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

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Interactions of C_{60}, C_{70}, C_{84} … with photons have attracted considerable attention, since fullerene family 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 succeeded in determining the total photoabsorption cross section curves of $C_{60(70)}$ at $h\nu$ = 1.3 to 42 eV by using photon attenuation method. Moreover, the yield curves of singly- and multiply-charged photoions from fullerenes were measured at $h\nu$ = 25 to 200 eV. We have studied the mechanisms and kinetics of sequential C_2-release reactions from the yield curves for $C_{60(70)-2n}^{z+}$ as a function of the internal energy of the parent $C_{60(70)}^{z+}$ ions. To gain more insight into the dissociation mechanisms we have constructed a velocity map imaging spectrometer for achieving the 3D velocity distributions of the fragments $C_{60(70)-2n}^{z+}$.

1. Photoabsorption Cross Section of C_{60} Thin Films from the Visible to Vacuum Ultraviolet[1)]

Absolute photoabsorption cross sections of C_{60} thin films are determined in the $h\nu$ range from 1.3 to 42 eV by using photon attenuation method. The spectrum shows a prominent peak of 1180 Mb at 22.1 eV with several fine structures due to single-electron excitation similarly to the case of C_{60} in the gas phase. The complex refractive index and complex dielectric function are calculated up to 42 eV through the Kramers-Kronig analyses. From the present data of C_{60} thin films the cross section curve of a molecular C_{60} is calculated with an assumption that the polarization effect of surrounding C_{60} molecules can be expressed by the standard Clausius-Mossotti relation. The spectrum thus obtained shows an excellent agreement with that of C_{60} in the gas phase measured independently.

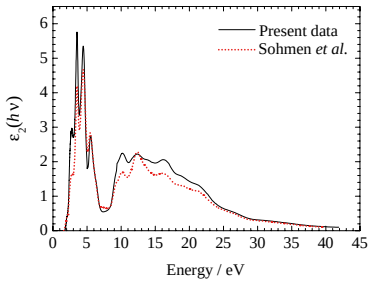

Figure 1. Dependences on $h\nu$ of $\varepsilon_2(\nu)$ of the complex dielectric function $\varepsilon(\nu) = \varepsilon_1(\nu) + i\varepsilon_2(\nu)$ of the C_{60} film.

2. Photoabsorption Cross Section of C_{70} Thin Films from the Visible to Vacuum Ultraviolet

Absolute photoabsorption cross sections of C_{70} thin films are determined in the $h\nu$ range from 1.3 to 42 eV by using photon attenuation method. The spectrum shows a prominent peak of 1320 Mb at 21.4 eV with several fine structures probably due to single-electron excitation. The complex refractive index and complex dielectric function are calculated up to 42 eV through the Kramers-Kronig analyses. From the present data of C_{70} thin films the cross section curve of a molecular C_{70} is calculated using the standard Clausius-Mossotti relation dealing with the correction of the local electromagnetic field, with a plausible assumption that the molecular rotation at room temperature could smear out the effect of the anisotropic molecular structure of C_{70}.

3. Performance Test of a New Velocity Map Imaging (VMI) Spectrometer[2)]

We have constructed a photoion imaging spectrometer to measure the velocity distributions of fragments produced by dissociative photoionization of fullerenes with synchrotron

radiation. The performance of this spectrometer has been tested using rare gas samples at room temperature. We have compared the images experimentally obtained with those generated by a simulation program based on a field free expansion of photoions. The experimental and simulated images agree well with each other, if we assume the Maxwell-Boltzmann velocity distribution and the Gaussian distribution for the defocusing of the images with a standard deviation σ of 2 mm.

4. VMI of C_{60} Molecular Beams[3)]

The speed and angular distributions of C_{60} molecular beams have been determined by using a VMI technique for photoions produced by irradiation of synchrotron radiation. The C_{60} powder in the sample cell was heated and the beam was generated in an effusive condition. The two-dimensional projection of the velocity distribution was recorded (Figure 2) as an image on the position sensitive detector (PSD), and was converted to the speed and angular distributions. The speed distribution was expressed by the Maxwell-Boltzmann distribution at the temperature of the sample cell, while the angular distribution was determined by the geometry of the fullerene beam source. The speed distribution of helium in thermal motion was used to calibrate the velocity scale.

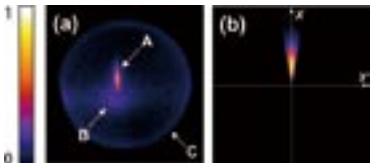

Figure 2. (a) Ion image of the fullerene beam at $h\nu$ = 70 eV. Pattern A is assigned to the signal of the C_{60} beam. (b) Ion image of the fullerene beam by computer simulation.

5. VMI Spectroscopy of Photofragments from C_{60} Beams

Simulations have been performed to calculate the scattering distributions of C_{56}^+ fragment ions produced by two different mechanisms of dissociative photoionization of C_{60}: (1) sequential ejection of C_2 units and (2) fission into $C_{56}^+ + C_4$. The simulated images for the two mechanisms can be distinguished clearly at T = 0 K, whereas their differences appear to be less obvious for bulk C_{60} at room temperature. Nevertheless, our VMI spectrometer is found to have an enough resolution under the beam condition to reveal such differences in the velocity distribution, because the transverse velocity of the beam is estimated to be less than 20 m s^{-1} even at T = 785 K.

6. Revision of our VMI Spectrometer[4)]

We have improved our earlier version of VMI spectrometer to be applied for measuring the momentum distributions of the fragments from fullerenes. The revised spectrometer is equipped with four electrostatic lens elements, a drift tube, a mass gate and a PSD. Application of an additional element to the conventional three-element lens system provides better focusing of an extended interaction region. Moreover, the electric field in the ionization region is kept cylindrically symmetric in spite of the field penetration from the oven and surface thickness monitor. The optimum arrangement and dimensions of the elements are determined from the calculations of ion trajectories of C_{56}^+, C_{58}^+ and C_{60}^+.

7. Measurements of Incident Photon-to-Current Efficiency (IPCE) and Photoabsorbance of Dye-Sensitized Solar Cells

We have fabricated dye-sensitized solar cells (DSC) comprised of Ru535 dye and PN50 electrolyte and measured their short current and the intensity of the transmitted light to estimate the wavelength dependence of the incidence photon-to-current efficiency (IPCE) and photoabsorbance (ABS) in the range of 300 to 1000 nm. In addition, we evaluated the quantum yield (EIQY) of DSCs for the electron injection from the excited orbital of Ru535 dye to the conduction band of TiO_2 nano particles. Our final goal is to develop DSCs with high performance and long lifetime by improving mainly ABS and EIQY in the near infrared region.

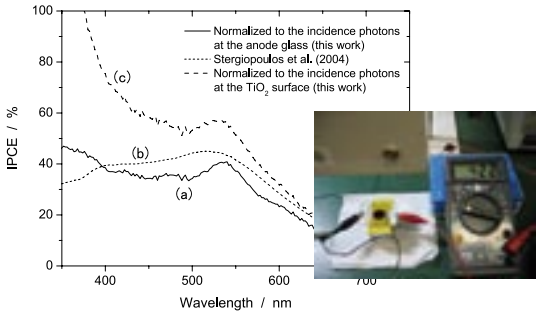

Figure 3. IPCE curves of dye-sensitized solar cells comprised of Ru535 dye and PN50 electrolyte. Normalization is made to the incidence light either (a) at the anode FTO glass or (c) at the TiO_2 surface. (b) Reported by Stergiopoulos *et al.* in 2004.

References

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