First Observation of Natural Circular Dichroism for Biomolecules in Soft X-ray Region using a Polarizing Undulator

Amino acids are well known chiral molecules, which have handedness or chirality. Right- and left-handed amino acids are called D- and L-amino acid. Life forms on the earth use only L-type amino acids to make proteins. This is known as the homochirality of amino acids (or proteins) in the body of life forms. Although almost all amino acids found in meteorites were a mixture of 50% D-amino and 50% L-amino acid (i.e., racemic), some meteorites such as the Merchison meteorite were found recently to have enrichment of L-amino acids [1]. Among various hypotheses for this enrichment, photochemical enrichment is studied extensively by several groups with the circularly polarized light from the ultraviolet-to-vacuum ultraviolet region using the abundant data of circular dichroism (CD), which is the difference in absorption coefficient μ between left and right circularly polarized lights; CD = $\mu_L - \mu_R$. However, no CD data was available in the soft X-ray region, at which the energy region interaction of electromagnetic waves and matter is violently stronger than the ultraviolet region. In this work, we attemped at the first time to detect the CD of biomolecules in the soft X-ray region [2]. The basic idea of this work is that the L- and D-amino acids should show CD spectra with the same magnitude but opposite signs and the racemic amino acid should show no CD just like the abundant data obtained in the ultraviolet region and the pioneering soft X-ray work of a metal complex by Goulon *et al.* [3].

The experiment was carried out at beamline **BL23SU** by mechanical switching the left and right polarized light with 0.1 Hz using a polarizing undulator. The values of μ_L and μ_R were determined from the sample photocurrent ***i*** divided by the incident photonumber I_0 estimated from the photocurrent of the focusing mirror M_3 for the left and right polarized light, respectively. Amino acid film samples were prepared on Cu-Be substrates by the vacuum sublimation technique. Film thickness was monitored during sublimation using a quartz oscillator thickness monitor and confirmed after sublimation by HPLC analysis. HPLC analysis also confirmed that no thermal decomposition occurred during vacuum sublimation. Figure 1 shows the molecular structures of L- and D-serine, and L- and D-phenylalanine used in this experiment.

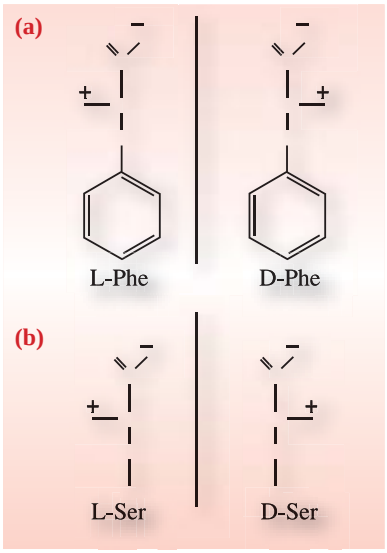

Fig. 1. Molecular structures of amino acids. **(a)** L- and D-phenylalanine, **(b)** L- and D-serine.

Figure 2 shows the absorption spectrum of a phenylalanine film (Fig. 2(a)) measured by us in the *K*-edge region of nitrogen atom, CD measured in this work (Fig. 2(b)), and result of the theoretical calculation (Fig. 2(c)) by Li Yang *et al.* [4]. As seen in the figure, the sign of CD spectrum of L-phenylalanine is opposite that of D-phenylalanine and the absolute magnitude of the CD spectrum of L-phenylalanine seems to be the same as that of D-phenylalanine. Although somewhat noisy, racemic phenylalanine seems to show no CD. Figure 3 shows, in the similar manner, the absorption spectra of serine film (Fig. 3(a)) in the *K*-edge region of oxygen atom, CD measured in this work (Fig. 3(b)), and result of the theoretical calculation (Fig. 3(c)) by Plashkevych *et al.* [5]. As seen in the figure, the sign of CD spectrum of L- serine is opposite that of D- serine and the absolute magnitude of the CD spectrum of L- serine seems to be the same as that of D- serine.

It should be noted that theoretical calculations by Yang *et al.* [4] and Plashkevych *et al.* [5] seem to reproduce our experimental result. However, the mechanism of CD is not yet clear. Both theoretical

calculations were carried out on the basis of the interference between the electric dipole (E1) and the magnetic dipole (M1) transitions. On the other hand, the ESRF group headed by Goulon ascribed many CD transitions in the hard X-ray region to be the E1-E2 interference mechanism. Moreover, in the UV-to-VUV region, the mechanism of CD is believed to be the E1-M1 mechanism. Because the soft X-ray region is the bridge energy region between UV and hard X-ray, the mechanism from which CD arises is a challenging subject for experimental and theoretical physicists and chemists.

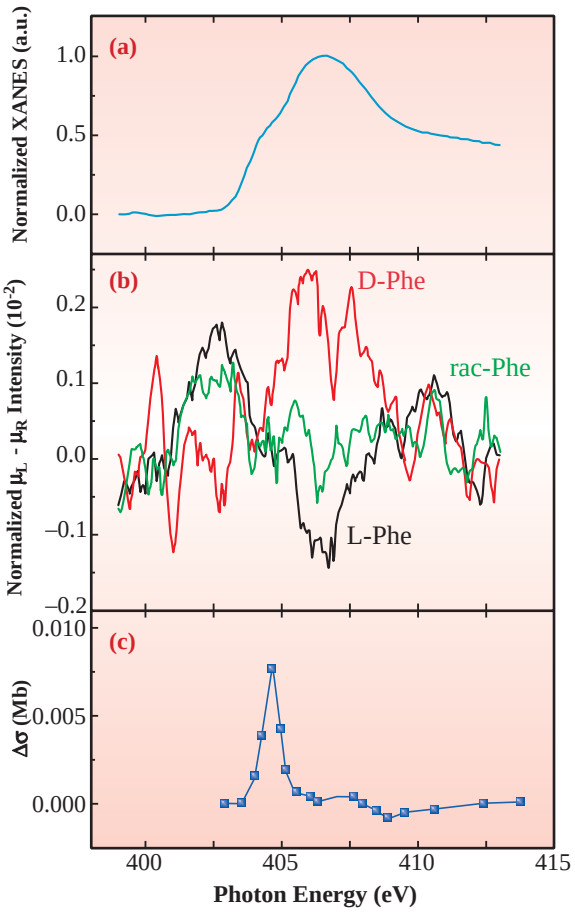

Fig. 2. **(a)** Absorption spectrum of a phenylalanine film. **(b)** CD spectra measured in this work. **(c)** Result of the theoretical calculation by Yang *et al.* [4].

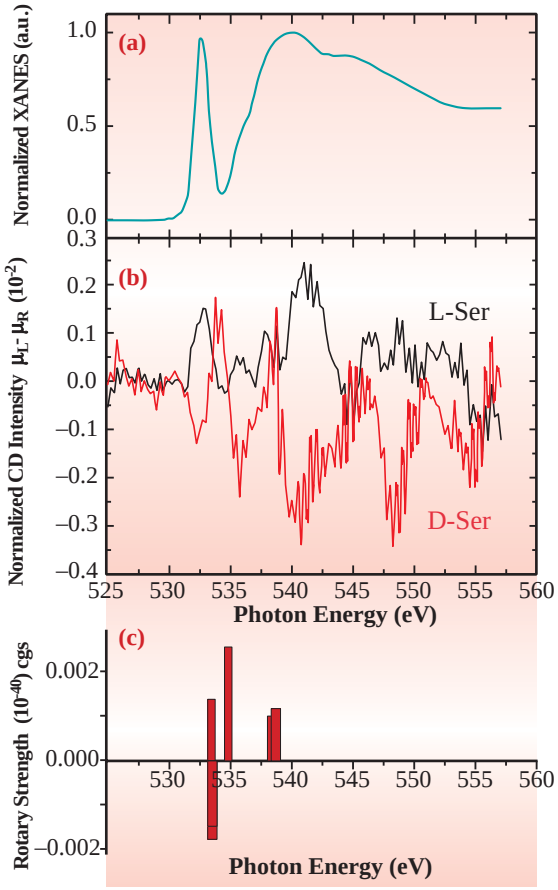

Fig. 3. **(a)** Absorption spectrum of a serine film. **(b)** CD spectra measured in this work. **(c)** Result of the theoretical calculation by Plashkevych *et al.* [5].

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References

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