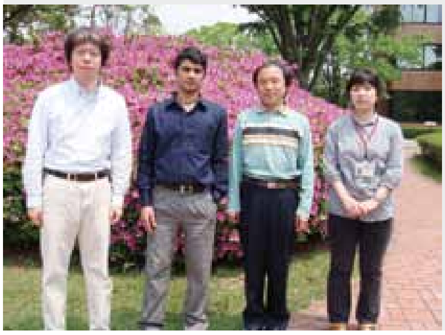
Photoabsorption and Photoionization Studies of Fullerenes and Development of High-Efficiency Organic Solar Cells

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



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We have observed the formation of multiply-charged photoions from gaseous fullerenes or aromatic hydrocarbons irradiated with synchrotron radiation at $h\nu$ = 25 to 200 eV. We thus studied the mechanisms and kinetics of consecutive C_2-release reactions on the basis of (i) the yield curves for the fragments $C_{60(70)-2n}{}^{z+}$ ($n \geq 1$, z = 1–3) as a function of the primary internal energy and (ii) the three dimensional velocity distributions of the fragments. The velocity distributions of $C_{60-2n}{}^{z+}$ and $C_{70-2n}{}^{z+}$ were measured for the first time. Concepts of the microcanonical temperature and Arrhenius-type rate constants for individual C_2 ejection steps allowed us to compare the experimental total average kinetic energy with theoretical kinetic energy release predicted from the “model free approach” developed by Klots.

In the second topic, we have fabricated dye-sensitized solar cells (DSSCs) containing ruthenium dye, iodide electrolyte, and platinum or carbon nanotube catalysts. The incidence photon-to-current conversion efficiencies (IPCE) and photoabsorbance (ABS) were measured in the range of 300 nm to 1 µm. We also evaluated the quantum yield (APCE) of DSSCs for the electron injection from the excited orbital of Ru dye to the conduction band of mesoporous TiO_2 nanoparticles. Our final goal is to develop DSSCs with high performance by improving ABS and APCE.

1. Photodissociation Dynamics of Fullerenes by Velocity Map Imaging with Improved Mass Resolution

We observed images of three-dimensional scattering velocity distributions of fragments produced by the photodissociation of the fullerenes, C_{60} and C_{70}, using a mass-resolved velocity map imaging spectrometer.[1,2] From the images we successfully obtained translational temperatures of the fragments and kinetic energy releases. Still the peaks of the fragments were found to be partially overlapped in their time-of-flight (TOF) mass spectra. We tried to improve the mass resolution of the imaging spectrometer by adding a focusing electrode to the Eppink-Parker type imaging electrode assembly.[3] This focusing electrode was designed after the ion lens device presented by Peši.

After introducing the focusing electrode, vertical stripes involving the fragment ions are completely resolved in the velocity vs. TOF maps, or y–t maps, and their masses are unquestionably identified. The y–t maps with improved mass resolution were obtained for C_{70} with the excitation photon energy $h\nu$ range of 70–125 eV. The translational temperature T_{trans} of each fragment was extracted from the map. The $h\nu$ dependence of T_{trans} exhibits the same propensity as that obtained previously[2] at low mass resolution. For $C_{60}{}^{2+}$ from C_{70} singularity in T_{trans} remains also in the present measurements. Probably the $C_{60}{}^{2+}$ formation mechanism is quite different from the stepwise C_2 emission from C_{70} that has widely been accepted for the other fragments.

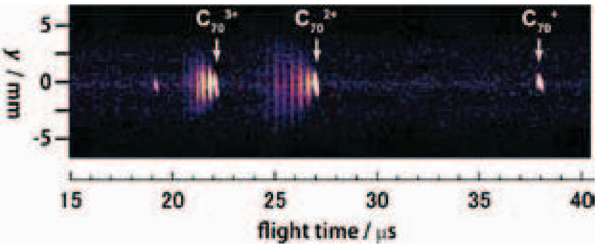

Figure 1. Y–t map of parent and fragment ions produced from C_{70} with the excitation $h\nu$ of 110 eV. The y coordinate is proportional to the y component of the ion velocity.

2. Estimation of the Translational Temperatures of High-Speed Fragment Ions Released from Sumanene and Coronene

Dissociative photoionization processes of polycyclic aromatic hydrocarbons (PAHs), sumanene $C_{21}H_{12}$ and coronene

$C_{24}H_{12}$, were studied by a mass-resolved velocity map imaging (VMI) technique. Since PAHs constitute the substructures of C_{60}, their behaviors in fragmentation are expected to have some analogies with those of fullerenes. Nevertheless, the y–t maps revealed a large difference in fragmentation mechanisms between PAHs and C_{60}. Main species produced from $C_{21}H_{12}$ and $C_{24}H_{12}$ were singly–charged ions with very high speed: CH^+, $C_2H_2^+$ and $C_nH_{n/2}^+$ ($2 < n < 13$). The translational energies of these fragments are so large that the scattering distributions extend beyond the coverage of our imaging apparatus. The peak profiles of the time-of-flight distributions were computer simulated on the basis of the ion trajectories calculated by the Simion–3D software. The translational temperatures of fragments from $C_{21}H_{12}$ were thus estimated to be 3000 to 30000 K (see Figure 2), depending on the number of carbon atoms in the fragments. A similar trend was observed for dissociation of $C_{24}H_{12}$. Our results suggest that dissociation of PAHs proceeds through the fission mechanism, which is not dominant in the fullerene cases.

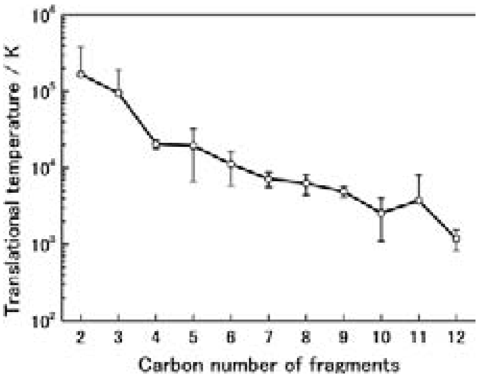

Figure 2. Translational temperatures of the fragment ions from coronene at $h\nu$ = 100 eV. Error bars show the standard deviations of repeated experimental runs.

3. Enhancement of the Solubility, Thermal Stability, and Electronic Properties of Carbon Nanotubes Functionalized by MEH-PPV

Multi-walled carbon nanotubes functionalized with poly [2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MWCNT-f-MEH-PPV) nanocomposites were successfully prepared by employing a "grafting from" approach.[4)] The content of the functionalizing MEH-PPV in the composites was observed as 76%wt. Compared with pristine MWCNT, p-MWCNT, the aqueous solubility and thermal stability of the former are significantly enhanced. The effect of covalently and non-covalently functionalized nanotubes on the performances of the DSSCs has been investigated. The cells having the counter electrodes coated with isolated MEH-PPV, p-MWCNT/MEH-PPV, and MWCNT-f-MEH-PPV/MEH- PPV were fabricated. The cells based on a MWCNT- f-MEH-PPV/MEH-PPV counter electrode demonstrate the best photovoltaic performance as observed by higher J_{SC}, V_{OC}, and FF values. The experimental phenomena can be explained by quantum chemical calculations: Charge transfer from MEH-PPV oligomers to nanotubes is greater when covalently functionalized than when non-covalently functionalized. These suggest that the improvement in the photovoltaic parameters of the cells containing covalently functionalized nanotubes results not only from the higher concentration present in the nanotube films of the counter electrode, but also from the greater electron delocalization between the oligomers and nanotubes. The obtained results are very useful for enhancement of functionalized nanotubes applied to DSSCs.

4. Gas Phase Spectroscopy of Carbon Nanotubes

Our efforts have been concentrated on elucidation of the electronic and optical properties of fullerenes as well as their reaction dynamics in the gas phase. Such knowledge is critical in applying fullerenes to molecular functional devices. Recently, we started to investigate the properties of gaseous carbon nanotubes (CNTs) which of course form another group of promising carbon material.

CNTs are vaporized by matrix assisted laser desorption ionization (MALDI) and analyzed by time-of-flight (TOF) mass spectrometry. Commercially available multiwall CNT powder and single-wall CNT aqueous dispersion were used as samples. We have checked several solvents and matrices to optimize the MALDI conditions. The images of electron microscope prove that the laser irradiation certainly gives rise to vaporization of the sample. A temporal increase in the pressure of the sample chamber also supports the vaporization during the laser irradiation. Nevertheless, the signal of whole CNTs has not been observed yet. Smaller fragment ions C_n ($n < 200$) were only detected. Interaction between matrices and dispersants may prevent effective ionization.

We will continue to seek for the suitable vaporization method and construct a new vacuum chamber for the gas phase CNT experiment. The chamber will be connected to the beamline 4B in the UVSOR facility. Photoabsorption and photoionization experiments will be performed using the same chamber at the outset.

References

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