BETA DECAY AND THE ORIGIN OF BIOLOGICAL CHIRALITY: NEW EXPERIMENTAL RESULTS

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ABSTRACT

The proposed connection between the parity-violating handedness of beta particles in radioactive decay and the sign (L) of biological chirality (the Vester-Ulbricht [V-U] hypothesis) is being investigated by measuring the theoretically predicted asymmetry in the formation of triplet positronium in amino acid enantiomers by low energy positrons under reversal of the helicity of the positrons. We find the asymmetry in leucine to be $(0.8\pm1.0)\times10^{-4}$, i.e. consistent with the theoretical prediction of 10^{-6} to 10^{-7}. The apparatus is now sensitive enough to test the predicted asymmetry in optically active molecules which have heavy atoms at their chiral centers. The connection between these results and asymmetry in radiolysis by beta-decay electrons is made, and the implications of our limits for the V-U hypothesis discussed. Although the above limits are 10^6 times lower than direct measurements of radiolysis, they are still not small enough to allow us to rule out the V-U hypothesis.

INTRODUCTION

Maximal optical activity, an identifying signature of life on earth (1), represents a mirror-asymmetric or parity-violating state. The origin of the sign of the chiral polarization η of this state ($\eta \equiv [n_L-n_D]/[n_L+n_D]$ with n_L, n_D the number of L,D molecules) e.g. $\eta = +1$ for amino acids, is still unknown and constitutes a question of fundamental interest in chemical evolution. We are now investigating the possibility, the Vester-Ulbricht (V-U) hypothesis (2), that the sign of η is

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causally related to preferential radiolysis of mirror image molecules by beta particles polarized as a result of parity non-conservation in the weak interaction. The weak interaction is the only one of the four universal interactions (the others being the electromagnetic, gravitational and strong interaction) which violates parity. Thus only the weak interaction can give rise to a causal, as opposed to random, choice for the sign of η.

It is now 25 years since the formulation of the V-U hypothesis. Since that time there has been no uncontested experimental demonstration of a connection between the sign of η and the weak interaction, and no theory which can quantitatively describe the entire process leading from a small induced asymmetry in an initially racemic mixture to the present state of enantiomeric purity. Recently, however, two theories (3,4) have been developed which do make quantitative predictions of weak interaction related asymmetries in the interaction of L versus D chiral molecules with handed beta particles. While these predicted asymmetries are far too small to be observed experimentally, one of the theories (3) also predicts the existence of a closely related asymmetry in the interaction of positrons with chiral molecules which is 10^5 times larger than the direct radiolysis asymmetry, and which is therefore accessible to measurement. We are performing such an experiment.

Before discussing our experimental results, we first review the theoretical model which allows us to connect the positron experiment to the L versus D asymmetry in radiolysis caused by handed beta decay electrons. The relation of the limits set on this latter asymmetry by our experiment to the V-U hypothesis is discussed at the end of the article.

BOUND HELICAL ELECTRON MODEL

A concept similar to handedness or chirality is helicity. The helicity (h_i) of a particle is defined to be $h_i = \hat{s}_i \cdot \hat{p}_i$, where $\hat{s}_i$ is the spin operator and $\hat{p}_i$ the momentum direction. The helicity of a beam of particles is the average of the individual helicities. Electrons bound within an atom or molecule can also have an average helicity, but because a bound state is not an eigenstate of helicity, it is more convenient to work instead with the helicity per unit volume or helicity density [$\mathcal{h}(\vec{r})$]. The helicity density becomes non-zero when the dissymmetric electrostatic fields of the core of a chiral molecule influence the electron spin orbitals through the spin orbit coupling. The size of $\mathcal{h}(\vec{r})$ depends on the molecular dissymmetry and, via the spin-orbit coupling, on $(\alpha Z)^2$, where α is the fine structure constant (α=1/137) and Z is the atomic number of the dominant heavy atom in the dissymmetric environment of the molecule.

Manifestation of $\mathcal{h}(\vec{r})$ occurs when a beam of electrons or positrons which itself has helicity is incident on a target of chiral molecules. The spin-dependent electron exchange interaction gives rise to asymmetric ionization (radiolysis) (A_R) when high-energy beta-decay electrons of helicity $h(e^-)$ are used. Writing $R^+(L)$, $R^-(L)$ as the radiolysis rate when electrons of positive or negative helicity are incident on an L enantiomer (and similarly for $R^+(D)$, $R^-(D)$), A_R is given by

$$A_R \equiv \frac{R^+(L)-R^+(D)}{R^+(L)+R^+(D)} = \frac{R^+(L)-R^-(L)}{R^+(L)+R^-(L)} = |h(e^-)|H_R(E_p,Z) \ .$$

H_R is essentially an average $\mathcal{h}(\vec{r})$ weighted by the electrostatic interaction between the projectile electron of energy E_p and the electrons of the target molecule. For projectile energies of order 10^5-10^6 eV, H_R is given by the relation (E_p measured in eV)

$$H_R(E_p,Z) \simeq \frac{14\eta_R'(\alpha Z)^2}{E_p[\ell n(E_p)-2.6]} \ .$$

The molecular asymmetry factor (η_R') takes into account the degree of dissymmetry in the molecular structure and is estimated to be of order 10^{-2}-10^{-3}. For $E_p \sim 10^5$-10^6 eV and Z=6, $H_R \sim 10^{-10}$-10^{-12}.

An alternative manifestation of $\mathcal{h}(\vec{r})$ which produces a much larger effect is the formation of the hydrogen-like electron-positron bound state called positronium (Ps). Ps exists in both the triplet and singlet states. Because Ps formation depends on the relative momenta of the positron and electron, and the triplet/singlet ratio depends on the relative spin directions, triplet (or orthopositronium, oPs) formation is dependent on both $\mathcal{h}(\vec{r})$ and the positron helicity at the time of of Ps formation, $h_f(e^+)$. Defining $f^-(D)$ as the fraction of positrons with negative helicity forming oPs on the D enantiomer (with similar definitions for $f^+(D)$ and $f^{\pm}(L)$), the asymmetry in oPs formation is given by

$$A_{Ps} \equiv \frac{f^+(L)-f^+(D)}{f^+(L)+f^+(D)} = \frac{f^+(L)-f^-(L)}{f^+(L)+f^-(L)} = |h(e^+)|H_{Ps}(Z) \ .$$

In this equation H_{Ps} is analogous to H_R, but, because Ps is formed in a narrow band of energies near 10 eV, the equation contains no direct projectile energy dependence. For Z=6, $H_{Ps} \sim 10^{-5}$ to 10^{-6}.

We can relate the measured value of H_{pS} to H_R through

$$H_R(E_p,Z) = H_{pS}(Z)(\eta'_R/\eta_{pS})\frac{14}{E_p[\ell n(E_p)-2.6]}$$

where η_{pS} is a molecular asymmetry factor similar to η'_R. The factor η_{pS} has been calculated (3) to be $\eta_{pS} \sim 10^{-2}$-10^{-3}. Although η'_R has not been calculated, it is expected to be of the same order of magnitude, but the relative sign of the two factors is not known at present. The determination of these factors awaits more accurate wave functions for the molecules under consideration or a direct measurement.

EXPERIMENT

As described in detail elsewhere (5), we produce a beam of monoenergetic positrons with an intensity of 1×10^5/sec, a measured initial helicity $h_0 = (0.48\pm0.02)$, and an energy adjustable between 2 and 2000 eV. The helicity may be reversed by means of a spin rotator. The apparatus is shown in Fig. 1.

The beam is focussed onto an amino acid powder sample which has been sublimated or deposited in a thin layer on a metal plate. The positrons, typically with energy 200 eV, enter the sample, lose energy, and within 10^{-12} second reach an energy near 10 eV where a fraction, typically 10-20%, form oPs, diffuse to the surface of the sample and escape into the vacuum, where they have a lifetime of 142 nsec. The other positrons either annihilate directly with an electron, form the short-lived (0.13 nsec lifetime) singlet positronium or form oPs which annihilates within the sample. All of these latter possibilities have lifetimes under 2 nsec. Thus by measuring the time between positron arrival and emission of the annihilation gamma rays we can separate the long-lived oPs from other species. To measure the fraction of events in which oPs is formed and escapes into vacuum, we count events with a time interval between positron entrance and gamma emission from 25 to 500 nsec. From this count we subtract the random background and normalize it to the total number of recorded positrons. This ratio, r, is then found for positive and negative beam helicity and the asymmetry, $A_{pS} \equiv (r^+-r^-)/(r^++r^-)$ is calculated. Helicity is reversed every 300 sec during a typical 8 day run. Asymmetries are measured for several D, DL, and L samples.

A major improvement in the present experiment over the preliminary one (5) is the method used to provide the positron arrival (t=0) signal. Within the beam the positrons strike a second set of tungsten vanes (see Fig. 1). With a 16%

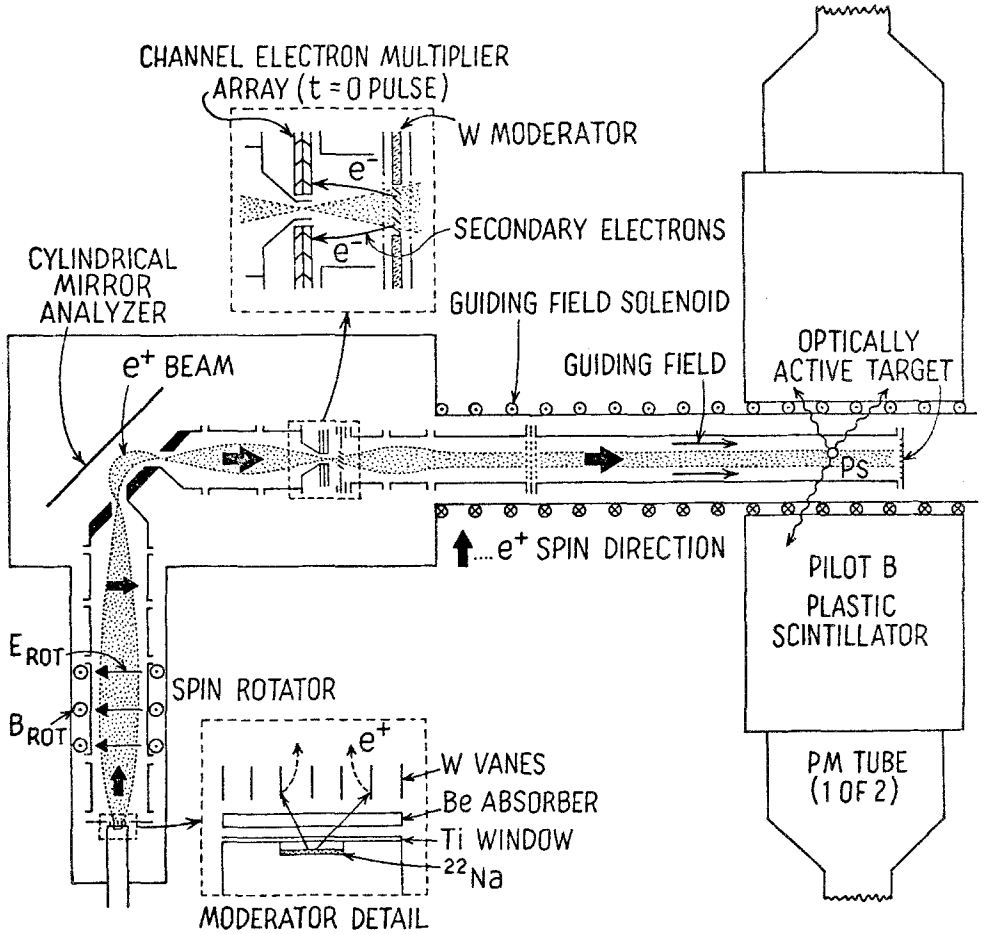

Figure 1: Experimental apparatus.

efficiency, they are remoderated and coincidentally emit a secondary electron which is detected by the channel electron multiplier array to provide the positron arrival signal. This new apparatus represents the first use of remoderation to both form and time a slow positron beam. The positrons are reaccelerated to 200 eV and transported to the amino acid target. With the positron timing system removed from the target region, instrumental asymmetries have been reduced to below 7×10^{-5}, and the options for producing samples of amino acid powders have been greatly expanded. In addition, in the new experiment, the initial helicity has been increased from 0.22 to 0.48, increasing experimental sensitivity by more than a factor of 2, and the beam intensity incident on the target has been increased by a factor of 6.

The value of $H_{PS}(Z)$ which is to be determined from the measured value of A_{PS} depends on the helicity of the positron at the time of Ps formation, $h_f(e^+)$. We previously estimated that a positron which enters the solid at 400 eV will have a final helicity of $h_f(e^+) = (0.2\pm0.1)$. Work on this calculation is continuing in collaboration with R. Hamm of Oak Ridge National Laboratory.

RESULTS

In the preliminary experiment (5), we found $A_{PS} < 4\times10^{-4}$ in tryptophan and cystine, and reported a possible effect of $A_{PS} = (16\pm4)\times10^{-4}$ in leucine. (We note that for notational consistency with ref. 3 we have redefined $A_{PS} \equiv (A_{PS}(L)-A_{PS}(D))/2$.) With the new apparatus we have remeasured the asymmetry in D, DL, and L leucine and find $A_{PS}(D) = (+2.7\pm1.5)\times10^{-4}$, $A_{PS}(DL) = (+0.5\pm1.5)\times10^{-4}$, and $A_{PS}(L) = (+1.2\pm1.5)\times10^{-4}$. Thus we conclude that in leucine the L versus D asymmetry is $A_{PS} = (0.8\pm1.0)\times10^{-4}$, i.e., it is consistent with a null result at the 10^{-4} level and with the theoretical value $A_{PS} = h_f(e^+)H_{PS} \sim 10^{-6}$-$10^{-7}$, taking $h_f \simeq 0.2$.

Using our present upper limit of the value of H_{PS} in leucine, $H_{PS} < 5\times10^{-4}$, we find the upper limit of the radiolysis effect in leucine, $H_R < 5\times10^{-9}$. Thus $A_R < 5\times10^{-9}$, in agreement with the theoretical estimate $10^{-10} < A_R < 10^{-12}$ for Z=6. We are now measuring asymmetries in selenocystine, an optically active molecule containing selenium (Z=34) at the chiral center. The overall spin-orbit coupling of selenium is approximately 100 times that of carbon. This, combined with other factors peculiar to selenocystine, gives an upper bound of 10^{-3} for A_{PS}, which would be observable at our present experimental sensitivity.

Experimental knowledge of A_R is needed in order to investigate the steady-state value of η (η_∞) which can be induced by asymmetric radiolysis. The value of η_∞ is found by studying linear rate equations for n_L and n_D -- the Mann-Primakoff equations (6). These equations, discussed in ref. 7, are linear, and thus do not describe autocatalysis or self-replication. The results of the analysis applied to the prebiotic ocean predict that for the actual experimental limit on A_R so far obtained in leucine ($A_R(expt) < 10^{-8}$, with the absolute value understood in what follows for both experimental limits and theoretical calculations), $\eta_\infty(expt) < 10^{-11}$, while for the theoretical value of A_R ($A_R(th) \sim 10^{-11}$), $\eta_\infty(th) \sim 10^{-14}$. These values of η_∞ assume combined β^- sources of ^{14}C and ^{40}K with the usually accepted concentrations of 3×10^{-12} and 4×10^{-8} respectively, and a temperature of -20°C (the freezing point of the ocean) at which the value of η_∞ is maximized. The time necessary for η to

approach η_∞ under these conditions is of order 2×10^8 yr (the thermal racemization time constant).

In order to consider the V-U mechanism as the cause of the sign of η currently observed, the value of η_∞ must be compared to statistical fluctuations present in η in a given system. For example, if we assume that A_R equals the maximum value consistent with our experiments, i.e. $A_R(\text{expt}) \sim 10^{-8}$ so that $\eta_\infty(\text{expt}) \sim 10^{-11}$, statistical fluctuations will be outweighed by asymmetric radiolysis if $n_L+n_D \sim 10^{23}$ molecules, assuming the fluctuations in the system to be Gaussian ($\sqrt{n_L+n_D}$). Obviously a system incorporating this number of chiral molecules is not unreasonable from the standpoint of size. However, the current experimental limit $A_R(\text{expt}) < 10^{-8}$ is considered to be an extreme upper limit (recall $A_R(\text{th}) \sim 10^{-11}$). Using $A_R(\text{th})$ and therefore $\eta_\infty(\text{th}) \sim 10^{-14}$ we need $n_L+n_D \sim 10^{29}$ (10^2 m^3 of saturated alanine solution) for η_∞ to exceed statistical fluctuations. In view of the current uncertainty concerning amplification (no amplification mechanism has been demonstrated experimentally, although mathematical models of such mechanisms exist (8)) one cannot rule out amplification incorporating the above mass of material.

Finally we note that the small value of $\eta_\infty(\text{th})$ discussed above is due in part to the small concentration of beta radioactivity thought to be present in the prebiotic ocean. The presence of larger concentrations of activity can lead to a maximum value of $\eta_\infty \sim A_R$ (7). We have recently analyzed evidence for beta sources of much greater specific intensity than ^{14}C and ^{40}K which may have been present on the prebiotic earth (9). Two sources which have been identified are detrital ^{235}U (β^- emitter) deposits (including those of sufficient specific activity to form natural reactors of the Oklo type) and ^{26}Al (β^+ emitter). Either can give rise to $\eta_\infty \sim A_R$ approached in times (depending on source concentration) of order 10^2-10^8 years. As noted above such sources would allow η_∞ to exceed statistical fluctuations in η in a system of size $n_L+n_D \sim 10^{23}$.

In summary, our primary experimental and theoretical conclusions to date are:

(1) $A_{PS}(\text{expt}) < 10^{-4}$ in leucine which implies $A_R(\text{expt}) < 5\times10^{-9}$.

(2) The limit $A_R < 5\times10^{-9}$ is 10^6 times lower than has been obtained from any direct radiolysis experiment but is still 10^2-10^3 times larger than theoretical predictions for leucine.

(3) Neither the experimental limits nor the theoretical estimates allow us to rule out a V-U mechanism as the cause of the sign of the presently observed η.

(4) Experiments now in progress using selenocystine may enable us to observe a preferential interaction between polarized beta particles and chiral molecules for the first time, thus securing a crucial experimental fact in the problem of the sign of η in biological systems.

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