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Natural circular dichroism of amino acid films Observed in soft X-ray and VUV region using polarizing undulator

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Abstract

We observed the natural circular dichroism NCD of amino acid films in the soft X-ray region for the first time [1]. Based on the success, a new generation of detection system is now under preparation. Vacuum ultraviolet NCD of amino acid films was measured successfully using a polarizing undulator [2] installed at the TERAS electron storage ring at AIST, Tsukuba, Japan. A result of NCD measurement for alanine films is described in detail.

Key words: Circular dichroism, Amino acid, Soft X-ray

1 Introduction

Natural circular dichroism (NCD) is well known to be the characteristic optical property of chiral systems such as molecules with asymmetric atoms. The NCD spectra at soft X-ray region of amino acid films were obtained recently [1] at the SPring-8 using the APPLE-2 undulater with the phase modulation technique. NCD of sublimated films of L-, D- and Racemic-phenylalanine (abbreviated as L-, D- and Rac-Phe, hereafter) and L- and D- serine (L- and D-Ser) were measured at the nitrogen and the oxygen K-edge energy region. For the Phe, a

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negative peak was observed at about 407 eV for the L-Phe spectra; on the contrary, a positive peak for the D-Phe spectra and no NCD signal for the Rac-Phe were observed. For Ser, positive CD peaks were observed at around 540 eV and 548 eV for the L-Ser spectra; on the contrary, negative peaks for the D-Ser. Observed NCD spectra were partly reproduced by the theoretical calculation by Plashkevych et al. [3] and Yang et al.[4] based on the E1-M1 transition mechanism.

Vacuum ultraviolet NCD of amino acid films are carried out using the Onuki-type polarizing undulator [2] installed at the TERAS electron storage ring at AIST (National Institute of Advanced Industrial Science and Technology), Tsukuba, Japan. Principle and instrumentation of the measurement will be reported by Yagi-Watanabe et al. [5] at this conference. Modulating the phase of the undulator mechanically at about 2 Hz, we succeeded to measure the NCD spectra of alanine films with the shortest wavelength of 130 nm.

Here we report the recent progress of NCD measurement with some emphasis on NCD in the vacuum ultraviolet region (VUVNCD).

2 Experimental procedure and result

Alanine (Ala) films were prepared by the vacuum sublimation technique [1] on the Suprasil P-20 fused silica substrates. Absorption spectrum of an Ala film (thickness 110 nm) is shown in Fig. 1(a).

Measurement of NCD spectra were carried out at the beamline BL-5 of the TERAS, AIST, Japan. Details of the measurement principle will be described elsewhere [6]. Briefly, right- and left- handed polarized light (RCPL and LCPL) were switched in 2 Hz. Here the magnitude δ of NCD was defined to be the difference between transmitted light intensity I_L of LCPL and the intensity I_R of RCPL ($I_L - I_R$) was divided with the half of ($I_L + I_R$), namely, $\delta = 2(I_L - I_R)/(I_L + I_R)$. Fig. 1(b) shows the spectra of δ for SiO_2 substrate (designated as S in the figure), Rac-Ala film (R), D-Ala film (D) and L-Ala film (L).

In order to check the absolute values of δ, we measured NCD of Ala films with a commercial CD spectrometer J-720WI (JASCO) from 185 to 220 nm.

3 Discussion

As seen from Fig. 1(b), apparent NCD signals were observed from 160 to 210 nm. Because such strong NCD signals were observed even without any sample, we concluded that the apparent NCD signal was originated from the optical distortion of optical components in this beamline.

In order to overcome against this difficulty and detect the true NCD, we fully utilized the advantageous nature of the amino acids; (1) NCD of D- amino acid should be of opposite sign but the same magnitude with that of L- amino acid. (2)

R-amino acid should have no NCD. Based on the point (2), we examined the NCD of the Rac-Ala shown in Fig 2. In the figure, ▲ symbols show the NCD of Rac-Ala subtracted by NCD of SiO_2 substrate. The curve A shows the derivative of the absorption spectrum of Rac-Ala (shown in Fig.1(a)) with respect to wavelength. A good agreement between curve A and symbols ▲ shows that the optical axis of LCPL and RCPL is slightly changed according to the phase modulation of the undulator to give the wavelength modulation.

Compensating this effect by differentiating absorption spectra of D- and L-Ala and subtracting those from the apparent NCD, we obtained a result shown in Fig. 3. As seen from the figure, obtained NCD spectra are in good agreement with the result of commercial CD photometer J-720WI (JASCO) in the longer wavelength region. Clear NCD peaks were observed at about 180 nm where sign of NCD of L-Ala is just opposite from that of D-Ala with almost the same magnitude.

Inagaki [7] studied the small shoulder at 180 nm in the absorption spectrum (Fig. 1 (a)) and ascribed it to be $\pi \rightarrow \pi^*$ transition in carboxyl group. From the comparison of Fig. 3 and Fig. 1(a), we found that an absorption peak around 168 nm does not show NCD. This means that NCD data is very useful to discriminate each transition from very broad absorption spectrum.

4 Soft X-ray NCD (SXNCD)

Based on the first successful measurement of SX NCD for biomolecules [1], we tried to detect SXNCD signals for other biomolecules. Here we report a preliminary result for Alanine (Ala). Thin films of L- and D-Ala were prepared at Kobe University with vacuum sublimation technique [1]. Thickness of these films was about 300 nm. Measurement of absorption spectra and CD spectra of Ala films were carried out at the beamline BL23SU of the SPring-8, Japan. All spectra were obtained thorough the drain current measurement with switching the polarity of circular polarization as described in the reference [1].

Fig. 1 shows CD spectra in the nitrogen K-edge region together with the ordinary absorption spectrum (ABS) obtained with the drain current measurement. The CD was defined to be $CD \equiv \mu_L - \mu_R$, where, μ designates the absorption coefficient and subscript L and R shows left- and right- circularly polarized light, respectively.

As seen from the figure, a CD peak at 406 eV of L-Ala is of the opposite sign from the peak of D-Ala. According to a theoretical calculation with E1M1 model by Plashkevych [3], a strong negative CD peak was suggested to appear at the absorption peak. Their suggestion is in good agreement with our experimental result. Although the magnitude of each peak at 406 eV is not equal, it is natural to ascribe the 406 eV peak to be the true NCD peak. The origin of difference in magnitude is not clear now. It may be due to some noise in measurement procedure. We are trying to improve our experimental system and data analysis procedure.

5 Acknowledgment

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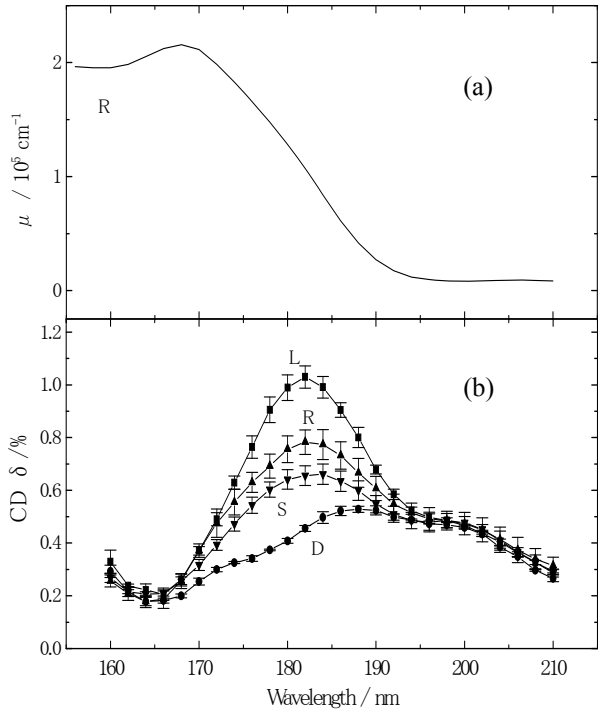

Fig.1 (a): Absorption spectrum of R-Ala film. (b): NCD spectra of SiO_2 substrate (S), Rac-Ala film (R), D-Ala film (D) and L-Ala film (L).

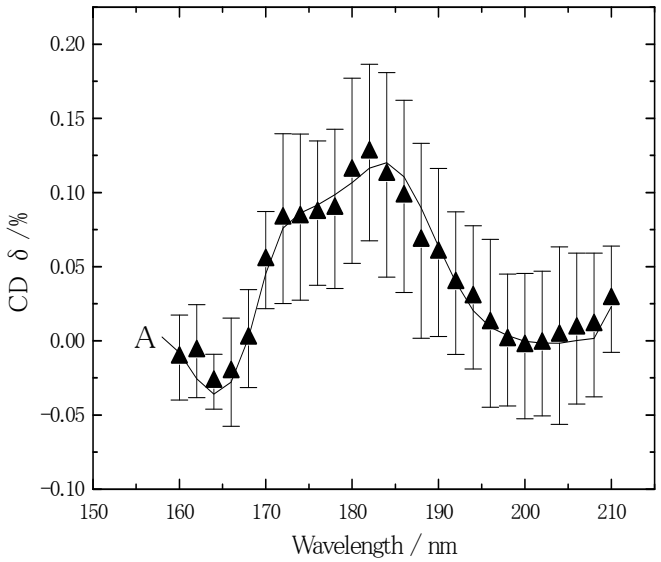

Fig. 2 Apparent NCD of Racemic-Ala film (▲) and the wavelength differential of apparent NCD (curve A).

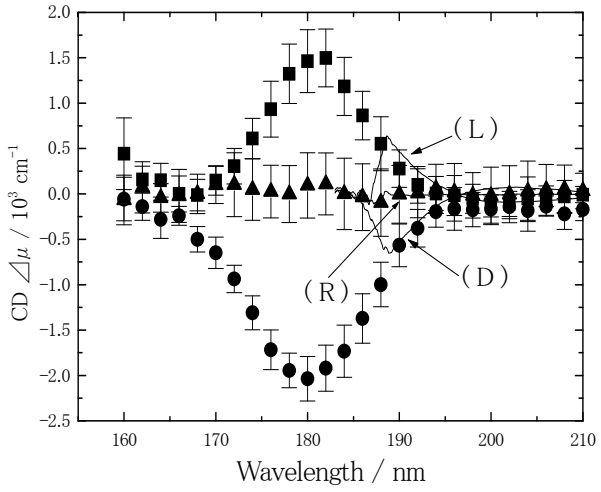

Fig. 3 True NCD of L-Ala film (■), D-Ala film (●) and Rac-Ala film (▲). A result by a commercial CD photometer is shown by curve (L), (D) and (R) for L-Ala film, D-Ala film and Rac-Ala film, respectively

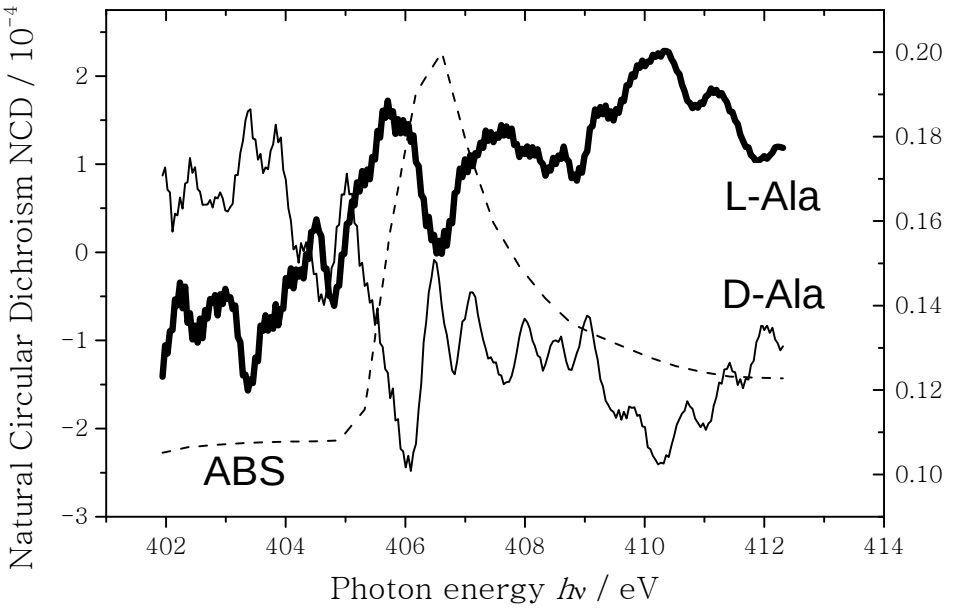

Fig. 4. Absorption spectrum of Alanine film (ABS) and natural circular dichroism NCD of evaporated films of L-Alanine (L-Ala) and D-Alanine (D-Ala) film, respectively.