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Origin of Homochirality in Amino Acids Induced by Ly α Irradiation in the Early Stage of the Milky Way

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Abstract

The enantiomeric excess (ee) of L -form amino acids found in the Murchison meteorite poses some issues about the cosmic origin of their chirality. Circular dichroism (CD) spectra of amino acids in the far-ultraviolet (FUV) at around 6.8 eV (182 nm) indicated that the circularly polarized light can induce ee through photochemical reactions. Here, we resort to *ab initio* calculations to extract the CD spectra up to the vacuum-ultraviolet (VUV) region (~ 11 eV), and we propose a novel equation to compute the ee applicable to a wider range of light frequency than what is available to date. This allows us to show that the strength of the induced ee ($|ee|$) in the 10 eV VUV region is comparable to the one in the 6.8 eV FUV region. This feature is common for some key amino acids (alanine, 2-aminobutyric acid, valine). In space, intense Lyman- α light of 10.2 eV is emitted from star forming regions. The present study provides a theoretical basis that Lyman- α emitter from an early starburst in the Milky Way plays a crucial role in initiating the ee of amino acids. (182/200words)

Key words: Lyman- α , Circularly Polarized Light (CPL), Symmetry-Adapted Cluster-Configuration Interaction (SAC-CI), Alanine (Ala), 2-Aminobutyric acid (Aba), Valine (Val)

1. Introduction

Amino acids are the basic building blocks of proteins, featuring two optical isomers, L - and D -forms, termed enantiomers. Most of the life forms on Earth makes use of the L -forms, whereas the D -forms are occasionally harmful, even though L - and D -amino acids are produced in equal amounts as racemic state by chemical syntheses *in vitro*. From this scenario, it can be inferred

that the dominance of L -amino acids (hereafter referred to as “homochirality”) must date back to the early stage of chemical evolution. The enantiomeric excess (ee) ratio is given by $\%ee = (C_L - C_D)/(C_L + C_D) \times 100$, where C_L and C_D are the amounts of each enantiomer. $\%ee$ is zero in a racemic mixture, and $\%ee$ becomes equal to 100 in homochiral all- L world. It has been shown that even if $\%ee$ is initially as low as a few percent, it can be amplified by the separation of L - and D -amino acids through polymerizations and recrystallizations. Even so, the astrophysical and molecular mechanisms responsible for the breaking of the chiral symmetry of amino acids remain an open issue (Meierhenrich 2008; Bonner 1991).

The detection of amino acids in the Murchison meteorite fallen in Australia in 1969 and the discovery of an amount of ee of L -amino acids above ten percent provided a basis for speculating on a cosmic origin of the homochirality (Cronin 1997; Engel 1997). Since the isotopic ratios of the meteoritic amino acids differ from the terrestrial ones and the abiotic species in this meteorite display positive ees, these are believed to be of extraterrestrial origin. More recently, available data of extraterrestrial materials and asteroid have been enriched by direct sample return to Earth by space missions such as the Hayabusa2. In Ryugu particles, at least 23 amino acids including complex α - and β -amino acids were detected, providing further support to the abundancy of organic matter formed on asteroids (Nakamura *et al.*, 2022). Enrichment of L -amino acids in Ryugu particles has not been detected, however, irradiation of circularly polarized light (CPL) is the factor supposed to be at the origin of the amino acid asymmetry (Rubenstein *et al.*, 1983).

Indeed, in laboratory experiments, the CPL irradiation induces the asymmetric photosynthesis and decomposition of amino acids leading to non-zero ee (Bailey 2000; Munoz Caro *et al.*, 2002; Nuevo *et al.*, 2007). From photolysis experiments and circular dichroism (CD) measurement of L -amino acids in the solid-state, the far-ultraviolet (FUV) region between 170 and 200 nm (7.3-6.2

eV) has been proposed to be the most effective to induce the homochirality in amino acids because of analogously large and positive magnitude of their CD spectra (Norden 1977; Meierhenrich *et al.*, 2010; Meinert *et al.*, 2012). In the gas phase, the CD active region is expected to be in a wider region of FUV ranging from 130 to 280nm (9.5-4.4 eV) (Meinert 2022). On the other hand, the CD spectrum at higher energy seems to be more limited only for L -Ala (Tanaka *et al.*, 2010a). In fact, the CD spectra of other amino acids, including 2-aminobutyric acid (Aba) and valine (Val), were observed in a photon energy range lower than 10 eV (Kaneko *et al.*, 2009; Tanaka *et al.*, 2010b). For energies above 10 eV, the CD features of amino acids have not been characterized experimentally to date.

In space, various light sources exist and are known to be responsible for different types of radiation field, however, the Kuhn-Condon zero-sum rule entails a cancellation of the CD contributions by summing over the entire wavelength range (Kuhn 1930; Condon 1937). Therefore, a non-zero ee cannot be originated by the irradiation of polychromatic CPL. This implies that a specific wavelength of CPL that gives the same sign of CD is required to promote the arising of ee of amino acids. In an early phase of the galactic evolution, the strongest emission in the pan-galactic light is Lyman- α ($Ly\alpha$) line, an emission peaked at 10.2 eV due to a relaxation from the first excited state to the ground state of a hydrogen atom. This early phase is categorized as $Ly\alpha$ emitters (LAEs) (Shibuya *et al.*, 2014).

In the present study, we inspect the arising of amino acid ee up to the 11 eV light region covering the LAE spectra by resorting to a high accurate theoretical methodology. In particular, we focus on optical properties and photolysis induced ee by the circularly polarized $Ly\alpha$ (CP- $Ly\alpha$) for three key amino acids; Ala, Aba and Val. All these amino acids were found in the Murchison meteorite, and their %ee were reported to be 1.2, 0.4 and 2.2, respectively (Cronin *et al.*, 1999).

2. Methods

In our computational approach, we first searched for the most stable conformations of the three targeted amino acids (L -Ala, L -Aba and L -Val). To this aim, we make use of the random connection (RC) method (Shoji *et al.*, 2022a) to evaluate all the possible conformations under fixed bond-connections in their zwitterionic forms. The geometry optimization and vibrational frequency calculations were done via quantum chemical methods within a B3LYP//6-311++G** level with the COSMO solvation procedure. Our former calculations have already shown that the B3LYP hybrid functional is able to reproduce total energies with an accuracy comparable to the CCSD(T)/cc-pVTZ level, and is applicable to optimizations, a large number of samplings and larger molecules (Shoji *et al.*, 2022a; Shoji *et al.*, 2022b; Hashimoto *et al.*, 2023; Mishima *et al.*, 2023). CD spectra were calculated at the SAC-CI/cc-pVTZ theoretical level for the L -amino acids. 150 excited states were included to evaluate the spectra up to 12 eV. The excited states of amino acids result as a combination of electronic and vibrational excitations. Because of this combination, the excitation spectrum of an amino acid features a certain bandwidth rather than separate discrete peaks at ultra-low temperature in space. We assumed a Gaussian distribution with a 0.30 eV bandwidth to compare with experimental absorption and CD spectra (Seino *et al.*, 2006; Yabana *et al.*, 1999). To compare with the experimental spectra of amino acids (Kaneko *et al.*, 2009; Tanaka *et al.*, 2010b), absorption and CD spectra are calibrated by assuming as references the values $\epsilon_0(6.6 \text{ eV}) = 1.0$ and $\Delta\epsilon_0(6.6 \text{ eV}) = 1.0$ in L -Ala. Relative values with respect to these references are used for a quantitative discussion. Further theoretical details are provided in the supporting information.

All the calculations were performed using the Gaussian16 program package (Frisch *et al.*, 2019). Molecular structures were illustrated by using the visual molecular dynamics program (Humphrey *et al.*, 1996).

3. Results

The most stable conformations of the three L - amino acids considered are shown in Figure 1(A). In the zwitterionic form, amino acids take only one conformation, and their conformational flexibility is due to side chains. Therefore, the conformations of their most stable state are structurally very similar. Specifically, Ala has one conformer, while both Aba and Val have three different conformers. The relative energies of the Aba conformers are 0.436 and 1.182 kcal mol⁻¹, while those of Val are 1.185 and 1.789 kcal mol⁻¹ as obtained at the of B3LYP//6-311++G** theoretical level with zero-point energy correction included. The relative Aba energies of 0.436 and 1.182 kcal mol⁻¹ contribute to the stability of the lowest energy conformer by 6.4 % and 0.06 % at the upper limit temperature of molecular clouds, 80 K. This suggests that the conformational contributions of these amino acids are minimal in molecular clouds. However, by comparing with the experimental CD spectra, observed at $T = 298$ K, their contribution ratios increase to 47.9 % and 13.6 %, respectively. Hence, we computed the CD spectra by including all the conformers. In the ongoing discussion, we first present the results obtained for the photoabsorption and CD features at 0 K, since this is a crucial reference temperature in molecular cloud conditions, and then we focus on these same spectra at higher temperatures up to 298 K providing an insightful comparison with experimental CD spectra.

<Figure 1>

In the most stable conformers of Figure 1(A), the photoabsorption (ε) spectra and CD difference of molar absorptivity between left- and right-CPL; $\Delta\varepsilon = \varepsilon(L) - \varepsilon(R)$, were calculated at the SAC-CI/cc-pVTZ theoretical level. For L -Ala, the calculated CD spectrum is peaked at 6.7 and 9.8 eV, which correspond to the experimental CD speaks at 6.8 eV and 10.2 eV (Tanaka *et al.*, 2010a). To compensate for the small photoenergy differences, we introduced the following calibration equation (Eq.),

$$y = 1.0978 x - 0.5171 \quad (1)$$

where x is the photon energy in eV unit before calibration, and y is the resulting scaled value. By applying Eq. (1), the peak positions of the calculated CD spectrum shift to 6.8 and 10.2 eV, thus becoming closer to the experimental values. In the following discussions, the Eq. (1) is applied to all calculations. The refined photoabsorption and CD spectra for L -Ala, L -Aba and L -Val are shown in Figure 1(B).

For a better comparison with the experimental data, the computed absorption and CD spectra at higher temperatures are reported in Figure 2. For L -Ala, calculated CD and absorption spectra are in good agreement with the experimental data (black dotted curve in Figure 2). Analogously, the experimental characteristic CD speaks at 6.8 eV (182 nm), 8.0 eV (155 nm) and 10 eV (122 nm) are well reproduced by our calculations and located at 6.8 eV (181 nm), 8.4 eV (148 nm) and 10.2 eV (121 nm), respectively. The two CD absorption peaks at 6.8 eV and 10.2 eV are both very pronounced and characterized by a positive and negative amplitude, respectively. The CD spectra computed for L -Aba and L -Val have very similar features with a large positive peak at 6.8 eV and a large negative one at 10.2 eV. By applying the proper thermal correction to the CD spectra of L -Aba, we observed a small shift of the 10.1 eV peak toward 10.2 eV, consistent with the experimental CD spectra which is located at a slightly lower value (9.5 eV). The thermal

corrections of the absorption and CD spectra resulting from conformations of these amino acids in higher energy states are nearly negligible at temperatures below 298 K. The similarity of the CD spectra of amino acids is due to the fact that their most stable conformations are common in their zwitterionic form. The CD spectra show that not only the positive CD peak around 6.8 eV region in the FUV region but also the native CD peak around 10 eV region are present in all these L-amino acids. All the absorption and CD spectra in ground and higher energy conformations are reported in Figure S1 of the supporting information.

<Figure 2>

Under the enantioselective photolysis, %ee has been estimated from the molecular absorption coefficients as

$$|\%ee_g| \geq \left(1 - (1 - \xi)^{\frac{|g|}{2}}\right) \times 100 \quad (2a)$$

$$g = \frac{\Delta\varepsilon}{\varepsilon} = 2 \frac{\varepsilon_L - \varepsilon_R}{\varepsilon_L + \varepsilon_R} \quad (2b)$$

where ξ is the extent of reaction and g the anisotropy factor (Balavoine *et al.*, 1974). Eq. (2a) indicates that %ee increases as the photolysis proceeds (ξ approaching the value of 1.0). By $\xi = 0.9999$, the computed %ee values (%ee_g) are plotted in Figure 3 (green curves), and the g value is the only variable determining %ee. The g value is obtained by dividing $\Delta\varepsilon$ by ε as expressed by Eq. (2b). Therefore, photons characterized by small ε values give large %ee values. Given this situation, values of %ee of about 6.8 eV become dominant compared to other photon energies. Nonetheless, it seems that this argument does not hold for the wide photon range considered in this study. Indeed, in our case ξ is expected to depend on $\varepsilon(\nu)$. By making use of the original derivation of ξ (Balavoine *et al.*, 1974), we obtain

$$\xi = 1 - \frac{1}{2}(e^{-k_L t} + e^{-k_R t}) \quad (3a)$$

$$= 1 - \frac{1}{2}\left(e^{-\varepsilon\left(1+\frac{g}{2}\right)t'} + e^{-\varepsilon\left(1-\frac{g}{2}\right)t'}\right) \quad (3b)$$

$$\approx 1 - e^{-\varepsilon t'} \left(1 + \frac{1}{2}\left(\varepsilon t' \frac{g}{2}\right)^2\right) \quad (3c)$$

$$\approx 1 - e^{-\varepsilon t'} \quad (3d)$$

where k is the reaction rate constant, proportional to the molar absorptivity (ε), and t' is the scaled time. Substituting Eq. (3d) into Eq. (2a), we obtain the following formula.

$$|\%ee_{CD}| \geq \left(1 - e^{-\frac{|\Delta\varepsilon|}{2}t'}\right) \times 100 \quad (4)$$

In Eq. (4), $\%ee$ depends on the time (t') and $\Delta\varepsilon$, but not on ε . Eq. (4) indicates that for small values of ε , the photolysis proceeds slowly but large value of g determines the $\%ee$ progress, whereas for large values of ε , the photolysis proceeds faster, while smaller g values decrease substantially the $\%ee$ contribution. Consequently, ε does not influence directly $\%ee$. Details of the simulation performed are provided in Figure S2 of the supporting information. By making use of Eq. (4), the $\%ee$ values ($\%ee_{CD}$) have been calculated and graphically shown in Figure 3 (red curves).

<Figure 3>

We made use of the newly derived ee formulation given by Eq. (4) ($\%ee_{CD}$) by setting an appropriate t' to generate a $\%ee$ value similar to the one given by the original formulation of Eq. (2a) ($\%ee_g$) in L -Ala at 6.6 eV. Photon energies with an identical $\%ee$ sign are colored in pink and cyan for positive and negative regions, respectively, in Fig. 3. A negative $\%ee$ sign is commonly obtained for three regions: 5.6-6.2 eV (220-201 nm), 7.4-8.3 eV (168-150 nm) and 9.5-11 eV (131-112 nm). Positive $\%ee$ values have been found only in the 6.5-7.3 eV (190-169 nm) range. The

absolute value $|\%ee_{CD}|$ in the 10.2 eV turn out to be substantially enhanced and comparable to the one of 6.8 eV region. The $\%ee_{CD}$ trends shown in our plots provide a new basis to rationalize the ee induction upon photolysis and corroborate the importance of the CD spectra in the 10 eV region in amino acids.

To complete our analysis, we calculated the convolutions of the derived $\%ee_{CD}$ spectra with an LAE spectrum to verify the generation of $\%ee$ by CP-Ly α (Figure 3). To this aim, ee employed a spectrum composed of 8 LAEs at a redshift near the value $z = 2.2$ of the luminosity z , as a typical average spectrum of LAEs (Shibuya *et al.*, 2014). The background continuum component ($h\nu < 10.17$ eV and $h\nu > 10.23$ eV) far from the intense LAE peak at 10.19 eV (121.66 nm) were not integrated, since the diffuse background continuum is expected to be non-polarized. The computed $\%ee$ values, with the LAE spectrum integrated within the ~ 0.0016 eV interval, are summarized in Table 1.

<Table 1>

The $\%ee$ values obtained by using the LAE spectrum compare very well with the $\%ee$ values estimated by 10.2 eV monochromatic light, as the LAE spectrum is considerably sharp with respect to the CD spectra of amino acids. All the three α -amino acids have in common an enhanced $\%ee$ not only at 6.8 eV but also at 10.2 eV region, and the signs of the induced $\%ee$ are inverted at 6.8 eV and 10.2 eV, respectively. By taking into consideration the fact that the CPL irradiation directly induces an amino acid excitation and its photo-dissociation, our results indicate that 10.2 eV L-CPL is responsible for the suppression of D -amino acids to a larger extent than L -amino acids. In other words, left-handed CP-Ly α enhances L -form ee ($ee_L = ee$) through the asymmetric photo-dissociation of amino acids.

4. Discussion

Former studies reported that ee_L is created by the R-CPL irradiation in the amino acid photosynthesis experiments (De Marcellus *et al.*, 2011; Modica *et al.*, 2014). Specifically, Modica *et al.* inferred that 10.2 eV R-CPL produces 1.04% ee_L of alanine and 6.6 eV L-CPL produced 0.71 % ee_L , respectively (Modica *et al.*, 2014). Although signs they obtained for the ee from the photosynthesis experiment are inconsistent with our theoretical results, the spectral peaks of the experimental CD spectra show a high correlation with our theoretical results in the photon energy. We expect that the experimental CPL radiation may induce a compositive photosynthesis which generates not only the amino acids but also its derivative or even other chiral molecules exist in interstellar environment. Generated chiral molecules may play a key role as the origin of chiral asymmetry of amino acids in the formation history. Amino acid precursors might be a solution to explain the origin of homochirality (Shoji *et al.*, 2023). Hori *et al.* reported that propylene oxide, a sole chiral molecule detected in space, has a negative CD absorption in the $Ly\alpha$ region (Hori *et al.*, 2022). To conclude these questions, further understandings regarding the synthetic mechanisms of biomolecules (i.e. synthetic reactions via radical species (Sato *et al.*, 2018)), molecular mechanisms of the enhancement of ee (Watanabe *et al.*, 2023), and even kinetics of various interstellar molecules on interstellar dust surface are requisite. Our study proposes the proper direction as a starting point of insight into the origin of homochirality.

On a speculative basis, all galactic bulges including the one in the Milky Way are thought to undergo a process of the LAE phase (Mori *et al.*, 2006). The $Ly\alpha$ emission on the LAE phase is 10^5 - 10^6 times stronger than in an individual star-forming region. Moreover, the bulge on the LAE phases is thought to be composed of substantial dust contents (Hayes *et al.*, 2013). Hence, the scattering and dichroic extinction by dust grains, aligned along a given direction of the interstellar

magnetic field, can produce an intense CPL in the Ly α band. In an interstellar molecular cloud, ammonium, aldehyde, and hydrogen cyanide are created and react each other to form biomolecules on icy dust upon UV irradiation (Nuevo *et al.*, 2007). Amino acids are synthesized from predecessor molecules through a number of chemical evolutionary processes occurring on icy dust surface in interstellar medium (Sato *et al.*, 2018; Kayanuma *et al.*, 2017). Regarding the observation data, CPL has been detected in star-forming regions in the Milky Way (Bailey 1998; Fukue 2010). In NGC6334 nebula, a strong circular polarization (CP) with a magnitude of 20% was found, and it was ascribed as the cause of dust scattering and dichroic extinction (Kwon *et al.*, 2013). Although this CP is observed in the infrared range, an analogous signal in the ultraviolet (UV) region is expected. Fukushima *et al.* simulated the CP generation and resulted the dependency of the CP degree on the relative distribution of dust grain in the forward position (Fukushima *et al.*, 2020).

The LAE phase in the Milky Way might correspond to an early starburst phase occurred several billion years ago in the bulge component (Mori *et al.*, 2006). Our solar system is located at 28 thousand light-years away from the galactic center in the disk component. Therefore, the intense Ly α emission was likely to have reached our planet from the solid angle collimated towards the galactic center in the whole sky. Peaky Ly α radiation could have been circularly polarized by scattering and dichroic extinction by dust grains aligned to the interstellar magnetic field in the proto-solar system (Whitney *et al.*, 2002). As the CP-Ly α was sharp enough, it could act as a galactic waveband filter. We suggest that these studies support the idea that the ancient polarized UV may be a crucial role to generate enantiomeric excess on the early biomolecule (represented as amino acids). It may be the trigger of breaking racemic state and thus could be the origin of homochirality in the solar system.

5. Conclusions

Our theoretical and computational approach has been shown to be able to reproduce with appreciable accuracy the experimental CD spectra of three amino acids, L -Ala, L -Aba and L -Val. Not only the positive CD magnitude around 6.8 eV is correctly obtained, but also the negative one around 10 eV is preserved in the temperature range typical of a molecular cloud (0-80 K). Moreover, we propose a new equation (Eq. (4)) extending the applicability of the calculation of ee to a wide wavelength range, showing that the ee induction upon photolysis is large in the 10 eV region and comparable to the one in the 6.8 eV region, which was so far considered to be most effective. In the early phase of the galactic evolution, the brightest spectral line of $Ly\alpha$ was emitted, then circularly polarization occurs because of dust scattering and dichroic extinction. As the CP- $Ly\alpha$ is sharp enough, it can act as a galactic waveband filter. Hence, our calculations provide clear evidence of the crucial role played by CP- $Ly\alpha$ in the origin of biomolecular homochirality on Earth.

Author Disclosure Statement

No competing financial interests exist for any of the authors.

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Supplementary Material

Supplementary information file containing computational details, comparison to experimental CD spectra and numerical simulation of *ee* induction in different ε condition, is available from Web site.

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