

Photofragment Imaging Apparatus for Measuring Momentum Distributions in Dissociative Photoionization of Fullerenes

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In dissociative photoionization of solitary fullerenes (C_{60} , C_{70}), we have measured the fragment (C_{60-2n}^{z+} , C_{70-2n}^{z+}) yield curves in the photon energy range of 45-150 eV [1,2]. From the results it is concluded that the excess energy is statistically distributed among the internal degrees of freedom of the parent ions (C_{60-2n}^{z+} , C_{70-2n}^{z+}) and C_2 units are ejected sequentially. Moreover, the results imply that the dissociation has no potential barrier and that no resonant state participates in the dissociation. To clarify these implications, we designed the photofragment imaging apparatus based on the time-of-flight mass spectrometer that we had constructed. From the photofragment images, we will be able to extract the kinetic energy and angular distributions of the fragments. These distributions reveal clearly whether there exist a barrier and/ or resonance.

We adopted the Eppink-Parker type velocity focusing electrodes [3] to achieve the kinetic energy resolution of ca. 0.01 eV on the photofragment images. To select a bunch of fragments having the same mass-to-charge ratio m/z from neighboring bunches ($m \pm 24$)/ z , for example, separating C_{58}^+ from C_{60}^+ and C_{56}^+ , we designed a mass gate which consists of a cylindrical potential switch and retarding electrodes. In order to optimize the dimensions of the setup, we performed ion trajectory simulations utilizing SIMION version 7.0 [4]. The most suitable dimensions were achieved

already as depicted in the Fig. 1.

The operation principle of this setup is as follows: As long as the tube of the potential switch is kept grounded, all fragments are reflected back by the retarding electrode and do not impinge an imaging detector. When an entire bunch of fragments having a desired mass enters inside the tube, the pulsed voltage is applied to the tube. The potential felt by the bunch are suddenly elevated and the bunch passes through the retarding electrode and thus can reach the 2D detector.

Parts of this setup are being fabricated at the machine shop in the Institute for Molecular Science. The parts will be installed in the end-station at the BL2B in the UVSOR facility, where the synchrotron radiation from bending magnet is dispersed by the 18-m spherical grating grazing incidence monochromator of dragon type. We are planning to examine the performance of the apparatus using SF_6 as a standard sample.

[1] J. Kou *et al.*, Phys. Chem. Chem. Phys. **7** (2005) 119.

[2] K. Mitsuke *et al.*, Am. Inst. Phys. CP **811** (2006) 161.

[3] A.T.J.B. Eppink and D.H. Parker, Rev. Sci. Instrum. **68** (1997) 3477.

[4] D.A. Dahl, SIMION 3D 7.0, Scientific Instrument Services Inc., Boise Idaho, 2000.

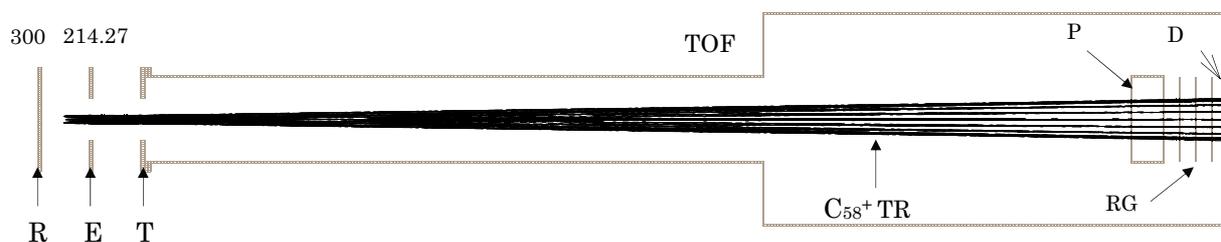


Fig. 1 Schematic 2D view of the imaging lens setup in combination with potential switch and kinetic energy analyzer. Trajectories of C_{58}^+ fragment ions having initial KE of 0.1 eV are drawn. R: Repeller; E: Extractor; T: Tube Electrode (grounded); TOF: TOF Tube; P: Potential switch; RG: Retarding grid; D: Detector.

Development of an Apparatus for Coincidence Measurements of Threshold Electrons and Ions Produced by Dissociative Photoionization of Fullerenes

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We developed an apparatus for threshold electron – photoion coincidence (TEPICO) measurement to make clear the photodissociation mechanism of gaseous fullerenes (C_{60} , C_{70}).

We had measured yield curves of photoions which were produced by dissociative photoionization of the fullerenes with the synchrotron radiation in the photon energy range of 45 – 150 eV [1,2]. We found that the fullerenes lose C_2 units sequentially. As a result, we concluded that the photodissociation mechanism can be described by statistical energy redistribution. We derived this conclusion from the comparison between the experimental yield curves and results of the RRKM calculation performed by us. In this comparison, in order to evaluate internal energies of parent fullerene ions, we assumed that the energy of the photoelectrons is zero. This assumption, however, is valid only at onsets of yield curves. At the onsets, it is appropriate that all the excess energy change to the internal energy of parent ions and zero kinetic energy (threshold) electrons be emitted. We thus could make the comparison only close to the onsets. Once high-energy electrons begin to be emitted, we cannot convert the photon energy directly to the internal energies of the parent ions because a portion of excess energy is transmitted to a kinetic energy of emitted electrons.

A photoelectron – photofragment coincidence measurement allows us to regulate the internal energies of the parent ions. Using the TEPICO technique, the internal energies are directly related to the energy of the synchrotron radiation. Development of a TEPICO apparatus enables us to discuss the dissociation mechanism beyond the onsets.

We designed a set of electrodes to perform the TEPICO measurement. The set was produced at the machine shop in IMS and installed in an endstation at the beamline 2B in UVSOR. Figure 1 shows sectional view of an assembly of the electrodes. The operation principle is as follows. We utilized “dark gaps” in which electron bunches were thinned out in a temporal profile of the synchrotron radiation. No ionization takes place during the dark gap. While the threshold electrons can linger at the ionization region even in the dark gap, high-energy electrons escape immediately. Only the threshold electron signals are detected by an application of a pulsed voltage to an electron repeller (b) after escaping of the high-energy electrons. Using the electron signal as a trigger to apply a pulsed voltage to an ion repeller (c),

photofragments produced simultaneously with threshold electrons can be detected.

Prior to an application to fullerenes, we examined the efficiency of our apparatus to select threshold electrons using helium and oxygen as samples. Figure 2 shows threshold electron spectrum of oxygen. A peak was observed at 24.56 eV and its energy corresponded to a transition to the c ($^4\Sigma_u^-$) state. The spectra, however, suffer from intense background. The background consists of high-energy electrons emitted by transitions to lower energy states than c ($^4\Sigma_u^-$) and electrons generated by stray light.

Although we succeeded in observing threshold electrons from gaseous samples, the background needs to be reduced to the utmost in order to perform the TEPICO measurement. It is necessary that we improve the efficiency to collect threshold electrons. Electron trajectory simulations to seek for the best design of the electrodes are under way.

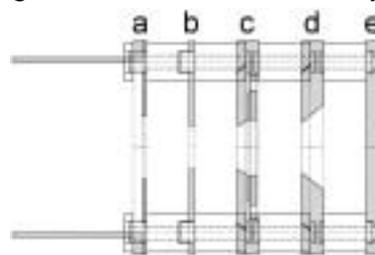


Fig. 1 Sectional view of the TEPICO electrode assembly. Symbols in the figure stand for a: entrance of ion TOF tube, b: electron repeller, c: ion repeller, d: ground plate, e: MCP support plate (made of Teflon). Ionization region is between b and c. Metal mesh is put at each hole.

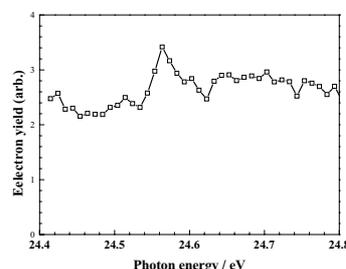


Fig. 2 Threshold electron spectrum of oxygen.

[1] J. Kou *et al.*, Phys. Chem. Chem. Phys. **7** (2005) 119.

[2] K. Mitsuke *et al.*, AIP Conference Proceedings **811** (2006) 161.

Improvement of the Horizontal Beam Size at the XES Endstation of BL3U

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Last year we constructed an XES (x-ray emission spectroscopy) endstation of the undulator beamline BL3U. High-resolution soft-x-ray emission spectroscopy generally requires small beam size at the sample position, because a smaller opening of the spectrometer entrance slit is needed to achieve higher energy resolution. At the XES endstation of BL3U, we have installed a transmission-grating spectrometer for high-energy resolution XES. In order to get the maximum energy resolution, the spectrometer demands a beam size of 1 μm in the energy dispersion direction, which is achieved by an entrance slit with an opening of 1-30 μm . In contrast to the conventional Rowland spectrometer, the present spectrometer demands a beam size less than 200 μm in the non-dispersion direction as well. This is because the spectrometer is equipped with an Wolter type I pre-mirror with a collection angle as high as 1.5×10^{-3} sr at the expense of a considerable aberration [1]. In the case of solid samples, where small grazing angle of 20° is used in order to avoid self absorption, horizontal beam size of less than 68 μm ($=200 \cdot \sin 20^\circ$) is required.

Since April 2005, the beam emittance of the operation mode of the UVSOR-II ring has been upgraded from 60 nm-rad to 27.4 nm-rad. The horizontal electron beam size at the BL3U undulator has been improved from 890 to 602 μm (σ), accordingly. As depicted in Fig. 1, the horizontal beam profile at the sample position is an image of the horizontal electron source profile demagnified by the M2X mirror (1/23.4). Thus, the horizontal beam size is expected to be smaller since April 2005 owing to the upgraded operation mode.

The horizontal beam size has been measured by using a knife-edge method. By fitting with an error function, we have obtained a full width half maximum FWHM for the horizontal direction of 41.2

μm at 115 eV as shown in Fig. 2, where the beam profile obtained in October 2005 is compared with the one taken in Dec. 2004. The results clearly show that the smaller emittance offered smaller beam size in the horizontal direction. The current horizontal beam size is 57 % of the one in 2004 in accord with the reduction of the electron beam size.

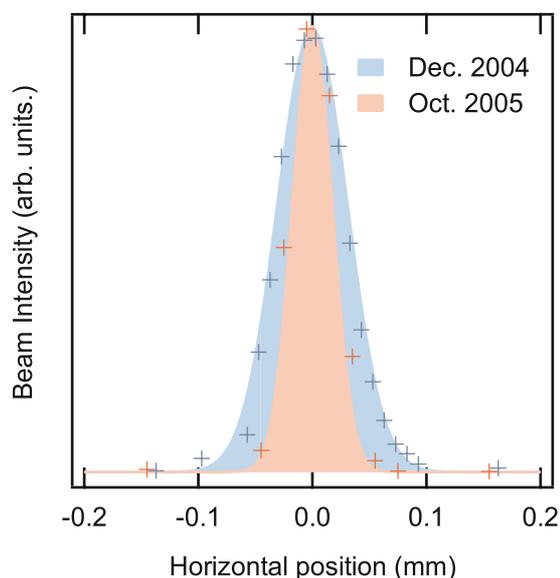


Fig. 2 Horizontal Beam Profile at the sample position ($h\nu = 115$ eV) measured in Dec. 2004 and October 2005 with FWHM of 72.1 ± 1.3 μm and 41.2 ± 1.46 μm , respectively.

[1] T. Hatsui, H. Setoyama, E. Shigemasa and N. Kosugi, *J. Electron Spectrosc. Relat. Phenom.* **144** (2005) 1059.

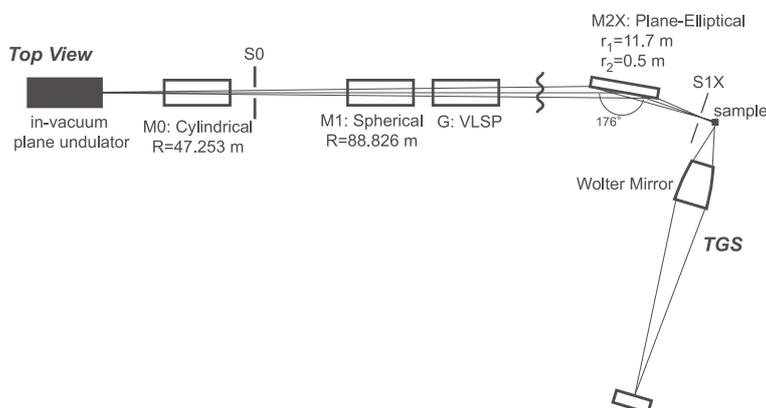


Fig. 1 Schematic Optical Layout of BL3U in XES mode.

Development of a Transmission-Grating Spectrometer for High-Resolution Soft X-Ray Emission Studies

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High resolution soft x-ray emission spectroscopy (XES) in combination with synchrotron radiation as incident soft x-rays has been extensively used to study valence states of solid, liquid, and gas phase systems. The design of their grazing-incidence spectrometer is based on the Rowland circle mount. In this case, the horizontal acceptance angle is mainly limited by the detector size. In order to achieve higher resolution, the Rowland radius, R , or the spectrometer size, should be larger due to the relationship of $\lambda/\Delta\lambda \propto R$. The detector size is however limited. It is therefore desirable to design a novel optical system which can focus the emitted x-rays not only in the (vertical) dispersion direction but also in the other (horizontal) direction. In addition, recent advances make the charge-coupled devices (CCD) a promising soft-x-ray detector. It is however not a trivial problem to adopt it in the high resolution Rowland spectrometer, since the CCD detectors have low quantum efficiency at the small grazing-incidence angle.

In order to overcome these difficulties, we have developed a transmission-grating spectrometer (TGS). This spectrometer is designed to realize a resolution $E/\Delta E$ up to 5000 in the energy region of 50–600 eV with high throughput (Fig. 1) [1]. The spectrometer has a Wolter type I premirror, a free-standing transmission grating (TG), and a back-illuminated CCD. The Wolter mirror with a high collection angle of 1.5×10^{-3} sr shows a slope error better than 0.4 arcsec [2]. A self-standing TG made of silicon carbide with a groove density of 6250 lines/mm has been developed [3]. The UHV compatible back-illuminated CCD has been developed [4]. By measuring the center of the electron charge cloud generated in

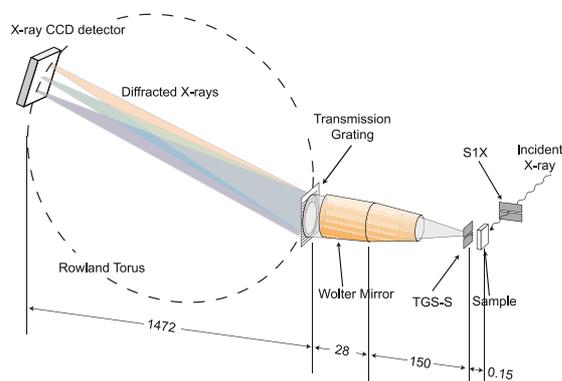


Fig. 1 Schematic Layout of the transmission grating spectrometer. The distances between the optical elements are shown in mm (not to scale).

depletion layer [4], the spatial resolution of the CCD was found to be less than $2 \mu\text{m}$ for photon energy larger than 500 eV. The CCD detector is mounted at 1.472 m downstream of the grating on a Rowland torus mount. Diffracted x-rays are detected in the normal incidence geometry, resulting in high detection efficiency. Ray-trace simulations using TGSGUI code [5] indicate that aberrations do not practically degrade the energy resolution as high as 5000 [1]. The energy resolution was examined by measuring the diffuse scattering of 114 eV photons. Without the entrance slit, TGS shows an energy resolving power of 3000 with high count rate, where the resolution is limited by the source size. Further evaluation of the performance by introducing the entrance slit has been carried out with a slit opening of $1 \mu\text{m}$. The results indicated that the energy resolution is better than 4500 at 114 eV (Fig. 2).

[1] T. Hatsui *et al.*, *J. of Electron Spectrosc. Relat. Phenom.* **144** (2005) 1059.

[2] Manufactured by A. Ohba, S. Onoda, and Y. Sugiyama (Hamamatsu Photonics).

[3] Manufactured by NTT-ATN.

[4] J. Hiraga *et al.*, *Jpn. J. Appl. Phys.* **40** (2001) 1493.

[5] T. Hatsui, <http://www.uvsor.ims.ac.jp/TgsguiHatsui/index.html>

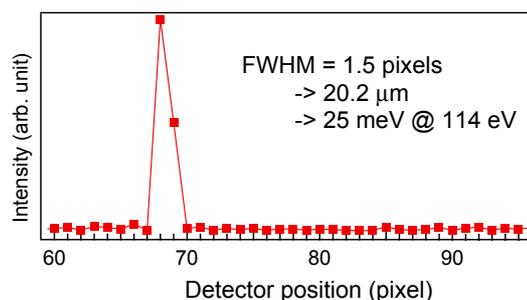


Fig. 2 Intensity profile of 114 eV x-rays on the CCD detector along the dispersion direction.

Beamline BL4A2 for Synchrotron Radiation Etching Using XeF₂ as Reaction Gas

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Synchrotron radiation etching has unique characteristics such as low damage, beam induced (spatially localized) process, and unique material selectivity. However, the etching rate, order of 10 Å/min, obtained by using the conventional etching gas such as SF₆ is too low to apply it to the micro-fabrication of MEMS devices, which require the etching rate of the order of 1 μm/min. So we have constructed an etching beam line using XeF₂ as an etching gas, which is known to give a rate of order of 1 μm/min in the fabrication of MEMS devices [1]. A unique anisotropicity and material selectivity between SiO₂ and Si are expected to appear by carrying out XeF₂ etching under the SR irradiation. Since XeF₂ is an extremely corrosion, the SR beam is introduced into the reaction chamber through the LiF window as shown in Fig. 1.

Furthermore, to reduce the damage of LiF window by the SR irradiations, the high energy part of the SR beam, which corresponds to the absorption region of LiF, is attenuated by reflecting ($\theta=25$ degree in Fig.2) the beam using a pair of Al coated plane mirrors attached to the mirror holders of the double crystal monochromator in BL4A2 (Fig.2). The spectrum distribution of the incident SR beam to the LiF window was calculated. Etching rates for Si and SiO₂, and the SR irradiation effects are going to be measured in the 2006 year beam time.

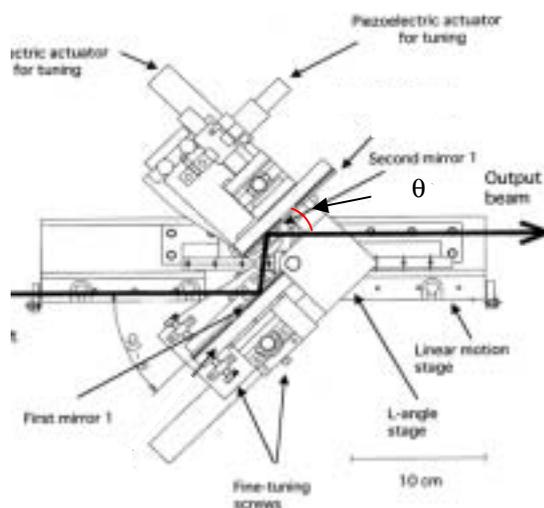


Fig. 2 Double crystal monochromator of BL4A2.

[1] B. Li, U. Streller, H.-P. Krause, I. Twesten and N. Schwentner, J. Appt. Phys. **77** (1995) 1.

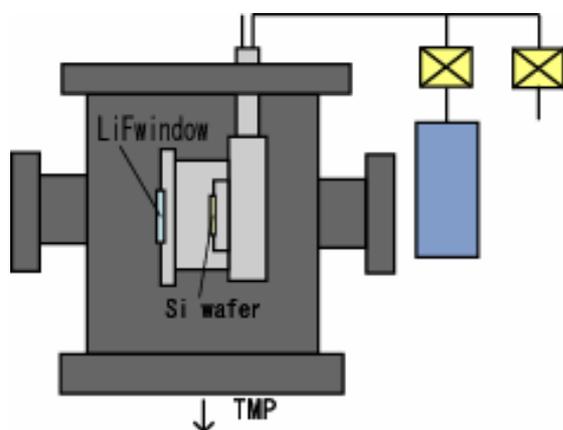


Fig. 1 Chamber for XeF₂ etching.

Development of Electron–Ion Coincidence Spectrometer for Studies on Decay Dynamics of Core Excited Molecules

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A new electron-ion coincidence spectrometer for studies on decay dynamics of core excited/ionized molecules has been developed. Energy and ejection angle of electrons, and momentum vectors of fragment ions are simultaneously measured in each event by means of a multi-coincidence technique. The coincidence spectrometer consists of a double toroidal electron analyzer (DTA), a three-dimensional ion momentum spectrometer which are followed by time- and position-sensitive detectors (PSD) as schematically illustrated in Fig. 1. The present system is based on the Auger electron–ion coincidence setup using the original DTA combined with an ion mass spectrometer [1].

The Auger electron is energy analyzed by DTA, while the ions are extracted from the interaction region by a pulsed electric field triggered by the detection signal of the electron, and the time-of-flight (TOF) of the ions and their position information on the ion PSD are obtained. The information gained enables the reconstruction of initial momentum vectors of fragments. In order to achieve high resolution for ion momentum measurements, we have newly designed the electrostatic lenses for ion trajectory focusing. The time focusing as well as space focusing conditions for the ions are satisfied by introducing the lens system, even in the pulsed electric field. A high performance pulse generator is the key to realizing the present experiments. We introduce a new high voltage pulse generator with the electronic time delay of 160 ns and rise time of 20 ns.

We have carried out photoelectron–ion coincidence measurements for the Ar $2p$ photoionization of Ar, as a performance test of the spectrometer. The TOF spectrum and two dimensional image of the Ar ions detected with the Ar $2p$ photoelectrons are shown in Fig. 2. Multiply charged Ar ions, which are produced through the Auger decay of the $2p$ hole states, are clearly resolved in the TOF spectrum. The narrow TOF peaks and the small spot on the image clearly indicate that the time and space focussing for the ions are well satisfied. So far the time focussing less than 17 ns (FWHM), and the space resolution of 2.8 mm (FWHM) have been achieved. The relative intensities of the product ions in this measurement are 84%, 14% and 2% for Ar^{2+} , Ar^{3+} and Ar^{4+} , respectively. The charge state ratio well agrees with the experimental result obtained by the photoelectron-ion coincidence spectroscopy [2]. This result suggests that the transmission of the momentum spectrometer and the detection efficiency of the ion PSD for various Ar ions are almost constant

without any calibrations.

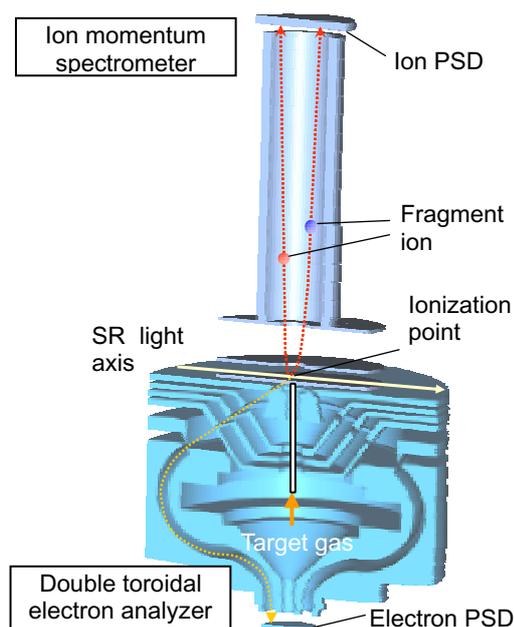


Fig. 1 Three-dimensional view of the electron-ion coincidence spectrometer.

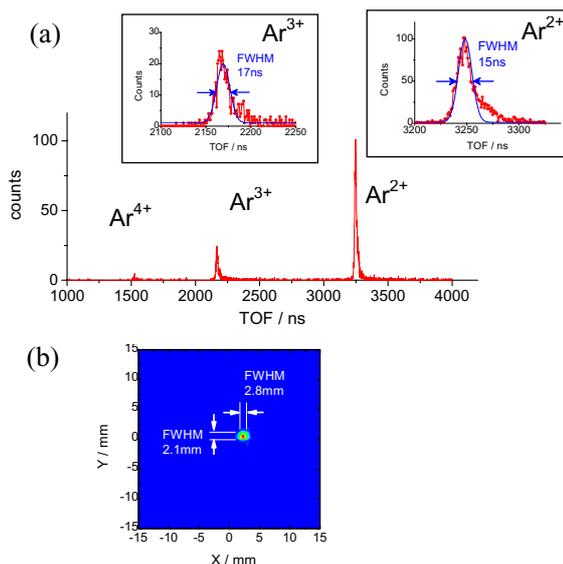


Fig. 2 (a) Time-of-flight spectrum of product Ar ions through the Ar $2p$ Auger transitions. The ions are extracted from the interaction region by pulsed electric field triggered by the detection of Ar $2p$ photoelectron. (b) Image of Ar ions on PSD.

[1] D. Céolin *et al.*, *J. Electron. Spectrosc. Relat. Phenom.* **141** (2004) 171.

[2] S. Brünken *et al.*, *Phys. Rev. A* **65** (2002) 042708.

Spatial Resolution of the THz Microscope

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Infrared synchrotron radiation (IR-SR) is a powerful tool for microspectroscopy and imaging not only in the IR but also in the terahertz (THz) regions because of its high brilliance. Then almost all IR-SR beamlines in the world equip commercial IR microscopes that are available only in the IR region. The commercial IR microscope has an advantage of the conventional apparatus but it is not suitable for the THz region. Then we install a newly designed IR microscope that covers down to the THz region.

The design concept is as follows; 1) Large working distance because some special experiments including at very low temperature, under high pressure, a near-field spectroscopy and so on are planned, 2) Covering down to the THz region because quasiparticle states of correlated materials and finger print vibration mode of proteins appear in the THz region. Then we employed a large-size schwarzschild

mirrors (140 mm in diameter, NA = 0.5, working distance = 106 mm) for covering the THz region [1].

After installation of the THz microscope, we checked the spatial resolution in the different wavenumber ranges in which the microscope covers as shown in Fig. 1. The THz microscope in conjunction with UVSOR-II covers down to 40 cm⁻¹ in contrast that with a globar lamp covers above 500 cm⁻¹. The spatial resolution and the intensity using UVSOR-II is much higher than that using a globar lamp in the whole wavenumber range. This indicates that the THz microscope using UVSOR-II is a very efficient means of microspectroscopy in the IR and THz regions.

[1] S. Kimura *et al.*, Infrared Sci. Tech. (2006) in press.

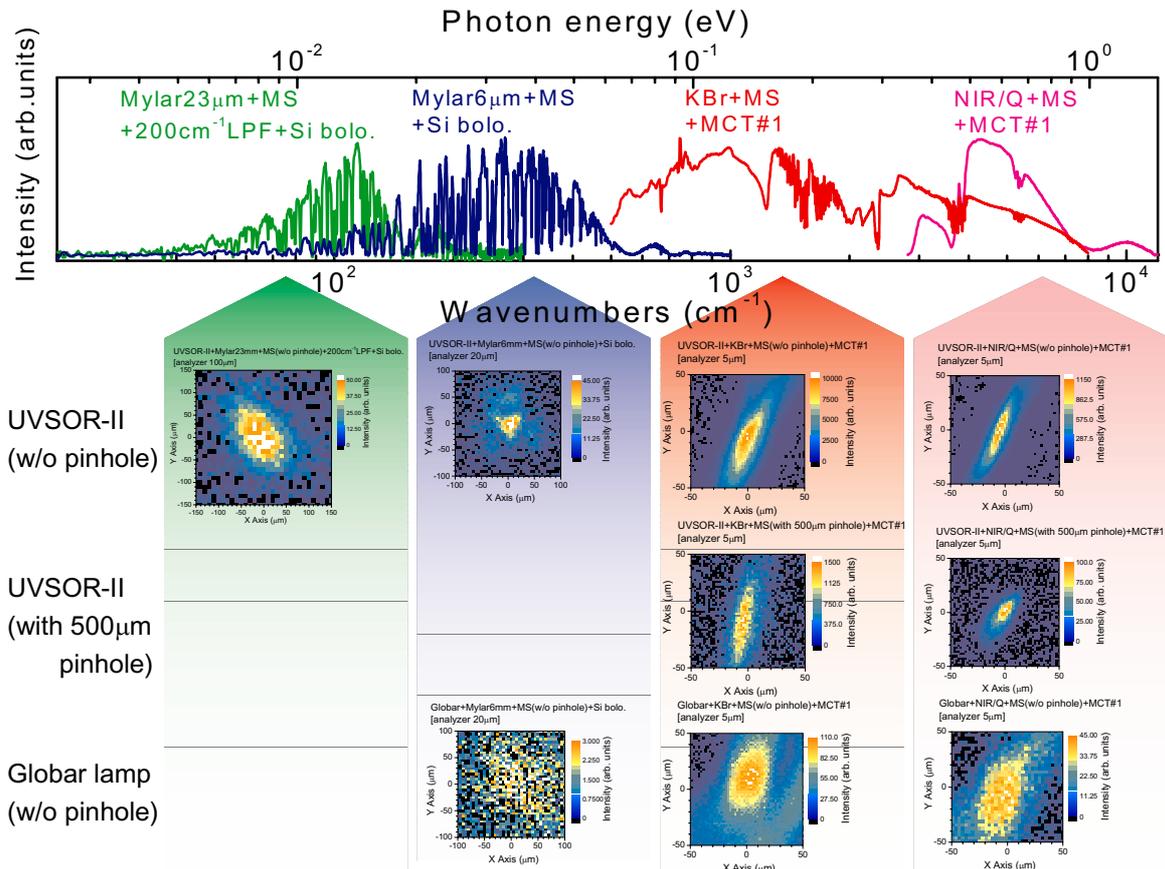


Fig. 1 Spectral shape and spatial resolution of THz microscope at different wavenumber regions using UVSOR-II compared with a globar lamp. Fine structures in the spectral shapes are due to the absorption of water vapor.