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Review

Photochirogenesis: Photochemical models on the absolute asymmetric formation of amino acids in interstellar space

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Abstract

Proteins of all living organisms including plants, animals, and humans are made up of amino acid monomers that show identical stereochemical L-configuration. Hypotheses for the origin of this symmetry breaking in biomolecules include the absolute asymmetric photochemistry model by which interstellar ultraviolet (UV) circularly polarized light (CPL) induces an enantiomeric excess in chiral organic molecules in the interstellar/circumstellar media. This scenario is supported by a) the detection of amino acids in the organic residues of UV-photo-processed interstellar ice analogues, b) the occurrence of L-enantiomer-enriched amino acids in carbonaceous meteorites, and c) the observation of CPL of the same helicity over large distance scales in the massive star-forming region of Orion. These topics are of high importance in topical biophysical research and will be discussed in this review. Further evidence that amino acids and other molecules of prebiotic interest are asymmetrically formed in space comes from studies on the enantioselective photolysis of amino acids by UV-CPL. Also, experiments have been performed on the absolute asymmetric photochemical synthesis of enantiomer-enriched amino acids from mixtures of astrophysically relevant achiral precursor molecules using UV-circularly polarized photons. Both approaches are based on circular dichroic transitions of amino acids that will be highlighted here as well. These results have strong implications on our current understanding of how life's precursor molecules were possibly built and how life selected the left-handed form of proteinogenic amino acids.

Keywords: Amino acids; Homochirality; Enantioselective photosynthesis; Asymmetric photolysis; Origin of life; Astrochemistry

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1. Introduction

One of the most interesting phenomena in Biology, Chemistry, and Physics is the homochirality of biomolecules, the origin of which remains unknown [1]: living organisms use carbohydrates, branched hydrocarbons, and amino acids that are asymmetric and are used as either right- or left-handed enantiomers [2]. Two major scientific challenges are linked to this phenomenon: i) the synthesis of chiral organic molecules from achiral starting materials and ii) the absolute asymmetric formation of enantioenriched chiral molecules. In recent years important progress has been made on both lines of research, in particular with respect to asymmetric photochemistry and the interaction of ultraviolet (UV) circularly polarized electromagnetic radiation with chiral organic molecules. These improvements involve the photochemical formation of amino acids out of C_1- and N_1-unit precursor molecules, which was experimentally achieved under simulated interstellar/circumstellar conditions [3,4]. Representative interstellar molecules such as H_2O, CH_3OH, NH_3, CO, and CO_2 were condensed on a solid surface cooled to 12 K while being irradiated mostly at Lyman-α. The organic residues obtained from these simulated interstellar/circumstellar ices were subjected, after acid hydrolysis treatment, to enantioselective gas chromatographic analysis allowing the identification of 16 different amino acids and diamino acids. The molecular composition of these residues was found to be similar, but not identical, to the amino acids and diamino acids extracted from meteorites, using the same protocol [5]. This review not only summarizes the most recent experimental data, but also comments on the chemical formation mechanism of amino acids in interstellar ice analogues and in meteorites involving photons and/or aqueous phase chemistry. The corresponding formation mechanisms are not necessarily identical and are the subject of recent scientific debate. This review pays particular attention to the fact that a hydrolysis step is required to increase the amount of 'free' amino acids in the organic residues of photo-processed interstellar ice analogues as well as in carbonaceous meteorites. This procedure makes the newly 'free' amino acids then detectable after a suitable derivatization step by gas chromatographic and liquid chromatographic separation techniques coupled to mass spectrometers.

As early as 1929 photochemical models have been proposed that are capable of inducing enantiomer-enrichments in chiral organic molecules [6–8]. Apart from asymmetric isomerization [9] and magnetochiral photochemistry [10–13], for inducing enantiomeric excesses (*e.e.*s) in chiral amino acids, we distinguish between enantioselective photolysis [14,15] and asymmetric photosynthesis. Enantioselective photolysis is based on the differential absorption of circularly polarized light (CPL) by amino acid enantiomers leading to *e.e.* formation. Recently it was shown that significant circular dichroic transitions in amino acids can be observed by extending circular dichroism (CD) spectroscopy to the vacuum-ultraviolet spectral range [16]. Circularly polarized light was thus shown to be capable of inducing *e.e.*s of the same handedness into proteinogenic amino acids. Interesting discussions concern circular dichroism spectra of alpha-methylated amino acids [17] that have been identified in carbonaceous meteorites with *e.e.*s of up to 18.5% [18]. Attempts to obtain an *e.e.* in amino acids have been performed very recently by condensing C_1- and N_1-unit precursor molecules such as H_2O, CH_3OH, and NH_3 under simulated interstellar/circumstellar conditions on a solid nitrogen-cooled surface at 80 K while being irradiated with synchrotron radiation of defined circular polarization [19]. After irradiation with UV-CPL, amino acids were recovered showing *e.e.*s of up to 1.34% [20]. We critically discuss these fascinating phenomena and put them into the context of current discussions on the origin of biomolecular homochirality.

In consideration of recent findings, it is assumed that amino acids and other prebiotic organic molecules form on interstellar dust grains in dense molecular clouds – the protostellar regions of space. These grains may accrete, resulting in the formation of various debris such as comets and asteroids [21–23]. Comets and asteroids can then be considered as vehicles delivering life's molecular seeds to the Early Earth [24,25]. Therefore comets are probably the best place to look for relicts of chiral organic molecules and enantiomeric excess. The European cornerstone mission ROSETTA was designed to land on the surface of the nucleus of comet 67P/Churyumov–Gerassimenko in 2014. ROSETTA's COSAC experiment includes an automatically operating enantioselective gas chromatograph that is coupled to a mass spectrometer [26]. This instrument was constructed in order to separate, identify, and quantify individual enantiomers of chiral organic molecules including amino acids in cometary matter *in situ* [27]. The scientific community looks forward to receiving and interpreting ROSETTA's results on the absolute asymmetry in cometary matter in 2014 and to relate these data to the results described above on evolved interstellar ice analogues.