POLARIZED BREMSSTRAHLUNG NOT THE SOURCE OF OPTICAL ACTIVITY

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Abstract. An evaluation is made of the previously proposed scheme (polarized β-particles → circularly polarized bremsstrahlung → optically active molecules) by which dissymmetry at the elementary particle level may be transmitted to the molecular level. The calculations suggest that much too small a fraction of the total energy of the electron appears as light, capable of causing photochemical resolution, to explain results obtained in the laboratory on the preferential radiation-induced decomposition of one enantiomer of chiral amino acids.

Shortly after the prediction (Lee and Yang, 1956) and verification (Wu *et al.*, 1957) of the violation of parity in weak interactions, Vester (1957) and Ulbricht (1959) suggested a connection between chirality at the elementary particle level and that at the molecular level. Specifically they suggested that it could be the inherent polarisation of β-particles which caused widespread occurrence of only one optical isomer of sugars and amino acids in biologically important materials. Some experiments have been reported in the last few years which were designed to examine the plausibility of this interesting suggestion in a laboratory situation. Positive evidence for this connection is claimed in two experiments wherein preferential decomposition occurred of one enantiomer (and, in each case, the one not found in nature): firstly, by Garay (1968) who irradiated dilute solutions of D and L amino acids with ^{90}Sr-Y β-particles (average energy $\approx$ 0.8 MeV), the other by Bonner *et al.* (1975) using crystalline racemic amino acids bombarded by a beam of polarised 0.12 MeV electrons. In other experiments no evidence for the transmission of dissymmetry was found (Vester *et al.*, 1959; Ulbricht and Vester, 1962; Gol'danskii and Khrapov, 1963; Lai, 1970; Bernstein *et al.*, 1972, Lemmon *et al.*, 1974; Bonner, 1974).

Vester and Ulbricht discuss possible pathways by which this could occur, favouring the one involving polarised bremsstrahlung (Vester, 1957 and 1974; Ulbricht, 1959, 1975a and 1975b, Bonner, 1973). Garay (1968) adopted this mechanism to explain his results, and Bonner *et al.* (1975) suggest that it may be the pathway in their case too. The mechanism proposed is indicated by scheme (1).

Longitudinally polarised high energy electrons	→	Circularly polarised bremsstrahlung radiation	→	Stereoselective photochemical decomposition, synthesis or resolution	(1)

The purpose of this Note is to point out that the above scheme cannot be responsible for the results obtained in the *laboratory*, because, of the total chemical change induced by the high energy electron, the fraction which occurs by the above scheme is much too small to account for the results obtained. Needless to say, this mechanism could be responsible for the asymmetry which is now built into living systems, because even a minute preference for one enantiomer may be amplified by

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replicative or autocatalytic steps into complete dominance during biological evolution.

In discussing the merits of scheme (1) as the source of preferential decomposition, several factors must be considered: (a) What fraction of the energy of the β-particle is deposited in the medium in the form of bremsstrahlung? (b) What fraction of it is absorbed by the amino acids in a photochemical process that could be stereoselective? (c) What is the degree of polarisation of this radiation? (d) What optical purity could arise from that stereoselective absorption? Let us call these factors F_a, F_b, F_c and F_d and try to estimate their product.

(a) High energy electrons in the 0.1 to 1 MeV range deposit most of their energy by ionisation and excitation, particularly in media of low atomic number ($\bar{Z}_{\text{effective}}$ may be taken as 6 ± 2 for amino acids or aqueous or alcoholic solutions). The fraction of the energy of an incident electron which appears as bremsstrahlung in a medium in which it comes to rest is approximately given by $E_o Z/1400$, where E_o is the incident electron energy in MeV (Johns, 1969). Thus, for 0.8 MeV electrons bombarding aqueous solution or solid amino acids we have $F_a = 3 \times 10^{-3}$.

(b) The spectral distribution of bremsstrahlung is constant from $h\nu = 0$ to $h\nu = E_o$ for a "thin" target (no significant degradation of the electron energy) but when stopped in the medium (regardless of Z) the total radiation produced has a spectral distribution such as that sketched in Figure 1 (Johns, 1969). In addition there will be "characteristic" X-radiation produced, which depends on the target atoms. K_α radiation from O atoms has an energy of 0.532 keV, from N, 0.392 keV and from C, 0.282 keV (Fine and Hendee, 1955); but this will only represent a few percent of the total photon flux when E_o is in the range 0.1 to 1 MeV. We need to estimate what fraction of the radiation is of sufficiently low energy to be absorbed by the amino acids in a "*photochemical*" process, because the high energy X-ray region will be reabsorbed by photoelectric and Compton processes – thereby creating another energetic electron to again repeat the cycle.

Figure 1 shows an essentially linear relationship between dI/dE and E so that Equation (2)

$$\int_0^{E'} dI = a \int_0^{E'} (E_o - E)\, dE \tag{2}$$

may be used to evaluate the amount of light emitted at photon energies between 0 and E', where a is independent of E and neglecting the characteristic X-radiation. The fraction of the total light having $h\nu < E'$ is then given by Equation (3).

$$F_b = 2E'/E_o - (E'/E_o)^2. \tag{3}$$

Let us assume, following Vester (1974), that photochemical absorption might extend out to $E' \leqslant 100$ eV ($\lambda \geqslant 12.5$ nm), then, for $E_o = 0.8$ MeV, we have $F_b = 2.5 \times 10^{-4}$.

It is worth noting at this point how the energy is dissipated. In media like aqueous solutions or solid amino acids, ionisations and molecular excitations cause chemical change with a typical efficiency of 3 molecules transformed per 100 eV of energy absorbed. For these systems, whether in direct or indirect processes, each 0.8 MeV electron typically decomposes 2.4×10^4 amino acid molecules. By (a) and (b) above

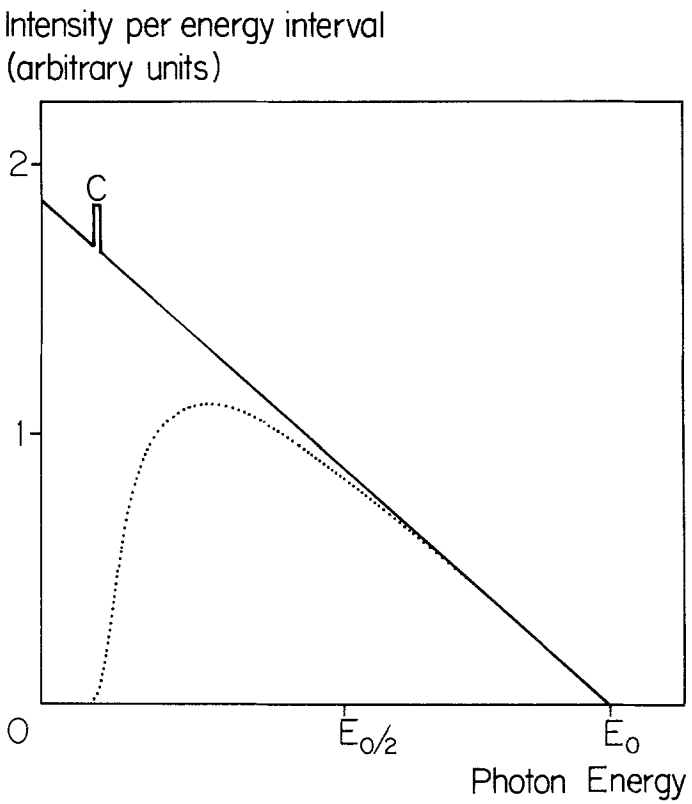

Fig. 1. Spectral distribution of bremsstrahlung radiation produced when electrons of initial energy E_o (in the range 0.1 to 2 MeV) are stopped in a target (solid line). The dotted line indicates the sort of distribution to be expected after "filtering" by the source and its housing (for instance, when an external β-source is used). Some characteristic K_α radiation is indicated at C. (Adapted from Johns, 1969.)

we have deduced that the same 0.8 MeV electron will, on average, release $0.8 \times 10^6 \times F_a \times F_b = 0.5$ eV of its energy as photons of 100 eV or less. Supposing these to be 5 eV photons which decompose amino acids with a quantum yield of unity, then the fractional decomposition by photochemical means would be $0.1/2.4 \times 10^4$, namely 4×10^{-6}*.

(c) McVoy (1957, 1958) has evaluated the extent of circular polarisation in the bremsstrahlung from 100% polarised electrons. His calculations predict that, whereas the polarisation of the light can be as high as 97% at $h\nu = E_o$ for relativistic electrons (>200 keV), the polarisation falls off sharply for low photon energies and is likely to be very small for $h\nu < 100$ eV. Vester (1974) estimated this to be $\approx 10^{-4}$. Let us merely assert here that $F_c < 10^{-3}$.

(d) The enantiomeric purity which may be achieved by selective photodestruction – except when a racemic mixture is almost completely destroyed (Kagan *et al.*, 1974) – is of the order of the dissymmetry factor, given by the extinction coefficients,

* Even if in a dilute solution case, such as Garay's (1968), the indirect effect is inhibited, (as it will be in that case by the alcohol present) there will still be a "direct" effect roughly proportional to the density fraction of amino acids in the system (say $\sim 10^{-2}$); in which case the above computed figure should become 4×10^{-4}.

$2(\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$. At favourable wavelengths this quantity is less than 10^{-2} for amino acids, so we may put $F_d < 10^{-2}$.

Our tally for $F_a \times F_b \times F_c \times F_d$ comes to $< 7.5 \times 10^{-12}$. Since the observed fractionations are about 10^{-2} (Garay, 1968 and Bonner *et al.*, 1975) scheme (1), invoking bremsstrahlung as an intermediate stage, should be discarded and some other mechanistic pathway sought.

Because of the absolute magnitude of the factors discussed above, it would be improper to infer experimental corroboration for the *non*involvement of bremsstrahlung (in transmitting dissymmetry) from the fact that Bonner obtained a negative result when using only bremsstrahlung (1974) and a positive result when using electrons plus their bremsstrahlung (1975). In fact, although F_a would equal unity, F_b would have been extremely small when using the external Sr source (1974), just because the material (containers, etc.) which stopped the electrons would also stop the "photochemical" bremsstrahlung (see dashed curve in Figure 1).

Radiation chemical changes occur by "direct" and "indirect" processes. In dilute solution the latter dominate so that retention of dissymmetry must be transmitted through reactive intermediates from the solvent. We studied this possibility using chiral solvated electrons but found that the stereoselective reactivity towards different enantiomers was less than we could measure, $\approx 10\%$ (Ulrich and Walker, 1975). On the other hand one would expect a direct effect, namely that polarised high energy electrons have different efficiencies for ionisation and excitation processes of valence electrons confined to right handed helical molecules as compared to left-handed ones; but is the difference measurable?

Acknowledgement

I am grateful to Prof. L. D. Hayward for helpful discussions and to the National Research Council of Canada for financial support.

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