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Enantiomeric Excesses of Aminonitrile Precursors determine the Homochirality of Amino Acids

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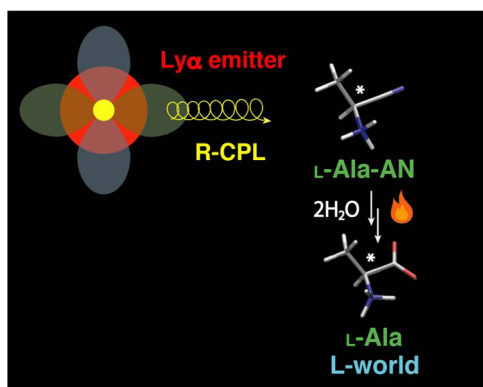
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ABSTRACT. High enantiomeric excesses (ee) of L-amino acids, including non-proteinogenic amino acid isovaline (Iva), were discovered in the Murchison meteorite, but the detailed molecular mechanism responsible for the observed ee of amino acids remains elusive and inconsistent, because Iva has an inverted circular dichroism (CD) spectrum with respect to α -H amino acids, e.g. alanine. To address this issue, we resort to accurate *ab initio* calculations for amino acids and their precursors in the Strecker synthesis. We evaluated their photolysis-induced ee in the range of 5-11 eV including the Lyman alpha emission line ($\text{Ly}\alpha$), the typical intensive 10.2 eV radiation ascribed to the early phase of galactic evolution. We show that only the aminonitrile precursors are characterized by positive ee in the $\text{Ly}\alpha$ region, explaining why right-handed circularly polarized $\text{Ly}\alpha$ (R-CP- $\text{Ly}\alpha$) induces homologous L-amino acids. This study shows that the homochirality of amino acids is produced at the aminonitrile precursors stage. (150/150words)

TOC GRAPHICS



KEYWORDS. Lyman- α ($\text{Ly}\alpha$), Circularly Polarized Light (CPL), Symmetry-Adapted Cluster/Configuration Interaction (SAC-CI), Alanine (Ala), 2-Aminobutyric acid (Aba), Valine (Val), isovaline (Iva)

Amino acids (AAs) are the fundamental building blocks of proteins in living organisms on Earth, and AAs, with the only exception of glycine, have a chiral center. Their enantiomeric forms, L- and D-AAs, are equally produced by nonbiological chemical syntheses. However, L-AAs are almost exclusively used in living systems.¹ This AAs homochirality is thought to have originated in the early stage of chemical evolution when the AAs were synthesized non-biologically. Even if the early enantiomeric excess (ee) is very low, it can be enhanced through recrystallizations and polymerizations.²⁻⁴ Since the first chiral symmetry-breaking event determines the selection of L-AAs or D-AAs, namely an L- or D-world on Earth, the origin of ee achieved by an asymmetrical event is of crucial importance.²

Their presence and related ee of AAs in the Murchison meteorite, fell in Australia in 1969, provided an unprecedented clue about a cosmic origin of homochirality.⁵ The detected AAs turn out to be not only proteinogenic but also abiotic, including β - and γ -amino acids, and their %ee were generally positive, where the %ee is defined as $(C_L - C_D)/(C_L + C_D) \times 100$ and C_L and C_D are the amounts of each enantiomer. Isotopic ratios of meteoritic AAs are different from the ratios of terrestrial ones, and high %ee were also measured in abiotic AAs such as isovaline (Iva). The observed %ee for AAs in the Murchison meteorite are 1.2, 0.4, 2.2 and 8.4 for alanine (Ala), 2-aminobutyric acid (Aba), valine (Val) and Iva, respectively.⁶ These results have opened a novel paradigm about the cosmic origin of the homochirality.⁵⁻⁸

It has been proposed that ultraviolet (UV) circularly polarized light (CPL) in star-forming regions might have played a significant role in inducing ee in interstellar organic molecules which, in turn, were probably subsequently delivered to the early Earth by meteorites.⁹ In star-forming regions, strong infrared CPL has been detected.⁹⁻¹¹ Laboratory experiments have shown that

circular polarized light (CPL) irradiation produces an asymmetric photosynthesis and decomposition of AAs eventually leading to ee.¹²⁻¹⁸ Based on photolysis experiments and circular dichroism (CD) measurement of *L*-AAs in the solid state, it has been proposed that the far-ultraviolet (FUV) region between 170 and 200 nm (7.3-6.2 eV) is the effective wavelength range to induce the homochirality, since the CD spectra have equally the positive and large magnitude for several key amino acids such as Ala, Aba and Val.¹⁹⁻²⁴ However, the CD spectra of Iva shows a reversed CD sign, suggesting that the production of *D*-Iva instead of *L*-Iva is induced by the FUV.²⁰ Furthermore, CD alternates in sign and sum to zero over the whole spectrum according to the Kuhn-Condon sum rule.^{25,26} Hence, to produce ee on AAs, the spectrum of UV CPL must be narrowed to a single band. It is known that strong Lyman- α ($\text{Ly}\alpha$) radiation, peaked at 10.2 eV, is emitted from ionized hydrogen (HII) in star-forming regions. In particular, in the early evolutionary stage, the Milky Way is thought to have been embedded in intense pan-galactic $\text{Ly}\alpha$ light. Such an early phase of galaxies is categorized as $\text{Ly}\alpha$ emitters (LAEs).^{27,28} Recently, it has been shown that high CPL of $\text{Ly}\alpha$ originates from scattering with interstellar dust.^{29,30}

Another unsolved issue is that the asymmetric photoreactions supposed to determine the final ee of AAs are not entirely clarified. Specifically, photosynthesis experiments have shown that 10.2 eV R-CPL produces 1.04 %ee of Ala¹⁸, whereas the CD values indicate that positive ee of α -H amino acids are achieved via L-CPL photodissociation. These results are mutually inconsistent. We remark that photoelectron circular dichroism (PECD) indicated that Ala, proline and serine are commonly photoionized by CP- $\text{Ly}\alpha$ with an identical angular anisotropy³¹⁻³⁴ and the main photoionized product of Ala by CP- $\text{Ly}\alpha$ is a fragment of $m/z=44$, identified as $\text{CH}_3\text{CH}=\text{NH}_2^+$ by releasing COOH .³⁵ Photoreactions of Ala have been fully characterized, but they are not sufficient to explain their photosynthetic reactions. To this aim, we considered the possible formation of

other chiral species prior to AAs, and these should be characterized. To address these crucial open issues, we investigated the initially induced ee for key AAs including Ala, Aba, Val, and Iva and all their precursors in the typical abiotic reactions, according to the Strecker synthesis (Fig. 1). Their computed CD spectra are obtained by an accurate *ab initio* method. Our computational results provide convincing evidence for a crucial chemical species responsible for the origin of homochirality in amino acids.

Strecker synthesis R = Alkyl

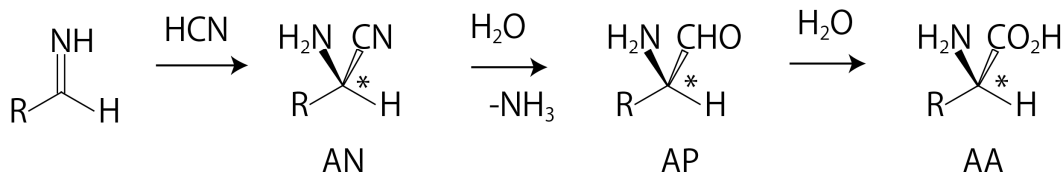


Fig. 1 Chiral intermediates leading to the formation of amino acid according to the Strecker synthesis. The precursors before *L*-amino acid (AA) are amino propanal (AP) and amino nitrile (AN).

In our computational approach, the most stable conformations of chiral molecules were identified using the random connection (RC) method.³⁶ This RC method makes use of a simplest force field in the initial geometry optimization for an extensive search in the conformational space. Details are reported in our former study.³⁶ We investigated the molecules in both zwitterionic/cationic and non-ionic forms, although the molecules on icy dust surface are expected to take the zwitterionic/cationic form. After discussing the results on the zwitterionic/cationic form, we focus on those for the non-ionic/gas form. The related energetics upon structural optimization and vibrational frequency analysis for zero-point correction were performed at the B3LYP//6-

311++G** theoretical level. For zwitterionic/cationic form in solvation, polarizable continuum model (PCM) was adapted. The DFT approach can reproduce the stable molecular structures with relative energies of accuracy comparable to those obtained by the higher accuracy CCSD(T) method for small size molecules.³⁶ Moreover, the DFT method has been shown to be applicable for a sufficient number of conformational samplings and larger size molecules.³⁶⁻³⁹ In the most stable conformations, photoabsorption (ϵ) and CD spectra have been computed. The CD value is defined as the difference of molar absorptivities between left-circular polarized light (CPL) and right-CPL, $\Delta\epsilon = \epsilon(L) - \epsilon(R)$. The CD spectra were calculated at the Symmetry Adapted Cluster/Configuration Interaction (SAC-CI/cc-pVTZ) theoretical level⁴⁰ for L-form enantiomers of Fig. 1. 150 excited states were included to evaluate the spectra up to the VUV region close to 12 eV. We assumed a Gaussian type distribution with a 0.60 eV bandwidth^{40,41} to compare with experimental absorption and CD spectra of alanine, and their relative values are provided in the discussion of the spectra. We set the base lines of $\epsilon_0(6.6\text{eV}) = 1.0$ and $\Delta\epsilon_0(6.6\text{eV}) = 1.0$ in L-alanine. This is a reasonable assumption since we introduced a scaled time parameter, t' in evaluating %ee (%ee_{CD}), which corresponds to ζ for %ee_g.³⁹ All the calculations were performed using the Gaussian16 program package.⁴² Molecular structures were drawn using the visual molecular dynamics program.⁴³ Further theoretical and computational details are reported in the supporting information. An extended view of the absorption and CD spectra for all the species considered are presented in the supporting information (Figs. S1-S8).

Molecular structures of Ala, Aba, Val and Iva in the amino acid form (=Ala-AA, Aba-AA, Val-AA, Iva-AA) and their computed %ee spectra in zwitterionic/cationic form are shown in Fig. 2 (A) and (B). All the %ee values (%ee_{CD}) are obtained by using the calculated CD values. As already discussed in our former study,³⁹ the %ee spectra for the first three AAs are rather similar

and comparable to their corresponding experimental CD spectra²⁴; %ee and CD values become positive in the FUV region around 6.6 eV and negative in the VUV region around 10 eV. Comparisons between calculated and experimental CD spectra of AAs in zwitterionic form are shown in Fig. S1 of the supporting information. The small positive peak of L-Aba-AA at 8.6 eV reduces in the spectra at 298 K by considering the contribution from the second stable conformation at 0.436 kcal mol⁻¹, but remains unperturbed at 80 K (Fig. S1).³⁹ The %ee spectrum of L-Iva-AA (Fig. 2(B)) is characterized by a feature roughly opposite to the spectra of other α -amino acids, i.e., negative at 6.7 eV (184 nm), positive at 7.5 eV (164 nm), negative at 8.7 eV (142 nm), and positive at 9.8 eV (127 nm). In the Ly α region around 10.2 eV, the %ee of L-Iva-AA is 0.5, hence reversed with respect to the negative %ee of other α -H amino acids.

In gas phase conditions, experimental CD spectra of L-Ala-AA, L-Aba-AA, L-Val-AA and L-Iva-AA were observed in the region 4.4-9.5 eV (280-130 nm).⁴⁴ The CD spectra of the former three AAs have similar shapes with a positive peak at about 5.9 eV (210 nm), a negative peak at about 7.3 eV (170 nm) and a following positive peak at about 8.3 eV (150 nm).⁴⁴ The CD spectra of L-Iva-AA is, instead, reversed, with a negative peak at 6.2 eV (200 nm), positive one at 7.0 eV (177 nm) and negative one at 8.1 eV (154 nm).⁴⁴ Our calculated CD spectra of the former three AAs in the non-ionic form are substantially unchanged in terms of positive (215 nm, 208 nm, 206 nm), negative (180 nm, 166 nm, 156 nm), and positive (156 nm, 149nm (convex upward but with a value still negative), 138nm) peaks for L-Ala-AA, L-Aba-AA and L-Val-AA, respectively, and inverted peaks with negative 5.8 eV (214nm), positive 6.7 eV (186nm) and negative 7.5 eV (165nm) amplitudes for L-Iva-AA (Fig. S2). The gas phase CD spectra was observed at 460 K. On the theoretical front, the computed spectra can be further improved by estimating the contributions from higher energy conformations (Fig. S2).⁴⁴ Here, we focus on the low temperature

photodecomposition property in molecular cloud conditions ($T < 80$ K), and their spectra by using the most stable conformations, being the contribution from higher energy conformations negligible.

Computed %ee spectra of AAs in non-ionic/gas form with the most stable conformations are shown in Fig. 3 (A) and (B). Although identical signs of %ee are induced at the 7.2 eV (172 nm) and 11 eV (113 nm) with negative and positive amplitudes, respectively (Fig.3(B)), these do not originate from the 6.6 eV and 10.2 eV regions, and most of these AAs are located near to the crossing points. Therefore, AA in both zwitterionic and non-ionic forms cannot provide a convincing explanation of the common L-form induction in both the 6.6 eV FUV and 10.2 eV VUV regions.

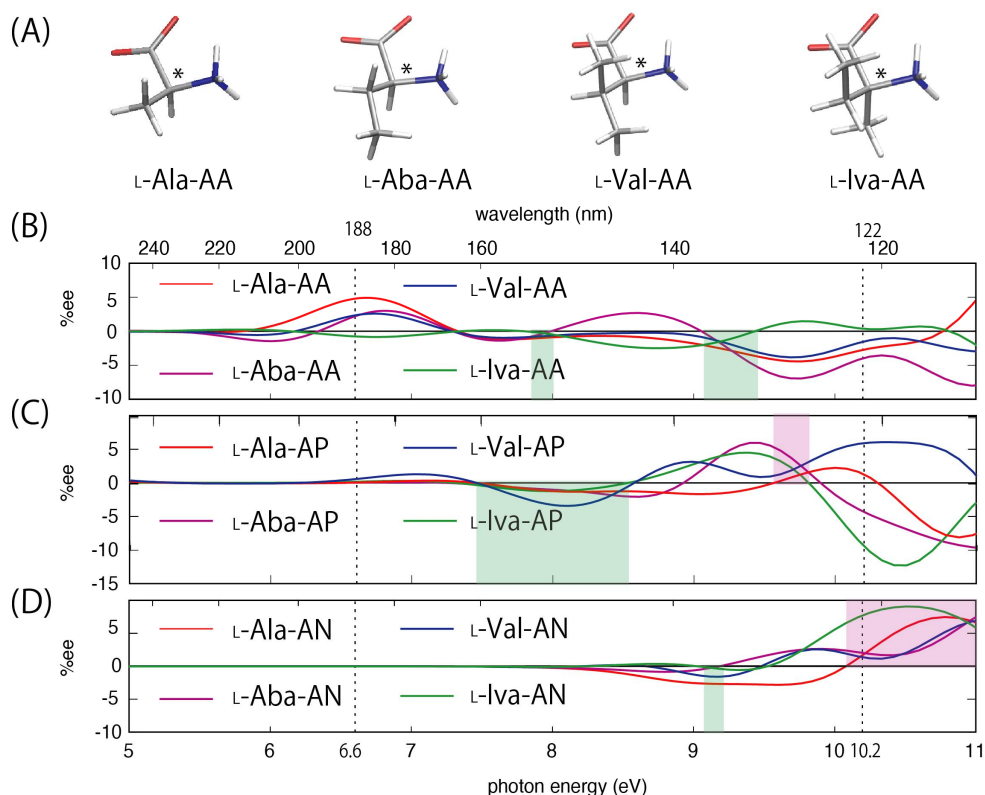


Fig. 2 (A) The most stable structures of L-amino acids: alanine (Ala), 2-aminobutyric acid (Aba), valine (Val) and isovaline (Iva) in zwitterion. The asterisks (*) indicate the chiral centers. AA

indicates the amino acid form. (B)-(D) Induced enantiomeric excess (%ee) of L-form chiral molecules by R-CPL in the range of 5-11 eV as obtained from the CD spectra calculated by the SAC-CI/cc-pvTZ method. Results for the (B) amino acid, (C) amino propanal (AP) and (D) amino nitrile (AN) forms in zwitterionic/cationic states are shown. Commonly induced regions with positive and negative %ee values are colored by red and green, respectively. Each CD spectrum is shown in Figure S3-S5.

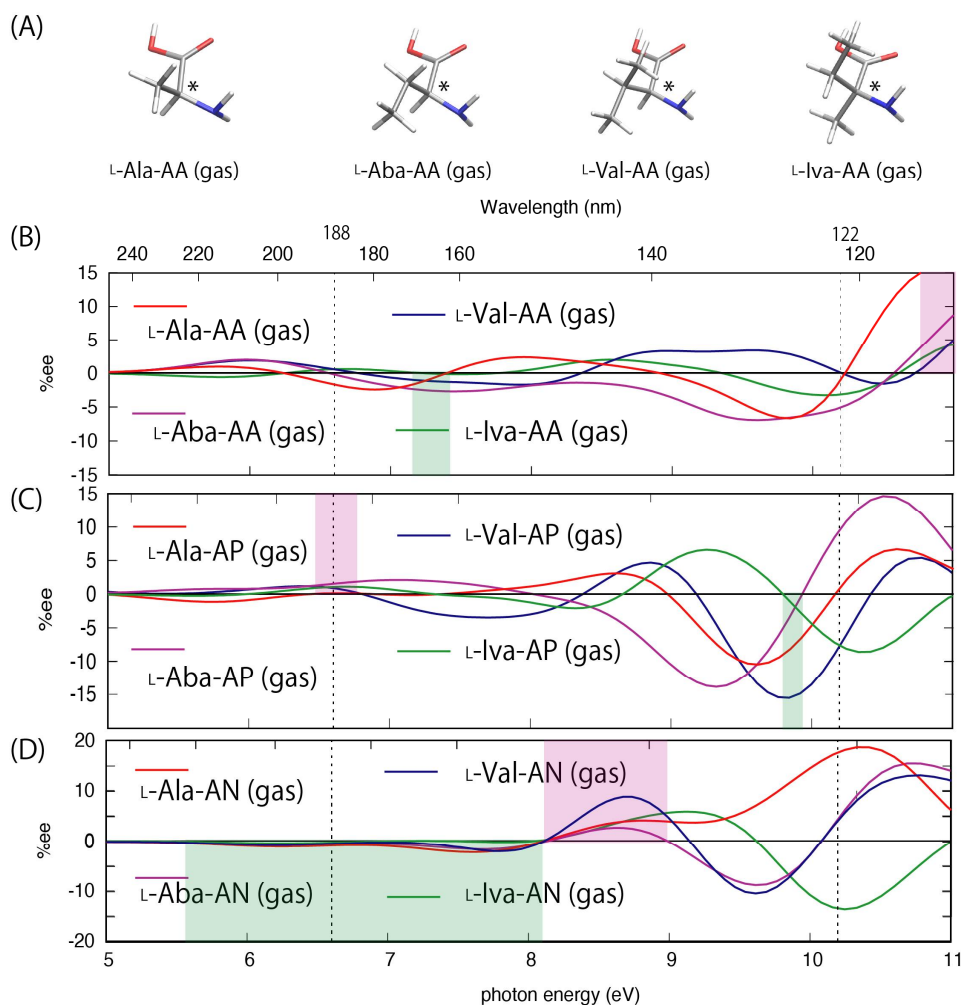


Fig. 3 (A) Most stable structures of L-Ala, L-Aba, L-Val and L-Iva in amino acid (AA) forms in gas phase. (B)-(D) Induced enantiomeric excess (%ee) of L-form chiral molecules by R-CPL in the

range 5-11 eV as obtained from the CD spectra calculated by the SAC-CI/cc-pvTZ method. Results for (B) amino acid (AA), (C) amino propanal (AP), and (D) amino nitrile (AN) forms in non-ionic gas forms are shown. Commonly induced regions with positive and negative $\%ee$ values are colored by red and green, respectively. Each CD spectrum is shown in Figures S6-S8.

The first amino acid precursor in the Strecker synthesis is the amino propanal (AP). In this form, the computed $\%ee$ are shown in Fig. 2 (C). An evident feature is the fact that these spectra are characterized by peaks deeply different from those of AAs. In particular, the strong peak at 6.6 eV is absent. In the AP species, the common signature of $\%ee$ is represented by the peaks centered around 7.5-8.6 eV (165-145 nm) and 9.6-9.8 eV (127-129 nm) as negative and positive values, respectively. In the Ly α region, negative and large $\%ee$ were obtained for $_L$ -Iva-AP and $_L$ -Aba-AP, whereas both large and small positive $\%ee$ were found for $_L$ -Val-AP and $_L$ -Ala-AP. In the gas phase, common signatures of $\%ee$ at 6.6 eV and 9.8 eV as positive and negative amplitudes, respectively (Fig.3(C)). In the Ly α region, $\%ee$ is positive for $_L$ -Aba, while $\%ee$ values for $_L$ -Val and $_L$ -Iva are negative. These results suggest that the AP species are unlikely to contribute to the origin of homochirality for all AAs.

The second amino acid precursor along the Strecker synthesis is amino nitrile (AN), for which we computed the $\%ee$ shown in Fig. 2 (D) and Fig. 3(D) for cationic and gas phase, respectively. The spectra in cation (Fig. 2 (D)) are further shifted toward higher energy regions, with typical signatures represented by the peaks at 8.0-9.2 eV (155-135 nm) and 10.1-11.0 eV (123-113 nm) with negative and positive amplitudes, respectively. Hence, in the Ly α region, the $\%ee$ values turn out to be positive for all the ANs. We remark that the $\%ee$ of $_L$ -Iva-AN results to be 7.4, which is

significantly larger in comparison with the 1-2 ‰ of other ANs (see Table 1). These estimated ‰ values are very close to the experimental ones in the Murchison meteorite. We remark that the magnitude of ‰ depends on the extent of the photolysis and these, in turn, are highly influenced by amplification processes in aqueous alteration. Anyhow, a direct comparison between the computed ‰ values and ‰ detected in meteorites is clearly insightful and provides a solid basis to draw meaningful conclusions. For ANs in gas phase (Fig.3(D)), ‰ spectra are rather similar in the range 5.5-8 eV (230-155 nm) and 8-9 eV (155-140 nm) with negative and positive amplitudes, respectively. The broad region extending from 5.5 to 8 eV can be interpreted as stability upon the shift of light wavelength. However, in the Ly α region, only Iva has a negative ‰ value, and the sign of ‰ is not the same for all ANs.

Table 1. Calculated enantiomeric excesses (‰) of chiral molecules: amino acid (AA), amino propanal (AP), amino nitrile (AN) under the R-CPL irradiation at 6.6 eV and 10.2 eV photon energies. Values in parentheses are at 6.6 eV.

	AA zwitterion	AP cation	AN cation	AA gas	AP gas	AN gas
Ala	-2.9 (4.8)	1.7 (0.1)	1.1 (-0.0)	-2.1 (-1.7)	0.1 (0.1)	17.7 (-0.7)
Aba	-4.3 (2.1)	-3.9 (0.1)	2.1 (-0.0)	-5.3 (-0.2)	8.5 (1.5)	3.3 (-0.5)
Val	-1.6 (2.4)	0.1 (0.4)	1.5 (-0.0)	0.4 (0.6)	-8.9 (0.9)	1.5 (-0.2)
Iva	0.5 (-0.7)	-8.5 (0.2)	7.4 (-0.0)	-3.2 (0.6)	-7.2 (1.1)	-13.3 (-0.4)

We note that strong correlations between ‰ and the parent body aqueous alteration have been reported in former works.^{3,8} This implies that the exact final ee values are not predictable. Nonetheless, the positive sign of ee is unaffected and on this aspect the present study is mainly

focused. We show in this work that the AN species in cation forms have common positive %ee values (L-amino acids are formed by R-CPL) in the Ly α region, which is consistent with asymmetric photosynthesis experiments by Modica et al.¹⁸ Modica et al.¹⁸ have shown that 6.6 eV R-CPL induced D-Ala (%ee < 0), in open contrast with the results of irradiation of 10.2 eV CPL. Values of %ee for ANs in the cationic form are close to zero in Fig.2(D), indicating that 6.6 eV CPL does not affect their asymmetric photolysis. Nonetheless, the broad and negative %ee of ANs in gas phase are consistent with the Modica's 6.6 eV result¹⁸. We expect that a minority of ANs take gas forms and are involved in asymmetric photolysis contributing to their non-zero %ee in the case of 6.6 eV irradiation.

Former theoretical studies have shown that hydrolysis of aminoacetonitrile to glycine is characterized by a higher electronic energy barrier ($\Delta E^\ddagger = 27\text{-}34 \text{ kcal mol}^{-1}$) than the energy barrier in the formation of aminoacetonitrile ($\Delta E^\ddagger = 8\text{-}9 \text{ kcal mol}^{-1}$).^{45,46} The high energy barrier for hydrolysis suggests that the AN form, and not the AP or AA forms, is dominant in molecular clouds at temperatures $T < 100 \text{ K}$. Elsila et al. reported that the carbon atom of the acid group of glycine is mainly derived from the carbon atom in HCN, not from other constituent such as CH₃OH.⁴⁷ This observation, obtained by isotopic labeling, is consistent with the fact that the acid group of an amino acid is formed by hydrolysis of nitrile group in the Strecker type synthesis. Moreover, it is also consistent with the typical observation that nitrile precursors are more stable under UV and cosmic rays irradiation in interstellar regions compared to amino acids.⁴⁸ Therefore, amino nitrile can survive longer on meteorites. In the high-mass star forming region SgrB2, amino acetonitrile, the precursor of glycine, was detected, but 2-aminopropionitrile, Ala-AN, has never been observed so far, because they are below the limit of detection.^{49,50} However, the detection of Ala-AN is a more practical probe with respect to the detection of Ala.

Our recent theoretical study also supports the notion that aminonitrile is the most stable molecule among the chiral precursors of AAs. This has been rationalized in terms of the minimum energy principle, namely, the most abundant molecule in the interstellar medium is directly correlated to its stability among all possible isomers.³⁶ Alanine and 2-aminopropanal (=Ala-AA, Ala-AP) are characterized by more stable isomers, N-ethylcarbamic acid and propenamide, with relative energies significantly lower by 10.3 and 23.9 kcal mol⁻¹, while 2-aminopropanenitrile (=Ala-AN) is the most stable among the isomers. Therefore, Ala-AN is expected to be the easiest chiral molecule formed in the Strecker synthesis to alanine.

In conclusion, our theoretical evaluation of the CD spectra of amino acid precursors via accurate *ab initio* method (SAC-CI) provide a clear indication on the induced ee of Ala, Aba, Val and Iva in their AA, AP and AN forms. From an astronomical standpoint, intense Ly α emissions around 10.2 eV are a dominant feature and can be strongly circular polarized. We found that a positive ee is present in all ANs in the 10.2 eV region, and is kept in the broad range of 10-11 eV. Therefore, we expect that aminonitriles are at the origin of homochirality of amino acids. Specifically, aminonitrile precursors are irradiated with R-CP-Ly α , and positive ee is formed upon photolysis. We can infer that the formation of amino acids is possible by aqueous alteration, which requires heat and water molecules. Kawasaki and coworkers have shown that the %ee of an α -AN (N-benzhydryl- α -p-tolyglycine nitrile) can increase up to 96% ee by spontaneous crystallization.⁵¹ The remarkable property of AN is achieved by the preferential formation of a conglomerate crystal accompanied by a faster racemization in solution compared to AAs.⁵¹ This result suggests that an amplification of ee can be achieved as soon as ANs are formed (and not AAs) along the Strecker synthesis. Nowadays, sample return of uncontaminated extraterrestrial material is possible as provided by the Japan Aerospace Exploration Agency's (JAXA's) Hayabusa2 mission. A variety

of amino acids of, at least, 23 species including β -amino acids were detected in Ryugu samples.⁵² We stress the importance of detection of aminonitriles and their %*ee* values in asteroids and meteorites, which may provide a direct validation of the present theoretical results. Further analyses and theoretical investigations for other prebiotic molecules related to D -sugars and nucleobases will provide new insights into the chemical evolutions of molecules and the origin of life.

ASSOCIATED CONTENT

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.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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