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Optical Activity Measurement of Amino-acid Films Irradiated with Circularly Polarized Lyman-α Light

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The origin of homochirality in terrestrial biomolecules (L-amino acid and D-sugar dominant) remains one of the most mysterious problems in the research for the origins of life. Rational explanations for the chiral asymmetry introduction into biomolecules are required through interdisciplinary collaborations. One of the most attractive hypotheses in the context of astrobiology is “Cosmic Scenario” as below [1, 2]; (1) Asymmetric reactions of prebiotic molecules on interstellar dust surfaces in molecular cloud circumstances were introduced by polarized quantum radiation sources in space, that is “chiral radiations”. (2) The chiral products were transformed into the complex organic materials including amino-acid precursors as “chiral seeds”. (3) The complex organic materials as “chiral seeds” were transported with meteorites or asteroids to primitive Earth and resulting in terrestrial biomolecular homochirality by some “chiral amplification” effect.

Among the polarized quantum radiation sources, circularly polarized light (CPL) in the space environment is thought to be one of the most likely causes of the enantiomeric excesses of terrestrial bioorganic molecules. A cosmogenic scenario has attracted attention, which proposes that the radiation fields of CPL induce new optical activity in organic molecules produced in the interstellar environment, leading to the enantiomeric excesses. The radiation fields of CPL are assumed to exist in the scattered light by magnetic field-aligned dust in massive star-forming regions [3] and in synchrotron radiation (SR) or gamma-ray bursts from neutron stars with strong magnetic fields [2]. Ultraviolet light with a wavelength shorter than 230 nm is highly absorbed by bioorganic molecules such as amino acids. Furthermore, this is in the region where the optical response to left- (L-) and right- (R-) CPL is of opposite sign, that is, optical activity is prominent.

To validate the cosmogenic scenario, several ground simulating experiments have been investigated using ultraviolet CPL from high-energy particle accelerators. We have already carried out irradiation experiments of ultraviolet CPL with different wavelengths (215, 180 and 155 nm) to investigate the photon energy dependence of chiral asymmetric reactions by using UVSOR beam lines [4, 5]. Photon absorption bands correspond with the chromophores from the characteristic electronic transitions of carboxyl and amino groups (n-π*, π-π* and n-σ*, respectively) of alanine molecule [6, 7]. The results of circular dichroism (CD) measurements strongly suggested that optical activity emergence depends on photon energy of the irradiated CPL.

In this study, we focused on a hydrogen Lyman-α wavelength of 121.6 nm, where strong emission lines are observed in star-forming regions. Furthermore, it is predicted by recent theoretical calculations that the hydrogen Lyman-α light is circularly polarized by the magnetic field-aligned dust scattering in massive star-forming regions. We have carried out irradiation experiments by using circularly polarized hydrogen Lyman-α light to investigate the further photon energy dependence of chiral asymmetric reactions. We formed thin solid film samples of racemic mixture of alanine (DL-alanine) on quartz substrates from crystal powders of

DL-alanine by using a thermal-crucible vacuum-evaporation system. The samples were irradiated with L- or R-CPL in hydrogen Lyman-α wavelength of 121.6 nm using the undulator beam line BL1U of UVSOR-III. The irradiated CPL wavelength are corresponding to photon absorption bands with the chromophores from the electronic transitions of carboxyl and amino groups (π -σ*) of alanine molecule [6, 7]. The samples were set in a vacuum sample chamber preventing attenuation by air absorption. The 121.6 nm wavelength radiation from the undulator is reflected by a gold-coated mirror located in the mirror chamber directly beam upstream of the sample chamber and then enters the sample chamber. On the beam entrance side of the vacuum sample chamber, a gate valve with an MgF_2 vacuum sealing window (0.5 mm in thickness) was mounted. The use of gold-coated mirror reflections has made it possible to suppress high-energy higher-order light from the undulator source expecting to reduce the transmittance loss of the MgF_2 window due to high-energy radiation induced defects. The sample substrate was set in the sample holder, in which magnetic and electric fields can be applied to perpendicularly to the sample surface. The total photon beam intensity irradiated on the sample was monitored with photoelectron current of a silicon photodiode settled at the beam downstream side of the sample holder.

CD spectra of the CPL irradiated films were measured using the SR-CD beam line BL-12 of HiSOR to clarify the optical activity emergence by CPL irradiation. CD spectroscopy can detect optical activity with a high accuracy because CD spectra sensitively reflects the steric structures of chiral molecules. Figure 1(a) shows spectra of DL-alanine films irradiated for 30 min with L- or R-CPL at 121.6 nm in wavelength. To delete the effects of linear dichroism components, the CD spectra at sample rotation angles (0, 45, 90, and 135 degrees) from both back and front directions of each were individually measured and averaged them. Comparing with CD spectra of irradiations at 215, 180 and 155 nm in wavelength, the observed optical activity emergence strongly depends on the irradiated CPL wavelength and the polarization helicity (L- or R-CPL). In addition, we have also examined the additional effect of applying a magnetic field to the sample to investigate the effect of the magnetic field in interstellar space (Fig. 1(b) and (c)). Detailed analysis of CD spectra is in progress supported by quantum chemical calculations. The clarification of full mechanism of the optical activity emergence potentially has relevance to the origin of terrestrial bioorganic homochirality stimulated by "chiral photon radiation".

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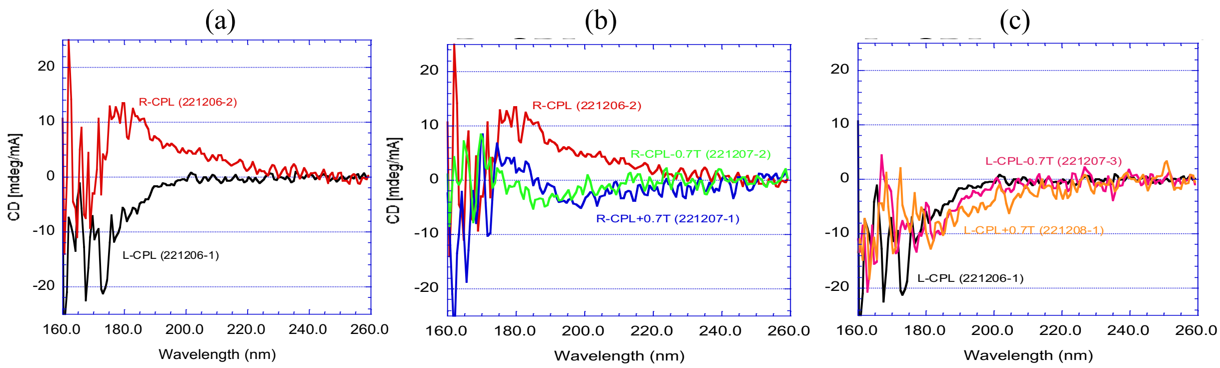

FIGURE 1. (a) CD spectra after right (R-) and left (L-) circularly polarized Lyman-α (121.6 nm) irradiation on DL-alanine films without magnetic field, (b) right (R-) circularly polarized Lyman-α irradiation with magnetic field (±0.7 T), and (c) left (L-) circularly polarized Lyman-α irradiation with magnetic field (±0.7 T).

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