Electrochirogenesis: The Possible Role of Low-Energy Spin-Polarized Electrons in Creating Homochirality

Richard A Rosenberg

Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA; rar@anl.gov

Received: 15 March 2019; Accepted: 8 April 2019; Published: 11 April 2019

Abstract: Electrochirogenesis deals with the induction of chirality by polarized electrons of which those with low energy (<15 eV) are seen to be the most effective. Possible sources of such electrons in the prebiotic universe are discussed and several examples where chiral induction by these electrons have been demonstrated are given. Finally, some possible scenarios where electrochirogenesis could have played a role in forming a chiral imbalance in a prebiotic setting have been speculated on and some possible future areas of research proposed.

Keywords: spin polarized electrons; homochirality; magnetism; prebiotic

1. Introduction

Pasteur first discovered the chiral nature of biological molecules in the 19th century. In the ensuing years numerous investigations have been devoted to trying to understand how chirality could have evolved in the prebiotic world. Despite all this effort, the editors of the 125th anniversary issue of Science Magazine in 2005 noted that among the 125 most important unanswered questions was the following:

“What is the origin of chirality in nature? Most biomolecules can be synthesized in mirror-image shapes. Yet in organisms, amino acids are always left-handed, and sugars are always right-handed. The origins of this preference remain a mystery.”

Fourteen years later, there is still no well accepted mechanism. Numerous reviews of research in this area have been written including one in the present issue [1–8]. Mechanisms are generally classified as biotic or abiotic. Biotic theories presuppose that the evolution of living matter inevitably resulted in chiral selection and homogeneity, whereas abiotic theories presume that the origin of life requires the prior development of chirality. Bonner categorized abiotic mechanisms as, determinate, chance and amplification [2]. A determinate mechanism presupposes that interaction of relevant organic molecules with a chiral physical force [1] led to an enantiomeric excess (ee). Perhaps the most invoked determinate mechanism is photochirogenesis, where the interaction of prebiotic molecules with spin-polarized ultraviolet (UV) photons is conjectured to lead to an ee [9–12]. In the present paper we examine the possible role of spin-polarized electrons in prebiotic chemistry, electrochirogenesis.

The interaction of longitudinally spin-polarized electrons (SPEs) has long been considered as a possible determinate mechanism for creating a chiral imbalance through their interaction with a racemic mixture of chiral molecules. Although spin-polarized electrons are not chiral particles, per se, longitudinally spin-polarized electrons are chiral, since as they propagate they trace out a helical path. The spin direction determines the helicity. Initial research in this area was stimulated by Vester and Ulbricht who proposed that the high energy spin-polarized electrons produced by parity violation in nuclear β decay [13,14] could indirectly play a role (V–U hypothesis) [15,16]. They hypothesized that the irradiation of polarized electrons with matter produced circularly-polarized “Bremsstrahlen”
photons, which subsequently induced stereoselective degradation or synthesis. Other researchers investigated the direct interaction of high energy SPEs with chiral molecules. Despite numerous investigations into both the V–U hypothesis and direct interaction of high-energy SPEs, no conclusive evidence was found to support either mechanism. Furthermore, Walker noted that the unpolarized secondary electrons produced by the high energy electrons would significantly dilute any chiral effects [17]. It is also worth noting that the high energy circularly-polarized “Bremsstrahlen” X-rays produced via the V–U hypothesis would have a very low absorption cross section for interacting with the low Z elements found in prebiotic molecules. Much of the research in this area was summarized in a 2011 review [18]. Although low energy electrons (<~15 eV) are very effective at inducing reactions in condensed molecular systems [19,20], the possible role of low energy SPEs at inducing chiral specific chemistry has been little discussed. In the present paper we will discuss recent progress in understanding the role of such low energy SPEs in creating an ee in an adsorbed chiral assembly.

2. Sources of Low-Energy Spin-Polarized Electrons

2.1. Valence-Level Photoionization by Ultraviolet (UV) Photons

In a ferromagnet the majority and minority valence electrons are unequally populated due to electron exchange interactions, which results in substantial spin polarization. Measurements on pure iron using 110 eV synchrotron radiation revealed polarizations as high as 45% [21]. Photoelectrons emitted from Ni single crystals show polarizations above 30% at threshold (5.2 eV) [22]. Even in the absence of no net magnetization, spin-orbit interactions can result in valence level polarized electrons. In the case of GaAs, spin polarizations of up to 40% have been observed following excitation with circularly polarized light in the range 1.5–3.6 eV [23]. As a result GaAs has found myriad uses as a source for SPEs in a variety of experiments. Polarizations as high as 15% have been found in gold using 6–9 eV CPL [24]. Since Au can also be used to self-assemble a variety of chiral molecules, it has been utilized as a substrate for spin-dependent transport measurements. Measurement using circular-, linear- and non-polarized light shown that there is an angular distribution in the emitted spin-polarized photoelectrons for a variety of non magnetic metals [25]. Using circularly polarized synchrotron radiation spin polarizations approaching 100% have been observed from adsorbed Kr and Xe excited by synchrotron radiation [26].

2.2. Secondary Electrons from a Magnetic Substrate

Any form of ionizing radiation (photons, electrons or ions) interacting with a solid will produce electrons. Primary electrons are emitted without any energy loss, but most electrons lose energy as a result of numerous collisions. The resulting secondary electrons (SEs) have very low energy, in the 0–10 eV range, as seen in a typical energy distribution curve shown in Figure 1b. In general, the electrons are unpolarized, but a high degree of polarization can be achieved if the material is ferromagnetic. The manner by which this is achieved is shown in Figure 1a. A ferromagnet has an imbalance between the number of majority and minority spin valence level electrons. The majority band in Figure 1a is totally filled while the minority band is partially filled. As the electrons scatter in the material, there is a higher density of minority band states available for occupation, so more electrons will scatter into them than into majority states. Hence the majority electrons have a longer mean free path than the minority ones, resulting in a net spin polarization of the former. Although subtleties exist in this model, it can be used to understand the basic process leading to SE polarization [27–31].
The incident electron becomes trapped in one of the lowest unoccupied molecular orbitals and forms a negative ion. Sometimes the incident electron also excites an electron in a molecule to a dissociative excited electronic state resulting in bond breaking. This is usually a minor process because the impact cross section is low, in the order of the absorption cross section, and there are relatively few electrons that have sufficiently high kinetic energy. The main route is called dissociative electron attachment (DEA). The incident electron becomes trapped in one of the lowest unoccupied molecular orbitals and forms a negative ion. Sometimes the incident electron also excites a second electron forming a one-hole, two-electron state or Feshbach resonance. These states are usually short lived and often these temporary negative ion states are dissociative, resulting in a negatively charged fragment and a neutral species. Dissociative electron attachment cross sections are about a factor of 100 or more higher than absorption cross sections in the hard and soft X-ray regimes and the cross section is maximum for positive ion injection.

Numerous measurements of the SE polarization have been made on various substrates using ions, photons or electrons. Polarization can range between ~10 to 70%. For a tabulation of secondary electron yield studies the reader is referred to Table 1 in Ref. [18].

2.3. Chiral-Induced Spin Selectivity (CISS)

As mentioned earlier, gold is the substrate of choice for the self-assembly of organic molecules. This property has enabled Naaman and coworkers to study the production of spin-polarized electrons as a result of spin filtering of chiral molecules adsorbed on Au using both circularly and linearly polarized laser light [32–38]. As a result even initially unpolarized electrons can become polarized by filtering of an organized chiral assembly, with polarizations reaching as high as 70% [38]. The rationale for this effect may be understood in terms of an effective Lorentz force acting on the electron. For a chiral molecule, the moving electron experiences a centripetal force in the direction perpendicular to the electron’s momentum. Furthermore, an effective magnetic field is produced along the axis of the chiral molecule, which introduces a spin-orbit coupling and thus a Zeeman splitting between the spin states of the moving electron. This results in a differential barrier height for the two spin states of the electron as it tunnels through the chiral bridge. Since the transmission probability depends exponentially on the barrier height, chiral molecules can act as very efficient spin filters. A number of recent articles have been devoted to detailing the mechanism by which this process occurs [39,40].

3. Chiral-Selective Chemistry via Low-Energy Spin-Polarized Electrons

Electrons have been shown to initiate chemical reactions in a variety of important biological molecules [41–43]. Dissociation primarily occurs by two main pathways. One possible dissociation process is a result of inelastic impact. A fast electron excites an electron in a molecule to a dissociative excited electronic state resulting in bond breaking. This is usually a minor process because the impact cross section is low, in the order of the absorption cross section, and there are relatively few electrons that have sufficiently high kinetic energy. The main route is called dissociative electron attachment (DEA). The incident electron becomes trapped in one of the lowest unoccupied molecular orbitals and forms a negative ion. Sometimes the incident electron also excites a second electron forming a one-hole, two-electron state or Feshbach resonance. These states are usually short lived and often these temporary negative ion states are dissociative, resulting in a negatively charged fragment and a neutral species. Dissociative electron attachment cross sections are about a factor of 100 or more higher than absorption cross sections in the hard and soft X-ray regimes and the cross section is maximum for positive ion injection.

Figure 1. (a) Schematic illustration showing how spin polarization of secondary electrons in a ferromagnet is achieved. Preferential scattering of minority electrons (red) into empty states above the Fermi level leads to a decrease in those electrons and thus a net spin polarization of the majority electrons (blue). (b) Permalloy secondary electron yield curve following excitation by 1190 eV X-rays.
slow electrons (<10 eV kinetic energy). As seen in Figure 1b there are a large number of secondary electrons in this energy range mainly because of inelastic scattering, which thermalizes the electron toward low energy, but also because such low energy electrons have a longer escape length so they are more likely to reach the interface region and react.

Since longitudinally SPEs are chiral particles, they should have chiral specific interactions with chiral molecules. The following sections will summarize recent experiments that demonstrate chiral specific reactions of adsorbed molecules initiated by SPEs.

3.1. Chiral-Specific Reactions Caused by Spin-Polarized Electrons from a Magnetic Substrate

Most experiments designed to see if a determinate mechanism can result in chiral specificity in a reaction start with a racemic mixture of molecules and then determine if the chiral physical force can impart an ee. The approach used in the work discussed here was to determine the reaction cross section, a more fundamental quantity, as a function of the chirality of the adsorbed molecule and the polarization of secondary electrons emitted from a magnetic substrate following X-ray irradiation. An easily magnetized permalloy (Fe$_{0.2}$Ni$_{0.8}$) substrate was chosen and a simple, model chiral molecule, (R)- or (S)-2-butanol (CH$_3$CHOHC$_2$H$_5$) was used as a reactant. Using X-ray photoelectron spectroscopy (XPS) changes in the intensity of the chemically shifted C–O peak were observed as a function of X-ray irradiation time. The chiral carbon on 2-butanol is bound to an –OH group. The intensity of the C–O peak decreases exponentially as a function of irradiation time as a result of cleavage of the C–O bond. The time constant ($\tau$) (reciprocal of the reaction rate) was determined by using the simple kinetic relationship, $I = I_0 \exp(-t/\tau)$, where $I_0$ = initial C–O peak area; $I$ = C–O peak area; $t$ = time, as a function of the spin polarization (magnetization direction) of the substrate secondary electrons and the chirality of the adsorbed molecule.

Figure 2 shows a series of C 1s XPS spectra of ~2 monolayers of (S)-2-butanol adsorbed on an argon ion sputter cleaned Permalloy surface, cooled to 90 K, obtained sequentially during 1190-eV X-ray irradiation. The C–H and C–O peaks decrease in intensity, while there is an increase in the C-M (carbon-metal) intensity. Kinetic analysis was performed by tracking the intensity of the C–O peak, since it directly probes the state of the chiral carbon atom. The time dependence of the C–O component is shown in the inset in Figure 2. Data points are shown by the red dots and the solid line represents an exponential fit to the data. Such measurements were performed 6–8 times for each magnetization direction and chirality. Results of the analysis are summarized in Figure 3a. The average time constants (seconds), with error bars, for (R)-2-butanol are shown in red, while those for (S)-2-butanol are in blue and the magnetization direction is denoted by +/−. These results clearly demonstrate that a dramatic change in the reaction rate for a given chirality is obtained by a reversal of the secondary electron spin polarization. For (S)-2-butanol this difference is 8.9 ± 3.5%, while for (R)-2-butanol, it is 10.9 ± 3.8%. The results for each enantiomer are mirror images of the other which further validates the proposed mechanism.

The results in Figure 3a indicate an average difference between the time constants for the two enantiomers of ~10%. In Figure 3b results of the ee for an initial racemic mixture as a function of reaction time is shown. The time spent acquiring the data in Figure 2, was 6900 s which equals 4.3 time constants. After this much time there would be 1.4% of the initial concentration remaining and the ee would be 25%. The ee would be 12% with 14% of the initial population remaining after a time equivalent to 2 time constants. Such values for enantiomeric excesses are significantly higher than those reported for experiments involving irradiation by circularly-polarized light or high energy SPEs.
Symmetry should be capable of filtering via the CISS effect as well [44]. When any substrate is subjected to ionizing radiation, secondary electrons will be produced. If chiral molecules are adsorbed on the surface then they could act as a spin filter for those initially unpolarized electrons. If additional ionizing radiation, secondary electrons will be produced. If chiral molecules are adsorbed on the surface then they could act as a spin filter for those initially unpolarized electrons. Additional experimental and theoretical studies indicate that higher energy (<15 eV) electrons by adsorbed chiral molecules resulting in spin polarizations as high as 70% [36, 38].

3.2. Chiral-Specific Reactions Caused by Natural Selection of Spin-Polarized Electrons

Section 2.3 discussed how the CISS mechanism can result in spin filtering of low energy (<1.5 eV) electrons by adsorbed chiral molecules resulting in spin polarizations as high as 70% [36,38]. Additional experimental and theoretical studies indicate that higher energy (<15 eV) electrons should be capable of filtering via the CISS effect as well [44]. When any substrate is subjected to ionizing radiation, secondary electrons will be produced. If chiral molecules are adsorbed on the surface then they could...
act as a spin filter for those initially unpolarized electrons. If additional chiral molecules are adsorbed on that layer then the SPEs should induce chiral specific reactions in those added molecules.

Figure 4 depicts a schematic diagram of an experiment designed to test this idea. The additional chiral molecule was (R)- or (S)-epichlorohydrin (C3H5ClO, Epi), which was adsorbed on a self-assembled monolayer of 70 base-pair long double-stranded DNA (dsDNA) cooled to 90 K. The dsDNA layer acts as a spin filter for the initially unpolarized secondary electrons produced by X-ray irradiation of the gold substrate. These secondary electrons then react with adsorbed Epi and the reaction kinetics were determined by the following changes in the Cl 2p XPS spectra in a similar fashion to Section 3.1 and quantum yields (QYs) were determined. When the two enantiomers were adsorbed on bare Au, the QYs were the same, but when adsorbed on the dsDNA layer the QY for S-Epi was ~16% greater than for R-Epi [45].

![Figure 4](image)

**Figure 4.** A schematic diagram showing how the Au secondary electrons produced by X-ray irradiation become spin polarized, with their spins aligned antiparallel to their velocity, and induce chiral selective chemistry in adsorbed (R)- or (S)-epichlorohydrin. This figure was originally published in Ref. [45].

The above work shows that dsDNA can act as an effective spin filter for secondary electrons in the energy range 0–10 eV (Figure 1b). However, additional studies indicate that dsDNA does not effectively filter higher energy (>30 eV) electrons [44]. The cause for this can be understood by examining the theoretically predicted polarization for a chiral overlayer as a function of wave vector, $k (E = 13.6 \, \text{eV} * k^2)$ shown in Figure 5. One can readily see that the relevant energy regime for chirality effects is $k = 0 – 1.5$ (0–30 eV) as shown in the inset and the effect decays very strongly at higher values [44].

![Figure 5](image)

**Figure 5.** Predicted electron polarizations as a function of electron energy in terms of wave vector $k (E = 13.6 \, \text{eV} * k^2)$ following scattering of electrons by a chiral overlayer. This figure was originally published in Ref. [44].
3.3. Chiral-Selective Adsorption

In a recent ground-breaking study, Banerjee-Ghosh, et al. demonstrated that the adsorption of a chiral molecule on a magnetic substrate is chiral specific [46]. They showed that if a substrate is magnetized in a particular direction one enantiomer adsorbs faster than the other, whereas if the magnetization is reversed, the opposite is true. This was determined by examining the initial adsorption rate of three different molecules: polyalanine, cysteine and DNA in solution, to a perpendicularly magnetized thin film covered with 5 nm of Au. In all cases the adsorption rate was dependent on the magnetization direction and the chirality.

In another recent paper Luque, et al. used XPS, ultraviolet photoelectron spectroscopy (UPS) and X-ray absorption spectroscopy (XAS) to monitor the bonding behavior of two different chiral molecules to a ferromagnetic thin film Co surface [47]. Using XAS they found that the ratio of the lowest unoccupied molecular orbital (LUMO) $\pi^*//\sigma^*$ peaks for one enantiomer was significantly different than for the other, which indicates that the hybridization between the molecular orbitals and the surface is chiral-dependent. Previously it had been found that the density of LUMO orbitals in self-assembled DNA films can be related to the secondary electron-induced damage cross section [48]. Therefore, the differences in the density of LUMO levels as a function of chirality may indicate that there may be a chiral dependence of the reaction rate in this case. It is also interesting to note that Luque, et al. [47] using UPS, found a significantly higher secondary electron background for two different enantiomers adsorbed on the Co surface. This indicates that there is a higher interaction of the secondary electrons for one adsorbed enantiomer as opposed to the other, which should result in a higher damage cross section for the former [49].

4. Mechanisms

The explanation for the chiral selective adsorption on a magnetic substrate can be understood by referring to Figure 6. When a chiral molecule binds to a surface, charge transfer occurs resulting in electric dipole polarization and excess of electrons and holes on opposite ends of the molecule. This charge polarization is accompanied by spin polarization via a CISS type mechanism [39,50], with the spin orientation determined by the chirality of the molecule. The substrate–molecule interaction will be stabilized via an exchange interaction if the spin of the electron on the end of the molecule bound to the surface and that of the ferromagnet (FM) are antiparallel (low spin state, Figure 6a) and destabilized if they are parallel (high-spin state, Figure 6b). For further details see Refs. [40,46].

![Figure 6](image_url)

**Figure 6.** Schematic diagram depicting the spin-dependent interaction between a ferromagnet (FM) substrate and chiral molecules. In (a) is shown a low spin interface where the spins of the molecule’s unpaired electron and that of the FM substrate are opposed whereas in (b) a high spin state is formed since the spins of the FM and the molecule are parallel.
In Sections 3.1 and 3.2 evidence was presented that demonstrated that low energy SPEs can produce chiral-specific reactions. By referring to Figure 6, symmetry arguments may be used to qualitatively understand the mechanism by which this may occur. The low energy secondary SPEs produced by irradiation of a magnetic substrate will have the same polarization as the majority spin electrons (spin up in Figure 6). The electron spin of the positively charged end of the chiral molecule is up in Figure 6a and down in Figure 6b. Thus, Pauli exclusion would favor the scattering of the free SPE into the same orbital as that of the electron in the positively charged end of the molecule in (b), which should stabilize the molecule. The opposite situation would exist for the chiral molecule in (a) so the SPE would tend to scatter into a higher lying orbital, producing a dissociative negative ion state via a Feshbach resonance [41]. Even in the absence of a strong adsorbate bond a chiral molecule will experience charge polarization and thus spin separation as a result of its dipole moment. Therefore, the SPEs produced by transmission through DNA (Section 3.2) will interact with an adsorbed chiral molecule in a similar fashion as discussed above, leading to chiral selective reactions.

5. Spin-Polarized Electrons in the Prebiotic Universe

Iron is one of the most common elements in the universe and numerous compounds based on it are magnetic. We have seen that irradiation of magnetic materials leads to low energy SPEs. Direct photoemission from a magnetic material by UV light will result in SPEs. If the UV light is circularly polarized, irradiation can result in SPEs from nonmagnetic material as well, although this effect is more dominant in higher Z materials.

A major component of the interstellar region is dust, which contains significant proportions of iron compounds, many of which are thought to be magnetic [51–54]. Analysis of meteorites has shown that there is a significant amount of iron- and nickel-based magnetic materials. Our nearest neighbor, Mars, is called the red planet due to the presence of various types of iron oxide in the soil, many of which have been determined to be magnetic [55]. Closer to home, numerous forms of magnetic materials are found on the earth’s surface and magnetic iron sulfide is a major component of hydrothermal vents [56].

One can imagine numerous possible scenarios where an electrochirogenesis mechanism could play a role in the formation of chiral, prebiotic molecules. It has been shown that UV irradiation of basic condensed molecules, analogous to those that form on dust grains in interstellar molecular clouds, results in the formation of prebiotic molecules such as (racemic) amino acids [57,58]. Ionizing irradiation of magnetic components of the dust particles will yield low energy, secondary SPEs, which could selectively react with a particular enantiomer yielding an excess of the other. There are numerous sources of magnetic fields in the universe. In fact Greenberg and Bonner have posited that circularly polarized synchrotron light produced by relativistic electrons orbiting a neutron start could produce an ee by irradiation of molecules condensed on dust grains of a passing molecular cloud [59,60]. The electrons are circulating due to the enormous magnetic field produced by the neutron star. This field could also align the magnetic domains in the dust particles thereby producing secondary SPEs as a result of irradiation by the synchrotron light or electrons. Such low-energy secondary SPEs would be very effective at producing an ee from a racemic mixture of adsorbed chiral molecules. Furthermore, gas phase amino acids (glycine) and chiral molecules (propylene oxide) have been detected in the interstellar region [61,62], as well as in comets [63]. If a magnetized dust particle were to interact with a chiral molecule it would tend to accrete one enantiomer over another via a CISS type mechanism (Section 3.3) [46].

Analysis of the Murchison meteorite revealed the presence of a wide variety of prebiotic molecules and, most importantly, chiral amino acids [64–67]. Meteorites, including the Murchison, are known to contain significant proportions of iron and nickel in a variety of magnetic states [68–71]. It is quite possible that low-energy, secondary SPEs produced by irradiation of magnetic domains in the meteorite could have selectively reacted with a particular enantiomer in an initial racemic adsorbate mixture leading to an ee of the other.
In a recent article, researchers investigating the structure of Martian meteorites have found an inventory of organic carbon species and have hypothesized that interactions between spinel group minerals, sulfides and brine enabled the electrochemical reduction of aqueous CO$_2$ to organic molecules [72] on Mars. Previous studies have shown that electrochemical reactions can play a role in the chemistry of important prebiotic molecules, such as amino acids [73,74] and purines [75]. If the electrodes are magnetic then spin-dependent chemistry may occur [76]. The particular minerals thought to serve as the electrodes are titano-magnetite, magnetite, pyrite and pyrrhotite, which have magnetic properties. Therefore, somewhere during the reaction cycle, SPEs could have induced chiral selectivity in the reaction products.

Hydrothermal vent systems have been postulated to be potential sites for prebiotic chemistry on Earth and possibly Mars and Titan [77,78]. Wang has suggested that magnetic material such as Greigite (Fe$_3$S$_4$) present in the vents can act as a spin filter under the action of an external magnetic field to produce SPEs or that irradiation of ZnS in the vents by circularly polarized light could produce SPEs, which could induce the synthesis of chiral organic molecules [79]. Further down the evolutionary cycle, the electrons released from the coenzyme NAD(P)H of amino acid synthase could become spin-filtered and polarized when they pass through the chiral α-helix structure of the enzymes to the site of amino acid synthesis at the other end of the helix producing only “spin up” electrons. The SPEs induce the reductive reaction between ammonia and α-oxo acid. As a result of the Pauli exclusion principle only L-amino acids are produced [80].

6. Further Research

Electrochirogenesis using low energy SPEs is a relatively unexplored area of research. Although, numerous avenues for further studies exist, the following possibilities could be very illuminating:

- Determination of an ee following X-ray irradiation of a racemic mixture of chiral molecules adsorbed on a magnetic substrate. The X-rays will produce low-energy secondary SPEs which should then selectively react with one enantiomer, leaving an ee of the other. If the cross sections for the two enantiomers differ by ~10% then the plot in the inset of Figure 3 indicates that there should be an ee of ~12% after 2 time constants of irradiation with about 14% of the material remaining. Such differences are well within the sensitivity range of modern chromatography techniques.
- Perform a Miller–Urey type experiment with a magnetized electrode. The magnetized electrode will produce low energy SPEs in the discharge which should selectively react with one of the enantiomers formed in the process. This should yield an ee of the other enantiomer and reversing the magnetization should yield an opposite ee.
- Irradiation of molecules condensed on a magnetic substrate by UV light. Previous work has shown that racemic amino acids can be produced by UV irradiation of simple molecules condensed on a non-magnetic substrate [57,58]. If the same experiment were performed using a magnetic substrate, SPEs would be produced which could result in the direct formation of a chiral amino acid or the destruction of a particular enantiomer from an initially formed racemic mixture. Reversing the magnetization directions should result in an opposite ee.
- Theory: although there has been significant progress made in modelling the manner by which SPEs are scattered by the gas phase [81] and adsorbed [82,83] chiral molecules, the mechanisms by which low energy SPEs cause chiral specific reactions are not well understood and could benefit from focused calculations using modern computational methods.

7. Conclusions

For more than 150 years scientists have been trying to determine what natural forces could have led to the prebiotic production of homochiral molecules which are essential for life as we know it. Electrons are the “glue” that hold molecules together, so it seems only natural that chiral electrons could have played a role. In this review we have discussed the possible role of electrochirogenesis, which deals
with the induction of chirality by polarized electrons of which those with low energy (<15 eV) are
seen to be the most effective. Possible sources of such electrons in the prebiotic universe have been
discussed and several examples where chiral induction by such electrons have been demonstrated.
Finally, some possible scenarios where electrochirogenesis could have played a role in forming a chiral
imbalance in a prebiotic setting have been speculated about and some possible future areas of research
proposed. This review is far from exhaustive and it is hoped that it will stimulate further activity in
this field.

**Funding:** The work performed at the Advanced Photon Source was supported by the U.S. Department of Energy,
Office of Science, Office of Basic Energy Sciences under contract No. DE-AC02-06CH11357.

**Conflicts of Interest:** The author declares no conflict of interest.

**References**

   [CrossRef] [PubMed]
   **2002**, *41*, 1139–1145. [CrossRef]
4. Feringa, B.L.; Delden, R.A.v. Absolute asymmetric synthesis: The origin, control, and amplification of
   [CrossRef] [PubMed]
7. Tsarev, V. Physical and astrophysical aspects of the problem of origin of chiral asymmetry of the biosphere.
   *Phys. Part. Nucl.* **2009**, *40*, 998–1029. [CrossRef]
   [CrossRef] [PubMed]
    *Orig. Life Evol. Biosph.* **2004**, *34*, 111–121. [CrossRef]
    Meierhenrich, U.J. Photochirogenesis: Photochemical models on the absolute asymmetric formation of amino
    [CrossRef]
    629. [CrossRef]
    **1959**, *46*, 68. [CrossRef]
18. Rosenberg, R.A. Spin-polarized electron induced asymmetric reactions in chiral molecules. In *Electronic
    and Mangetic Properties of Chiral Molecules and Supramolecular Architectures*; Naaman, R., Beratan, D.N.,


54. Hoang, T.; Lazarian, A. Polarization of magnetic dipole emission and spinning dust emission from magnetic nanoparticles. Astrophys. J. 2016, 821, 91. [CrossRef]


58. Muñoz Caro, G.M.; Meierhenrich, U.J.; Schutte, WA.; Fineran, I.A.; Jewell, P.R.; Remijan, A.J.; Blake, G.A. Discovery of the interstellar chiral molecule propylene oxide (CH₂CHCH₂O). Science 2016, 352, 1449. [CrossRef]


61. Cronin, J.R.; Pizzarello, S. Cometary glycine is a carbonaceous meteorite perspective. Acc. Chem. Res. 2006, 39, 231–237. [CrossRef]


78. Fortes, A.D. Exobiological implications of a possible ammonia–water ocean inside titan. *Icarus* 2000, 146, 444–452. [CrossRef]


