil fragments, produced from the intersection region of the VUV light and the C₆₀ beam, were accelerated by a two stage electric field and detected by a three-stage microchannel plate detector (MCP) after mass-to-charge separation by a conventional Wiley-McLaren type TOF mass spectrometer. The ions provide the stop signal to a time-to-digital convertor (TDC). Photoelectrons, accelerated in the opposite direction with respect to the positive ions, were recorded by a two-stage MCP, providing the start signal to the TDC. No active energy analysis has been made for electrons, but the electric field between the ionization region and the two-stage MCP is more favorable for faster photoelectrons.

The detection efficiencies of the ions and electrons have been estimated by photoionization measurement of rare gases. The performance of the electron analyzer has been tested by measuring the total electron yield (TEY) spectrum and PEPICO spectroscopy of krypton in the $h\nu$ range of 90-96eV.

Results and Discussion

Parent ion C_{60}^{z+} ($z=1-3$) and fragments ions C_{60-2n}^{z+} ($n \geq 1, z=1-3$) were measured at $h\nu=50, 60, 90$ and 120eV , respectively. For all photon energies, no small carbon cluster ion C_m^{z+} ($m=1-5$) were observed. Therefore, the emission of neutral carbon cluster rather than C_m^{z+} is the main fragmentation channels of C_{60} in the present energy region. As for the singly charged fragments, C_{58}^+ and C_{56}^+ were just detected at very narrow $h\nu$ range. At $h\nu \geq 60\text{eV}$, their intensities become negligibly weak. This probably means that the singly charged fragments emit another electron at $h\nu \geq 60\text{eV}$ and are converted to fragments with the same size but with higher charged state.

Taking mass spectra with scanning the monochromator we could measure the ion yield curves for C_{60-2n}^{z+} as a function of $h\nu$. The total relative photoionization cross section of C_{60} can be calculated from the total ion yield (TIY) curves of C_{60} and agrees well with the reported results.^[9]

The ratios between the relative photoionization cross sections of C_{60-2n}^{z+} ($n \geq 1, z=1-3$) and that of C_{60}^+ were calculated by using the ion yield curves of C_{60-2n}^{z+} ($n \geq 1, z=1-3$) and C_{60}^+ . Fig 1 shows the ratio of photoionization cross section of C_{58}^{2+} to that of C_{60}^+ . The previous data of Reinkoster *et al.*^[2] and Juranic *et al.*^[3] are also displayed in this figure. The reported results show that the ratios almost keep constant after passing the maximum value. In contrast, our data exhibits a pronounced decrease after the maximum on the ratio curve. The cross-section ratios for C_{56}^{2+} and C_{54}^{2+} also have similar tendencies. The detailed dissociative mechanism of C_{60} was discussed in the presentation.

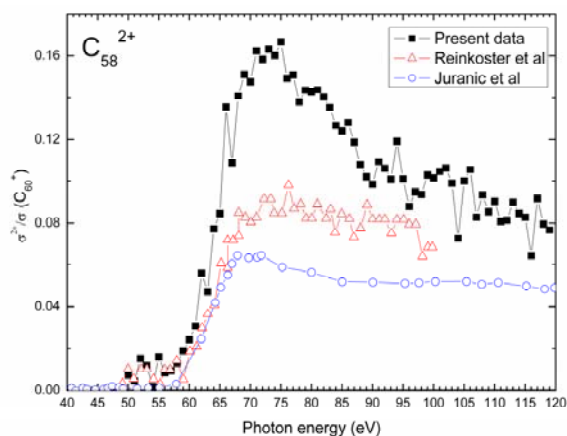


Fig. 1 Double-to-single photoionization cross section ratio of C_{58}^{2+} as a function of photon energy

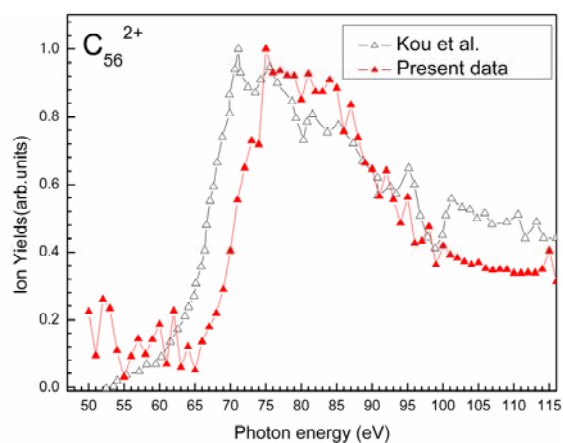


Fig. 2 Ion yield curves of C_{56}^{2+} as a function of photon energy

The appearance energies (AE) of the fragment ions produced from C_{60} were derived from their yield curves or the curves of the cross-section. In comparison to the previous results reported by Kou *et al.*,^[7] we found the present AEs and peak positions of the yield curves of the fragment ions shifted to higher photon energies. The yield curves of C_{56}^{2+} in Fig. 2 exhibits this shift very clearly.

Kinetic energy release of unimolecular dissociation of molecule reveals important information about the dissociation reaction. The kinetic energy release in fragmentation of C_{60} was calculated from the peaks of the produced fragments in the mass spectrum.

References

1. Yoo, R.K. *et al.* J. Chem. Phys., 1991. **96**(2): p. 911-918.
2. Reinkoster, B. *et al.* J. Phys.B. At. Mol. Opt. Phys., 2004. **37**: p. 2135-2144.
3. Juranic, P.N. *et al.* Phys. Rev. A, 2006. **73**: p. 042701.
4. Foltin, M. *et al.* J. Chem. Phys., 1993. **93**: p. 9624-9634.
5. Jensen, J. *et al.* Nucl. Instrum. Methods in Phys. Res. B, 2003. **205**: p. 643-650.
6. Walch, B. *et al.* Phys. Rev. Lett., 1994. **72**: p. 1439.
7. Kou, J. *et al.* Phys. Chem. Chem. Phys., 2005. **7**: p. 119-123.
8. Mitsuke, K. *et al.* AIP Conf. Proc., 2006. **811**: p. 161-166.
9. Mitsuke, K. *et al.* J. Phys. Chem. A, 2007. **111**: p. 8336-8343.