

ASTRONOMICAL SOURCES OF CIRCULARLY POLARIZED
LIGHT AND THEIR ROLE IN DETERMINING MOLECULAR
CHIRALITY ON EARTH

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ABSTRACT. The major source of circularly polarized flux potentially capable of inducing asymmetric photolysis of a racemic mixture of chiral molecules on the primitive Earth is the daytime sky. The degree of circular polarization (q) depends on the slope and orientation of the local terrain which obscures part of the sky. After allowance for dilution by direct sunlight values of $|q|$ range between about 10^{-4} and 10^{-5} . The rates of (1) asymmetric photolysis, (2) chiral selection by the electro-weak process and (3) racemization are not yet well enough known for the relative importance of these processes to be definitely established.

1. INTRODUCTION

Currently favoured mechanisms to explain why terrestrial biochemistry is based on L-amino acids and D-sugars involve a difference in either (i) the rate constants of molecular synthesis and destruction reactions of L-and D-isomers; or (ii) the electronic binding energy, ΔE between the two isomers, which originates in the parity non-conservation associated with weak neutral currents. Recent investigations indicate that a very small ΔE is sufficient to overcome the randomising effect of thermal fluctuations on reaction sequences ($\Delta E > 10^{-17}$ times the thermal energy, kT) and to lead to chiral selectivity in favour of the naturally occurring L-amino acids (Kondepudi and Nelson, 1983; Mason and Tranter, 1983, 1984). However because the bias associated with ΔE is so small, class (i) mechanisms might still override (ii) (which henceforth we refer to as the electro-weak process). While the action of spin polarized electrons emitted in beta decay has been discussed in some detail (though no detectable effect on racemic mixtures has yet been observed (Bonner, 1984)) the other class (i) mechanism, the action of ultraviolet and visible circularly polarized light on such a mixture, has received little astronomical attention, although it has been covered from the laboratory point of view (see e.g. Flores, Bonner and Massey, 1977). Here we assess the role of astronomical sources of circularly polarized light (CPL).

2. SOURCES OF CIRCULARLY POLARIZED LIGHT

Asymmetric photolysis by CPL of a racemic mixture of chiral molecules on the primitive Earth would have proceeded at a rate proportional to the circularly polarized flux of radiation illuminating the mixture, ie on the product of the degree of circular polarization, q , and the total flux, I . The two daytime sources of illumination, namely direct sunlight and the light of the daytime sky, would have dominated the photolysis produced by night-time sources mainly because of the much greater daytime flux and also because of the low net value of q from night-time sources : the great majority of individual stellar sources have low values of $|q|$ ($< 10^{-4}$) and with no preferred handedness of the circular polarization of these sources we anticipate $|q|_{\text{NIGHT}} < 10^{-6}$. Although a class of stellar sources with high circular polarizations is known, namely isolated magnetic white dwarfs with $\langle |q| \rangle \sim 10^{-2}$ and magnetic white dwarfs in binary systems with $\langle |q| \rangle \sim 10^{-1}$, these stars are too faint and too few to influence significantly the above limit on $|q|_{\text{NIGHT}}$. We also note that the suggestion by Rubenstein et al (1983) that a nearby supernova might be a relevant source of CPL has been discounted by Roberts (1984).

2.1. Daytime Sources : Sun and Sky

Broad-band continuum circular polarization is observed in sunspots in the range $|q| \sim 10^{-3}$ to 10^{-4} at wavelengths between 0.37 and 4.5 μm (Kemp and Henson, 1983). Away from sunspots the circular polarization is much lower and its absolute value is difficult to measure : at the centre of the solar disk $|q| < 1 \times 10^{-6}$ in the mid-visible (Kemp, 1984). The circular polarization, both in and away from sunspots, almost certainly has a magnetic origin but the mechanism is not fully understood (Kemp, Macek and Nehring, 1984). Differential measurements over the Sun (away from spots) suggest a north/south difference in $q \sim 3 \times 10^{-7}$ which might have its origin in a global field (Kemp, 1981, 1984). The net value of q for sunlight is much less than that for an individual sunspot. This is firstly because of the very good balance between positive and negative magnetic flux in bipolar regions and the larger complexes of solar activity (Gaizauskas et al., 1983); this should lead to an effective cancellation of the circular polarizations, with an upper limit to the net value of q for all solar active regions $\sim 10^{-5}$. Secondly after allowance for dilution of the polarization due to the small fractional area of the solar disk covered by spots ($f \sim 10^{-3}$), the net value of q for sunlight is dominated by the regions away from spots, ie $q_{\text{SUN}} < 10^{-6}$. Solar activity may have been greater in the past (Barry, Hege and Cromwell, 1984), in particular at the epoch when photolysis may have occurred on the primitive Earth, but the above limit on q_{SUN} is still reasonable even if f were as large as 10^{-1} .

The circular polarization of the daytime sky arises from multiple scattering of sunlight by atmospheric aerosols. For a

normal aerosol content the range of predicted (Hitzfelder, Plass and Kattawar, 1976) and observed values of q (Wolstencroft, 1984) are in reasonable agreement : at visible wavelengths typical values are $|q| \sim 10^{-3}$, with values approaching $\sim 10^{-2}$ in selected directions. The circular polarization observed at a fixed point of the sky as a function of time (Fig. 1) illustrates that $q = 0$ along the solar meridian and is equal in magnitude but opposite in sign in directions symmetrically placed either side of the meridian.

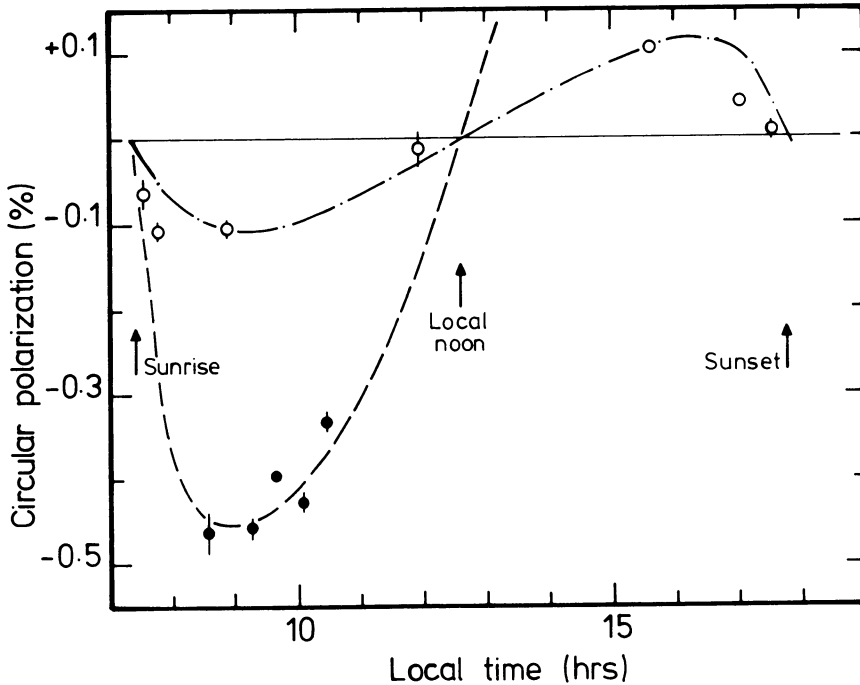


Figure 1. Degree of circular polarization (q) of the daytime sky as a function of local time in a fixed direction (34° altitude, due south) during two very clear days at Sutherland, South Africa. Open and filled circles represent observations at 5825\AA and 3500\AA respectively. The curves illustrate the anti-symmetric behaviour of q relative to the solar meridian.

Thus for a smooth spherical Earth with homogeneous atmospheric and surface properties we expect the net value of q_{SKY} for light received from all parts of the sky to be identically zero at all points of the Earth's surface at all times. For the real Earth a small net value of q_{SKY} can result if there is a significant tilt of the local terrain where unequal amounts of sky are sampled on either side of the solar meridian. Sloping terrain has the maximum effect

when the azimuth of the 'missing' sky is 45° away from the north or south directions and has no effect when oriented north or south. For example with 10% of the sky obscured by sloping terrain at the NE horizon, the time averaged value for light received from all accessible parts of the sky is $|q|_{\text{SKY}} \approx 1$ to 5×10^{-4} depending on wavelength. For a 10% obscuration at the NW horizon the value of q_{SKY} is of the same magnitude but of opposite sign. At a more typical site with about 1% of the horizon obscured we anticipate values of q_{SKY} in the range $+3 \times 10^{-5}$ to -3×10^{-5} . With allowance for dilution by direct sunlight ($q_{\text{SUN}} < 10^{-6}$, $I(\text{Sun})/I(\text{Sky}) \approx 3$ at $0.4\mu\text{m}$) the effective circular polarization from both sky and Sun is in the range $q_{\text{DAY}} = +1 \times 10^{-5}$ to -1×10^{-5} , the precise value depending primarily on the orientation of the local terrain. The mechanism of asymmetric photolysis by CPL on the primitive Earth would have been most effective in a region where there was a preferred orientation for the terrain (other than N-S or E-W), such as in the vicinity of a major mountain range. The above estimates of q_{DAY} are based on conditions today. If in the past the aerosol optical depth, τ , was much greater, at least for limited periods - perhaps due to volcanic activity - then the circular polarization would have been correspondingly greater. An increase from $\tau = 0.25$ (present day) to $\tau = 4$ would have increased q_{SKY} by an order of magnitude (Plass, Kattawar and Hitzfelder, 1976) and at the same time reduced the dilution by direct sunlight by at least an order of magnitude. In the example cited above of a typical site of sloping terrain the range of q_{DAY} would have been about $+2 \times 10^{-4}$ to -2×10^{-4} .

3. TIME SCALES FOR ASYMMETRIC PHOTOLYSIS, RACEMIZATION AND THE ELECTRO-WEAK PROCESS

Since low values of circular polarization are involved it is important to consider whether the rate of racemization exceeds the rate of asymmetric photolysis: if it does, then progressive photolysis will not take place. The racemization rate of amino acids depends significantly on temperature and whether they are incorporated into water-insoluble polymers (Dose, 1981). For four amino acids (phenylalanine, aspartic acid, alanine, isoleucine) under water-free conditions the range of half lives for racemization are 2×10^5 to 4×10^6 yr at 0°C and 2×10^3 to 4×10^4 yr at 25°C . Few laboratory determinations of the rate of asymmetric photolysis have been made: in one study by Flores, Bonner and Massey (1977) of (RS)-leucine an enantiometric excess (percent LH minus percent RH) of about 2% was produced using a 100% circularly polarized laser source in about one day. If the same rate constants apply when the polarization of the source is only $q_{\text{DAY}} \sim 10^{-5}$ then we predict, allowing for some uncertainty in the ratio of laboratory and solar power factors, that the same excess would be achieved in 10^4 to 10^5 years: the most optimistic prediction is $q_{\text{DAY}} \sim 10^{-4}$ for which the time scale is $< 10^4$ years. It is clear that asymmetric photolysis is more likely to overcome the racemization barrier at the lower

temperatures cited above, and that the above time scales do not rule out the success of asymmetric photolysis on the primitive Earth. However further laboratory studies are needed before a more positive statement can be made.

The rate at which the electro-weak process will proceed has been discussed by Kondepudi and Nelson (1984). They show that the minimum time scale, τ_M , varies inversely as $V(\Delta E/kT)^2$ where V is the volume in which the chemical reactions are occurring. Using the values of $\Delta E/kT$ calculated by Mason and Tranter (1983) for L-alanine and L-peptides in the α -helix and β -sheet conformation, Kondepudi and Nelson (1984) derive a crude estimate of $\tau_M \sim 10^3$ yr (assuming $V \sim 10^3$ litres). The biological relevance of the choice of reaction parameters needs to be fully explored before this estimate is useful for comparison with the timescale for asymmetric photolysis.

If racemization is shown to be unimportant, it seems likely that chiral selectivity would have been achieved first at those terrestrial sites where the net circular polarization of the daytime sky favoured asymmetric photolysis acting in the same sense as the electro-weak process. This bias in favour of the naturally occurring amino acids would have been present provided the rate of asymmetric photolysis was not too large.

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