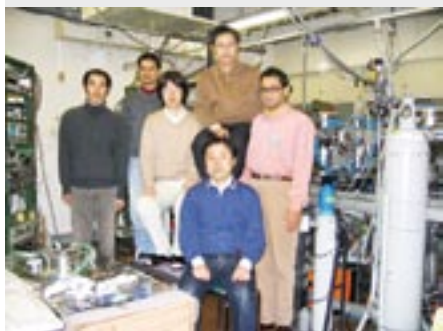


Extreme UV Photoionization Studies of Fullerenes by Using Synchrotron Radiation and High-Temperature Mass Spectrometer

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The interactions of C_{60} , C_{70} , C_{84} ... with high-energy photons have attracted considerable attention, since fullerenes provide unique molecular systems characterized by exceptionally stable electronic structures associated with dense and highly degenerated molecular orbitals and by extremely large vibrational degrees of freedom. In UVSOR we have investigated the yield curves of singly- and multiply-charged photoions from fullerenes by using a grazing incidence monochromator in the $h\nu$ range from 25 to 200 eV. We succeeded in absolutizing the partial and total photoionization cross section curves of $C_{60(70)}$. Moreover, we have measured the yield curves for $C_{60(70)-2n}^{z+}$ from $C_{60(70)}$ as a function of the internal energy of the parent $C_{60(70)}^{z+}$ ions to study the mechanisms and kinetics of sequential C_2 -release reactions.

1. Relative Partial Cross Sections for Single, Double and Triple Photoionization of C_{60} and C_{70} ¹⁾

Partial cross sections for the photoion formation from C_{60} and C_{70} were determined from the yields of singly, doubly and triply charged ions at $h\nu = 25$ –120 eV. The dependence of the detection efficiencies on the mass-to-charge ratio was evaluated by using the formula proposed by Twerenbold *et al.* Corrections of the detection efficiency were found to be critical to obtain accurate partial cross sections. Revisions were made of the partial cross-section curves for single and double photoionization of C_{60} and C_{70} . The curve for triple photoionization of C_{70} was newly proposed. The ratios between the cross sections for double and single photoionization increase with $h\nu$ and reach saturated values of 0.78 at 85 eV for C_{60} and ~ 1.3 at 100 eV for C_{70} . In contrast, the ratios at 120 eV between the cross sections for triple and single photoionization of C_{60} and C_{70} amount to be 0.14 and ~ 0.38 , respectively. Formation mechanism of multiply-charged fullerene ions was discussed in terms of valence-electron excitation to antibonding unoccupied orbitals and/or spherical

standing waves inside the cavity of a fullerene. This excitation could be followed by Spectator Auger processes and transmission of the excess electronic energy among numerous vibrational degrees of freedom.

2. Absolute Total Photoionization Cross Section of C_{60} in the Range of 25–120 eV²⁾

The absolute total photoionization cross section of C_{60} has been measured at $h\nu = 25$ –120 eV. Evaluation has been made on the detection efficiency of fullerene ions in different charge states. The present total photoionization cross section curve has been combined with the absorption cross section curves of C_{60} at $h\nu = 3.5$ –26 eV in the literature, after appropriate alterations of the vapor pressure being taken into account. The oscillator strengths are calculated from the combined cross section curve to be 230.5 and 178.5 at $h\nu = 3.5$ –119 and 3.5–40.8 eV, respectively. These oscillator strengths agree well with those expected from the TKR sum rule. Moreover, the total photoionization cross section curve of the present study is

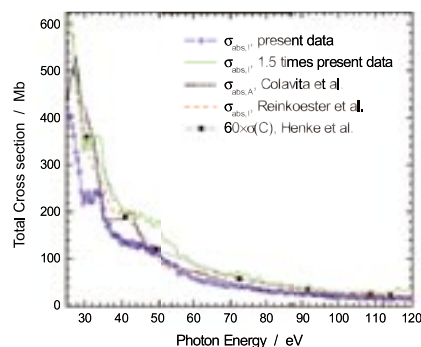


Figure 1. ○, total photoionization cross section $\sigma_{\text{abs,I}}$ of C_{60} of the present study; —, $\sigma_{\text{abs,I}}$ of the present study multiplied by 1.5; ---, experimental $\sigma_{\text{abs,I}}$ by Reinkoester *et al.*; ■, theoretical total photo-absorption cross section $\sigma_{\text{abs,A}}$ by Colavita *et al.*; ■, 60 times $\sigma_{\text{abs,A}}$ of a C atom by Henke *et al.*

consistent with those of recent experimental and theoretical studies (see Figure 1).

3. Relative Partial Cross Sections for Single, Double and Triple Photoionization of C₈₄

The partial cross sections for the photoion formation from C₈₄ were newly determined from the yields of singly, doubly and triply charged ions at $h\nu = 55\text{--}120$ eV. The ratios between the cross sections for double and single photoionization increase with $h\nu$ and reach saturated values of ~ 0.9 at 80 eV. In contrast, the ratios at 120 eV between the cross sections for triple and single photoionization amount to be ~ 0.18 , respectively.

4. Kinetic Energy Analysis of the Fragment Ions Produced from C₆₀ and C₇₀³⁾

We reported the yield curves of the fragments C_{60-2n}^{z+} and C_{70-2n}^{z+} ($n \geq 1, z \geq 1$) produced from C₆₀ and C₇₀, respectively, at $h\nu = 45\text{--}150$ eV. Then the mechanism of sequential loss of C₂ units has been proposed on a basis of comparison between the experimental ion yield curves and theoretical fractional abundance curves. The latter curves have been derived by employing the RRKM theory to individual unimolecular reactions, C_{60-2n+2}^{z+} \rightarrow C_{60-2n}^{z+} + C₂. More reliable calculations of the rate constants of these reactions are needed before closer comparison between the two curves. For such calculations we should know precise values of the activation energies for the reactions, together with the vibrational spectra of the transition states. This induced us to develop a new spectrometer for the fragment ions. It is likely that the magnitude of the potential barriers can be estimated from the average kinetic energy release measured by this spectrometer.

5. Scattering Distributions of the Photofragments from Fullerenes

We are developing an imaging spectrometer to measure the three-dimensional momentum distributions of the ionic photofragments produced from fullerenes at $h\nu > 50$ eV. High kinetic-energy resolution is expected to be achieved on the images by adopting the Eppink-Parker type velocity focusing lens system. We will be able to distinguish the two possible mechanisms of fragmentation of fullerene ions, *i.e.* stepwise C₂ ejection and direct fission into two species, since different momentum distributions result in different projected images on the position sensitive detector.

6. ZEKE Photoelectron Spectroscopy Using the Dark Gap of the Storage Ring

We have constructed a threshold photoelectron spectrometer for the purpose of measuring the signal of threshold electron-photoion coincidence (TEPICO), using the dark gap

of the UVSOR facility. Such measurements provide us with the detailed information about the excitation/de-excitation and decay processes of C₆₀ and C₇₀. We already succeeded in observing the electron signal from He and O₂ samples, but the spectra suffered from intense background counts. The background needs to be reduced to the utmost for performing the TEPICO measurement. It is also necessary to improve the efficiency of the spectrometer for threshold electrons. We are therefore developing an improved version of the spectrometer which has the capability to significantly reject the electrons with high kinetic energies and to guide slow electrons ($KE = 0$ to 10 meV) to the detector.

7. High Resolution Photoelectron Spectroscopy of Gaseous C₆₀

Photoelectron spectroscopy (PES) of solid C₆₀ has been performed by several groups to clarify its electronic structure. However, comprehensive PES studies of gaseous C₆₀ are few and the energy resolution was ~ 100 meV at the best. This resolution was not enough to distinguish closely spaced bands, though many degenerate bands are located in the 7–40 eV ionization energy range. We are developing an apparatus of high-resolution angle-resolved PES. Our goal is to carry out PES of various kinds of fullerenes with a total energy resolution of ~ 20 meV at the UVSOR facility. The partial photoionization cross section and anisotropy parameter of each band are expected to be determined at $h\nu = 25\text{--}150$ eV.

8. Photodissociation of Butyl Cyanides and Butyl Isocyanides⁴⁾

Photodissociation process to produce the electronically excited CN(B Σ^+) fragment has been studied for four structural isomers, *n*-C₄H₉CN, *t*-C₄H₉CN, *n*-C₄H₉NC and *t*-C₄H₉NC by using synchrotron radiation. Photoexcitation spectra for the CN(B² Σ^+ \rightarrow X² Σ^+) transition were measured in the excitation wavelength range of 85–165 nm (7.5–14.5 eV) and the CN(B² Σ^+ \rightarrow X² Σ^+) emission spectra were dispersed at several wavelengths in the range of 57–140 nm. Quantum yields for the production of the CN(B) state from photodissociative excitation of the isocyanides were larger than those from the cyanides. The quantum yields from the molecules consisting of a *tertiary*-butyl group were larger than those from the *normal*-butyl compounds.

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