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Present status of vacuum ultraviolet natural circular dichroism measurement system using polarizing undulator at TERAS BL5 beamline

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ABSTRACT

The study of natural circular dichroism (CD) in the vacuum and extreme ultraviolet (VUV and EUV) regions has been providing us with chirality and structural information on biomolecules. We have developed the beamline BL5 at TERAS, Tsukuba, which is equipped with a compact Onuki-type polarizing undulator. This beamline is dedicated to measuring the CD spectra in the VUV and EUV regions for the photon energy region of 5–40 eV. The use of a polarization modulation technique with a polarizing undulator is essential for detecting a weak CD signal. Using this CD system, the natural CD spectrum has been measured in the EUV region up to 40 eV for the first time. In addition, the differences and the similarities between the CD spectra of four amino acid films (alanine, valine, leucine, and phenylalanine) in the VUV region up to 9.5 eV are determined.

1. Introduction

Polarization modulation spectroscopy is a powerful technique for detecting weak signals that are usually buried in noise. The technique has been applied to measure circular dichroism (CD), which is the difference in optical absorption between left and right circular polarized light. Natural CD has been widely utilized for analyzing protein secondary structures and determining the chirality of molecules, and magnetic CD has been used to determine the magnetic properties of magnetic materials.

For typical polarization modulation spectroscopy in the visible and ultraviolet regions, polarized light is generated by transmission-type photo-elastic modulators (PEMs). In addition, by using PEMs, some synchrotron radiation facilities have developed beamlines for measuring natural CD in the vacuum ultraviolet (VUV) region up to a photon energy of 8.5 eV [1–3]. The measurable region of the CD system is strongly restricted by the optical absorption of PEMs and/or polarizer.

Because most organic molecules exhibit strong absorption in the VUV and extreme ultraviolet (EUV) regions, CD studies in these regions are conducted for conformational analysis of many chiral substances. For CD measurement in higher energy regions, such as the EUV and X-ray regions, a polarizing undulator is the most powerful light source. By using a DC method with a polarizing undulator, the natural CD spectra of biomolecules and crystals [4–7] as well as that of magnetic CD have been measured in the X-ray region. However, for more precise observation of weak CD signals, a polarization modulation spectroscopic technique using a polarizing undulator is essential for higher energy regions.

A CD measurement system for the VUV and EUV regions was recently developed at beamline BL5 in TERAS, Tsukuba, Japan, for using the polarization modulation technique with a polarizing undulator [8–11]. The natural CD spectrum of biomolecules in the EUV region (up to 15.5 eV) has already been observed for the first time with this CD system [12].

In this paper, we report on the recent progress of our CD system and natural CD study of biomolecules, especially the obvious expansion of the CD measurable region in the EUV region up to 30 eV. This paper is organized as follows. Section 2 summarizes our CD system and recent improvement to the system. Section 3 presents the CD spectra in the VUV region (VUV-CD) up to 9.5 eV of some amino acid films and describes the differences and similarities between these spectra. Finally, Section 4 presents the recent progress of CD spectra measurements in the EUV region (EUV-CD) up to 30 eV.

2. Performance of CD system at TERAS

The beamline BL5, which is designed for modulation spectroscopy in the VUV and EUV regions, is equipped with a four-period Onuki-type undulator as a light source [13,14]. This undulator can emit the desired polarization (left and right circular polarization and vertical and horizontal linear polarization) by

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adjusting the relative phase retardation between its crossed magnetic fields. An electromagnet undulator based on the Onuki-type undulator is used to obtain CD in photoelectron spectroscopy [15]. The peak energy of undulator radiation can be selected by changing the electron energy E in the storage ring and the strength of magnetic field, which is determined by the vertical distance between the magnets of the undulator (undulator gap). We usually vary the value of E from 350 to 650 MeV and the undulator gap from 60 (minimum value) to 70 mm for spectroscopic experiments in the VUV and EUV regions.

This undulator consists of four pieces of periodic magnets 80 mm long, and its overall length is only 320 mm. This compact undulator can easily drive the magnet arrays; thus, it can modulate the polarization state of the undulator radiation up to a modulation frequency of 5 Hz. This is sufficient for detecting weak signals such as CD by the modulation spectroscopic method. Because this undulator has only four periods of periodic magnets, it radiates relatively low light intensity, which prevents organic materials from decomposing by irradiation.

Recently, we introduced a new motor-driven Scotch–Yoke mechanism for horizontal movement of the magnet arrays instead of the former slider-crank mechanism. The Scotch–Yoke mechanism gives sinusoidal modulation of polarization, which is essential for highly sensitive modulation spectroscopy. In contrast, the previous slider-crank mechanism needed to modify the crank angular speed by computer control of the stepping motor to approximate sinusoidal modulation [11]. This undulator is consequently suitable for modulation spectroscopy of organic materials.

The beamline BL5 consists of simple optics such as a pre-focusing mirror and monochromator in an attempt to minimize the polarization degradation from the undulator as much as possible. The pre-focusing mirror, which can be coated by Al, Au, or Pt, focuses the light at an incident angle of 7.5°. The Seya-Namioka-type mount, which is popular for spectroscopy in the VUV and EUV regions, is used as the monochromator. The monochromator is equipped with three interchangeable holographic concave gratings (G1: 2400 grooves (gr)/mm with Al + MgF_2 coating, G2: 2400 gr/mm with Pt coating, and G3: 3600 gr/mm with Pt coating). By selecting the appropriate mirror and grating, this beamline can cover the photon energy region from 5 to 30 eV. Details on the beamline have been given in our previous reports [11,12].

This undulator can emit left circular, right circular, and vertical linear polarization (LCP, RCP, and VLP) with almost the same intensity. The light polarization varies in the order of RCP–VLP–LCP–VLP–RCP with a typical modulation frequency of 2 Hz. Fractional differences in the optical absorption with polarization modulation are detected by a lock-in-amplifier with a referring frequency of undulator modulation. Our system has achieved CD detection with a sensitivity of about 0.01%.

Currently, samples in thin films and a liquid state are available at this beamline. For CD measurements of solid samples, the contribution of linear anisotropy in the recoded CD signal is seriously validated in an attempt to obtain accurate CD spectra [16]. A simple method for validation is to measure the CD spectra by changing the sample rotation angle [10]. The sample can thus be rotated about axes either parallel or perpendicular to the light axis. A detail explanation of the validation method has been described elsewhere [10]. For liquid samples, a compact cell utilized for VUV spectroscopy has been developed with a temperature control unit [17].

For modulation spectroscopy using a polarizing undulator, the degree of polarization onto a sample is carefully evaluated to obtain accurate signal. This is because the polarization state varies as a function of photon energy; this is determined by experimental conditions such as E, the undulator gap, and degradation caused by reflection in the optical system. We developed a method for determining wavelength dispersion of the degree of polarization in the VUV and EUV regions using a multiple-reflection-type polarimeter [18]. This method introduces a calibration factor (G_{1f}) for calibration of the CD signal. The recorded CD signal is divided by the G_{1f} value to obtain the real CD. G_{1f} mainly depends on the circular polarization (P_c) emitted from an undulator and the polarization characteristics of the optical system. The procedure for determining the G_{1f} value has been described in our previous report [18].

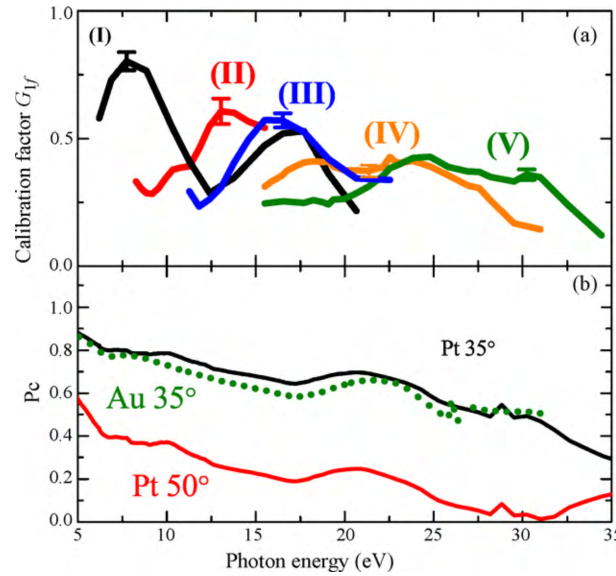

Fig. 1. (a) Experimental values of calibration factor G_{1f} expressed as a function of photon energy under several experimental conditions; these conditions are (I): black line, (II): red line, (III): blue line, (IV): orange line, and (V): green line. (b) Calculated variations of P_c values from perfect circular polarization (P_c = 1) when reflected off mirrors coated with Pt or Au. Detailed parameters for each condition are summarized in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Grazing-type monochromators such as the Seya-Namioka-type mount require a careful evaluation of G_{1f} to obtain accurate CD spectra. The obtained G_{1f} spectra under the G3 grating and various experimental conditions are shown in Fig. 1(a). The conditions are summarized in Table 1. The experimental errors in the G_{1f} values were estimated to be ±7%. The maximum values of G_{1f} clearly decreased with an increase in photon energy. Because the undulator emits the polarization of P_c which was calculated to be 0.9 [12], this degradation originates from the polarization characteristics of the optics. The P_c degradation caused by the reflection was predicted as shown in Fig. 1(b). This spectra was calculated by using the optical constants for Au and Pt [19] under the assumption that an undulator emits perfect circular polarization (P_c = 1). The calculated spectra at the incident angle of 35°, which is a half of the deviation angle for the Seya-Namioka-type mount, reasonably predicted the decrease in G_{1f} values. If the system is equipped with a normal-incidence-type monochromator, degradation of G_{1f} caused by reflection can be prevented.

Table 1
Experimental parameters for calibration factor measurements.

Condition	E (MeV)[a]	Gap (mm)[b]	Mirror
I	400	60	Au
II	500	60	Au
III	500	70	Pt
IV	650	60	Pt
V	650	65	Pt

[a] Electron energy in the storage ring.
[b] Undulator gap distance.