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Hiroyuki Yoshida

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Low-energy inverse photoemission spectroscopy using a high-resolution grating spectrometer in the near ultraviolet range

Hiroyuki Yoshida[a)]
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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An inverse photoemission spectroscopy (IPES) apparatus using a Czerny-Turner grating spectrometer is demonstrated. Previous IPES instruments based on grating spectrometers used a concave grating and operated in the vacuum ultraviolet range. The reflectance of such gratings is lower than 20% and the aberration cannot be finely corrected leading to an energy resolution of up to 0.1 eV. In the present study, employing the low energy IPES regime [H. Yoshida, Chem. Phys. Lett. **539–540**, 180 (2012)], incident electrons with a kinetic energy below 5 eV are used, while photon emission in the range of between 250 and 370 nm is analyzed with a 10-cm Czerny-Turner grating spectrometer. The signal intensity is at least 30 times higher than the previous apparatus. The resolution of photon detection is set at 0.07 eV though the ultimate resolution is one order of magnitude higher. The experiment is performed both by sweeping the electron energy (isochromat mode) and by simultaneously analyzing the photon of whole wavelength range (tunable photon energy mode). © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4822119]

I. INTRODUCTION

Inverse photoemission spectroscopy (IPES) is an experimental technique for examining the unoccupied states of solid materials or surface.[1,2] IPES is often regarded as the compliment of photoemission spectroscopy (PES) which examines the occupied states. In IPES, an incident beam of electrons induces photon emission and a photon emitting as a result of the radiative transition to a low lying unoccupied state is detected. The IPES spectrum is measured either by sweeping an electron kinetic energy with detecting photons at a fixed energy, called the isochromat mode, or by analyzing the photon energy at a constant electron kinetic energy, called the tunable photon energy (TPE) mode, as shown in Figure 1.

The main drawback of IPES is the low cross section for photon emission. According to the theoretical studies, the cross section of IPES is only 10^{-3} of that of PES in the X-ray range and 10^{-5} in the vacuum ultraviolet (VUV) range.[3–5] Therefore high collection efficiency and high sensitivity are crucial in the design of the photon detectors of IPES apparatus. Most IPES studies were carried out in the isochromat mode using bandpass photon detectors.[6,7] The bandpass detector is a combination of a photon detector with a sensitivity from 9 eV (e.g., Geiger-Müller tube[6–17] or alkali-halide sensitized electron multiplier[18–22]) with a alkali-earth halide plate with a cut-off energy at 10 eV. These detectors have a bandpass centered around 9.5 eV. This type of photon detector possesses a large acceptance angle (typically 0.8 sr) and high quantum efficiency[1,22,23] which fulfills the requirement for the photon detector for IPES. However, the sensitivity is governed by the combination of materials, consequently the energy resolution is low, the photon energy is fixed, and often the sensitivity has a long tail. If the resolution is improved, the sensitivity drops rapidly.[14–17] The energy resolution of practically useful bandpass detectors is limited to 0.4 eV.

On the other hand, grating spectrometers are standard equipment for photon analysis. The photon energy and resolution are easily adopted, and the sensitivity curve is well-defined. So far, IPES has been performed using grating spectrometers in the vacuum ultraviolet (VUV) range, with photon energies between 10 and 100 eV.[24–32] There are several drawbacks. First, the collection efficiency of photons is limited by the solid angle of the grating. Unlike the bandpass detector, the incident light is dispersed due to the interference of light in the grating spectrometer. Therefore the light should originate from a point source or be well collimated. In a practical spectrometer, the entrance slit serves for this which, together with the dimension of grating, inherently limits the collection efficiency. In practice, the collection solid angles are between 3×10^{-3} sr[24] and 0.1 sr[31] which is at most one order of magnitude less than typical bandpass detectors.

Second, in the VUV range, the reflectivity of the gratings and mirrors is low. An aluminum coating is widely used because of its high reflectance in the visible and ultraviolet ranges. However, the reflectance of the aluminum coated mirrors is low in the VUV range (particularly below 170 nm) and the surface easily deteriorates in air.[33] In order to design a spectrometer without mirrors, a concave or toroidal grating has been used for IPES at grazing angles,[24] and at the normal angle with the Roland circle[25–28] or off-Roland circle[29–32] configurations. The diffraction efficiency of such gratings is in the range of 4%[27,31] to 15%.[25]

Third, the instruments are much more complicated and expensive than those that use a bandpass detector. All these optical components must be installed in vacuum to avoid the absorption of the VUV light by oxygen and makes it more difficult to construct and tune these devices. So far, such grazing spectrometers usable for IPES are not commercialized and have to be specially designed and constructed by researchers.

a)Email: yoshida@e.kuicr.kyoto-u.ac.jp. Tel.: +81-774-38-3083. FAX: +81-774-38-3084.

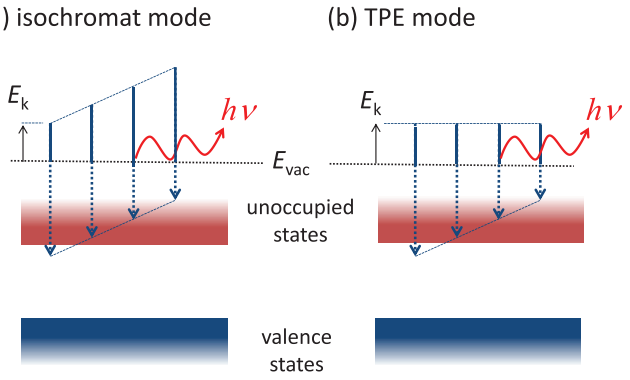

FIG. 1. Principle of inverse photoemission spectroscopy in (a) the isochromat and (b) tunable photon energy (TPE) modes.

Recently, we have demonstrated Low Energy IPES (LEIPS) operated in the near ultraviolet (NUV) range.[34] In this photon energy range, multilayer dielectric interference filters[35] can be used for the photon bandpass detection. The bandwidth of the filter typically ranges between 0.05 and 0.2 eV, improving the high energy resolution compared with conventional bandpass detectors. Further, the measurements are made with the electron energy ranging from 0 to 5 eV which is below the damage threshold of most of organic materials.[36] Thus the method is particularly suitable to examine organic materials such as organic semiconductors and biomolecules. The energy range observed by IPES is limited to the photon energy from the vacuum level as shown in Figure 1. Since photon energies up to 6 eV (corresponding to 200 nm) are detected in LEIPS, the unoccupied states as low as −6 eV with respect to the vacuum level can be examined. Organic materials of which electron affinities are mostly less than 5 eV can therefore be examined by LEIPS.

Another advantage of LEIPS is the ease of the photon detection. In the NUV range, various optical components are available. Lenses and windows made of quartz are widely used and the reflectance of aluminum coated mirror is beyond 90%. The NUV light can be handled in air because the photons in this energy range are not absorbed by oxygen. Using these optics, it is possible to build grating spectrometers with higher resolution and transmittance. If such a spectrometer is applied to LEIPS, an apparatus with higher performance can be realized. Further, there are two possible modes, the isochromat and TPE modes, in IPES as mentioned above. In the TPE mode, the photons in the whole spectral region can be detected simultaneously using a one- or two dimensional detector. Thus, more efficient measurement is possible than the isochromat mode. From a view point of the physics involved, the initial state can be selected in the TPE mode. This provides us with precise data on highly excited anionic states and transition probabilities. For these measurements, the photon intensity must be analyzed as a function of photon energy at a constant electron energy so a spectrometer becomes indispensable.

In this work, we demonstrate LEIPS using a grating spectrometer in the Czerny-Turner configuration covering the wavelength ranging between 250 nm and 370 nm. The measurements are made both in the isochromat and TPE modes.

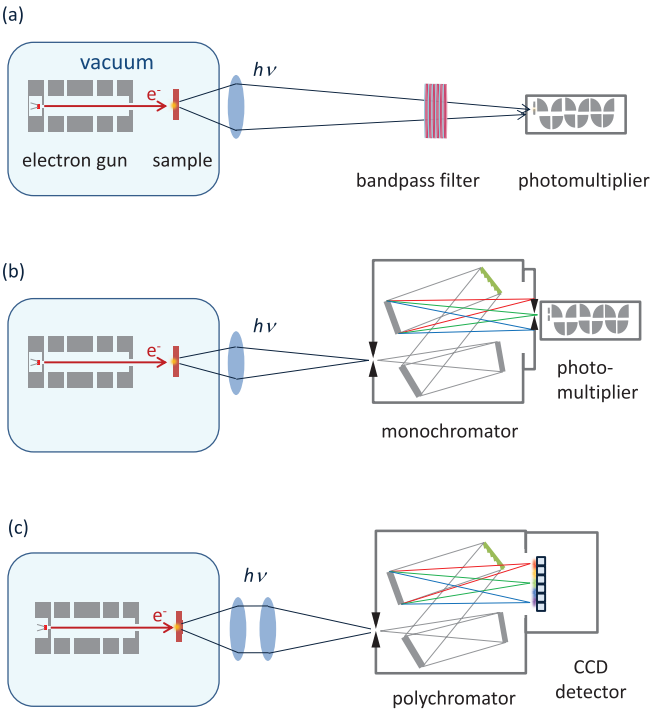

FIG. 2. Schematic diagrams of the experimental setups. The photons are detected using (a) the multilayer bandpass filter and photomultiplier, the same as the previous work,[34] (b) the monochromator and photomultiplier in the isochromat mode, and (c) the polychromator and CCD detector in the TPE mode.

The performance is discussed in comparison with the reported IPES apparatus with the grating spectrometers[24–32] and the previous LEIPS apparatus using the bandpass filter.[34]

II. EXPERIMENTAL

The experimental setup is shown in Figures 2(b) and 2(c) compared with the bandpass filter arrangement in Figure 2(a) which was reported previously.[34] The three setups are essentially the same except for the photon detection system. The vacuum chamber was evacuated below 2×10^{-7} Pa. The electron beam was produced from an Erdman-Zipf type electron gun.[37] The electron current ranged from 1 to 2 μA and the diameter of electron beam was 4 mm leading to the current density of 10^{-5} A cm^{-2}. The emitted photons, transmitted through the sample and vacuum window, were focused into the entrance slit of the grating spectrometer using quartz lenses with the diameter of 50 mm. The first lens is placed just downstream of the quartz window and about 100 mm distant from the sample, resulting in the focal ratio (f-number) of f/2 or the solid angle of 0.2 sr.

The Czerny-Turner grating spectrometer (Bunkokeiki, M10-TP) had a focal length and focal ratio of 100 mm and f/3, respectively. The grating had a nominal blaze wavelength of 300 nm with a groove density of 1200 lines mm^{-1}. This apparatus can be used as a monochromator by installing an exit slit as well as a polychromator when a position sensitive detector is installed.

The IPES measurement in the isochromat mode was carried out with the setup shown in Figure 2(b). The

monochromated photons are detected by a photomultiplier (Hamamatsu, R585). The widths of both entrance and exit slits are 1 mm resulting in the resolutions of about 7 nm. This value corresponds to 71 meV at 350 nm and 96 meV at 300 nm. The overall energy resolution, which is approximated by the convolution of this photon detector resolution and the thermal spread of electrons (0.25 eV),[34] is estimated to be 0.26 eV. The IPES spectrum is recorded as the photon intensity as a function of electron kinetic energy E_k.

In the other setup shown in Figure 2(c), the IPES spectrum was measured in the TPE mode. The exit slit of the monochromator was removed and photomultiplier was replaced with a CCD detector (Andor, Newton DU970N-UVB). The detector has an image area 25.6 mm wide and 3.2 mm high, with the pixel size of 16 × 16 μm^2. The CCD detector was operated without using the electron multiplier mode and cooled to −100 °C to suppress the thermal noise. The spike noise called the cosmic ray noise was removed using a median filter. The stray light in the near infrared range from the electron gun was removed by a NUV transmitting filter (Hoya U330). The remaining background noise was separately accumulated and subtracted from the spectrum. The spectrum is taken with the wavelength ranging between 250 nm and 370 nm at a fixed electron energy E_k.

III. RESULTS AND DISCUSSION

A. LEIPS in the isochromat mode

Figure 3 shows the spectra of CuPc measured in the isochromat mode. The upper panel shows the IPES spectrum measured using the bandpass filter with the center wavelength of 285 nm as a reference. The lower panel shows the spectra measured with the monochromator at the photon energy of 250 nm, 300 nm, and 350 nm. The whole energy scan took 11 h for each spectrum. Note that we have already confirmed that the samples are not damaged after at least 14 h under this experimental condition.[34] The result clearly shows that the resolution, throughput, and signal-to-noise (S/N) ratio of the monochromator in the near ultraviolet range meets the requirement for LEIPS.

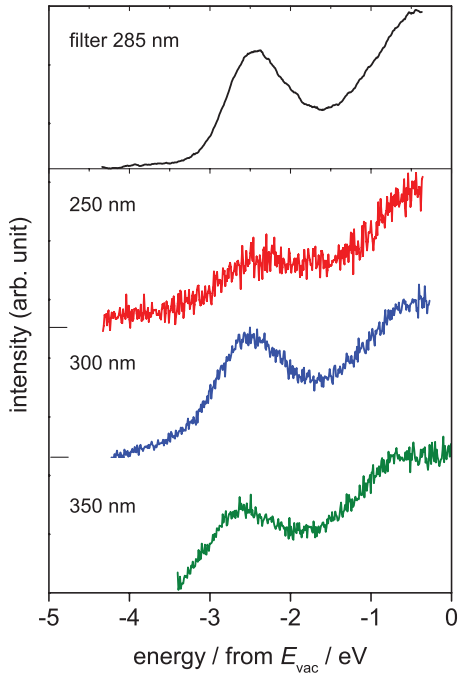

FIG. 3. The IPES spectra of CuPc. The spectrum in the upper panel was taken using the bandpass filter (setup shown in Figure 2(a)). The spectra in the lower panel are measured in the isochromat mode using the monochromator (Figure 2(b)) at the wavelength of 250, 300, and 350 nm.

Although sufficient signal was obtained using the monochromator, the signal intensity is about one order of magnitude smaller than that measured with the bandpass filter. The reason can be explained by the difference in the collection efficiency and transmittance of light in the monochromator. The collection efficiency of the first lens is the same between the two setups shown in Figures 2(a) and 2(b). In order to match the focal ratio of the monochromator (f/3), the image of the sample is magnified by a factor of 1.5 meaning that only one fourth of the focused light (approximately 6 mm in diameter) can enter the entrance slit (1 × 5 mm^2) of the monochromator. On the other hand, the effective area of the bandpass filter and photomultiplier (5 × 8 mm^2) is large enough to detect all the photons that are collected by the lens. From this consideration, the spectrometer with a small focal ratio has advantage of the high collection efficiency of photons. The focal ratio of the spectrometers used in the earlier studies ranges from f/45[24] to f/2.8.[28] The spectrometer used in this work is comparable to the best one in terms of the collection efficiency.

The transmittance of the monochromator is governed by the reflectance of the mirrors and the grating. The reflectance of the aluminum mirror is typically 90% in the NUV range, while that of the plane blazed grating is 70% around the blaze wavelength and rapidly falls towards shorter wavelengths. This leads to an overall transmittance of 40%, about a half of the bandpass filter. Overall, the signal intensity is decreased by a factor of 0.1 in the present setup which is in a good agreement with the above observation. Since the photon signals are mostly lost at the entrance slit, the intensity may be improved at the cost of resolution by increasing the slit width or the focal ratio of the monochromator, or tightly focusing the electron beam so that the image size is smaller than the entrance slit.

B. LEIPS in the TPE mode

Now that we find that the grating spectrometer has sufficiently high signal throughput, we try IPES in the TPE mode. In the measurements, the electron kinetic energies E_k were fixed to 0.28, 0.53, 0.76, and 0.97 eV, the photons $h\nu$ are recorded in the wavelength between 250 and 370 nm. In each spectrum, the photons were accumulated for 2 h. The photon energy is converted to the binding energy E_b using the relation, $E_b = h\nu - E_k$.

Figure 4 shows the IPES spectra of CuPc. The width of the energy region is limited to about 1.6 eV according to the wavelength range of the polychromator and NUV transmitting filter. The window of the observed range in E_b shifts as

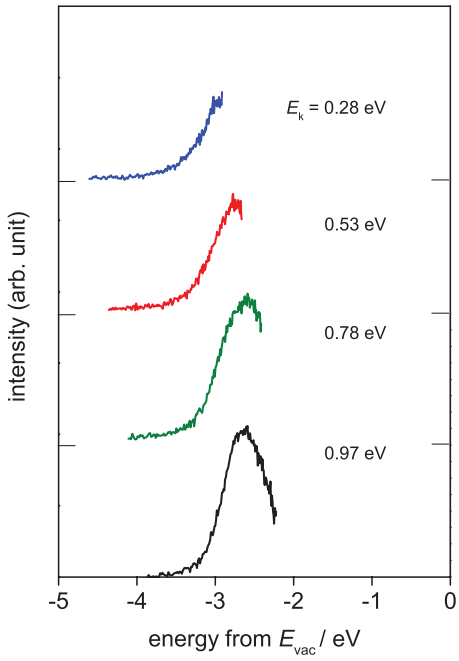

FIG. 4. The IPES spectra of CuPc taken in the TPE mode. The electron energy was fixed to E_k and the wavelength ranged between 250 and 370 nm are detected simultaneously using the polychromator and CCD detector (Figure 2(c)).

$h\nu$ increases as shown in Figure 4. The spectral line shapes are independent of E_k and similar to those obtained in the isochromat mode shown in Figure 3. It is therefore certain that the IPES spectra of CuPc are observed.

The signal intensity was 100 cps eV^{-1} at the sample current of 1.6 μA around the HOMO-derived feature of CuPc spectrum. Assuming the 1 photon makes 1 count of the CCD detector,[38] the value corresponds to 6×10^7 count C^{-1} eV^{-1}. The reported signal intensity from the grating spectrometer is in the range between 1.8×10^4 [25] and 10^6 count C^{-1} eV^{-1} [29–32] for the Fermi edge or sp band of Au. Since the intensity is similar between the Fermi edge of Ag and the HOMO-feature of CuPc,[34] the signal from the Fermi edge of Au and the HOMO of CuPc should be comparable. Taking the quantum efficiency of the photon detectors into account,[38] the obtained signal by the present setup is at least a factor of 30 more intense than the conventional setup. The reason can be explained by the higher reflectance of the grating and mirrors (40% of the present work vs 4%–15% of the earlier apparatus) as well as the higher collection efficiency (0.2 sr of the focusing lens vs 0.1 sr, giving at least 4 times larger).

To discuss the signal intensity, the resolution should also be considered since the signal intensity is usually proportional to the reciprocal of the resolution. In this work, the resolution of the spectrometer was fixed at 0.07 eV. This can be further improved by narrowing the slit width at the cost of signal intensity. Note that the resolution arbitrary chosen here is even better than 0.084 eV of the best resolution achieved by a conventional bandpass detector.[16] On the other hand, the reported resolution of the photon detector is between 0.1 and 0.2 eV[24–32] and further improvement seems to be difficult. The ultimate resolution of the concave grating spectrometer is worse than the Czerny-Turner spectrometer because of aberrations.

The resolution of a spectrometer is usually proportional to the photon energy. The low photon energy of 4–5 eV in the present work compared with 10–100 eV of the previous ones has obvious advantages in terms of resolution. The same condition (the slit width and focal ratio etc.) gives several times better resolution. For example, the experimental setup with the resolution 0.1 eV at 20 eV should give 0.025 eV at 5 eV. If the resolution is the same, the collection efficiency can be a factor of four higher. The resolution of the present apparatus is comparable to the best achieved, which in turn suggests the collection efficiency of photons is several times higher in the present apparatus.

On the other hand, resolution and energy range is compromised in the grating spectrometer. In the present study, a rather small energy range of about 2 eV is covered. Although the range can be increased by decreasing the groove density of grating, it cannot exceed 5 eV. This is substantially smaller than that covered by the VUV IPES where the energy ranges are reported to be 10,[26,27] 20,[29] and 30 eV.[25,28,32] Thus LEIPS in the TPE mode is suitable to examine the narrow energy region with high resolution. There are no such limitations in the isochromat mode.

IV. CONCLUSION

We have demonstrated the low energy inverse photoemission spectroscopy using a Czerny-Turner grating spectrometer in the near ultraviolet range (250–370 nm). The two possible modes of IPES, namely the isochromat and TPE modes, were shown. The resolution chosen in this study was about 0.07 eV which can be improved down to a few meV by narrowing the slit width. The focal ratio of the spectrometer was f/3. The grating spectrometer is installed in air which greatly facilitates building the apparatus and making the measurements.

This is in a marked contrast with the conventional VUV IPES; a spectrometer must be specially designed and installed in vacuum to avoid the photon absorption by air. The best resolution achieved by a grating spectrometer in the VUV range so far was between 0.1 and 0.2 eV[24–32] which is comparable to the present spectrometer whereas the signal intensity is at least a factor of 30 lower. This can be explained by the lower collection efficiency of photons (the focal ratio which is related with the collection efficiency is at most f/2.8[28]) and the lower reflectance of light in the VUV range.

We have already shown that the LEIPS has advantages in the higher energy resolution and lower damage to organic samples.[34] This study has, on the other hand, demonstrated a significant advantage in handling light; photons with wavelengths longer than 200 nm can be manipulated in air using high quality optics such as quartz lenses and aluminum-coated mirrors. As a result, the high resolution and throughput grating spectrometer in the Czerny-Turner configuration is able to be used for IPES. Currently, the overall resolution of IPES is limited by the energy spread of electrons (typically 0.25 eV) rather than the photon detector.[15] The present spectrometer design aims at the high resolution

unnecessary for IPES. The specially designed spectrometer for higher throughput with a moderate resolution will certainly be more satisfactory.

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[38]According to the specification of Newton EMCCD series Andor Inc. (http://www.andor.com/scientific-cameras/newton-ccd-and-emccd-cameras/newton-970), the sensitivity is 0.8–3 e^-/count. Here, we assume the lowest values to estimate the lower limit of the LEIPES intensity. The quantum efficiency of the UVB-type CCD detector between 200 and 380 nm is 33% which is about 2 factors larger than the CsI coated microchannel plate (Ref. 1).