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**CHIRAL SYMMETRY BREAKING PRODUCED BY
MAGNETIC AND ELETRIC STATIC FIELDS: THE
ENANTIOMERIC EXCESS IN CHEMICAL SYSTEMS**

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CHIRAL SYMMETRY BREAKING PRODUCED BY MAGNETIC AND ELECTRIC STATIC FIELDS: THE ENANTIOMERIC EXCESS IN CHEMICAL SYSTEMS

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ABSTRACT

A chiral symmetry breaking occurs when optical active molecules, taken as two-level systems, are placed in parallel magnetic and electric static fields. We analyse how this symmetry breaking can be used to amplify the production of one enantiomer in chemical systems.

KEY WORDS: optical active molecules in magnetic and electric static fields, two-level model, asymmetric synthesis.

1. INTRODUCTION

As is well known,¹ Earth biochemistry is overwhelmingly dissymmetric or chiral. Living organisms are characterized by the presence of optically active and enantiomerically pure molecules. Proteins are composed of L-amino acids while nucleic acids contain only D-sugars. Pasteur, long ago, regarded the violation of mirror symmetry in biomolecules as the most important material attribute of life. However, the transition from racemic geochemistry to homochiral biochemistry remains up to now a major problem of chemical evolution. Plausible mechanisms have been proposed to explain the origin of biased molecular handedness in biochemistry, as one can see in many review articles.²⁻⁶ As pointed out by de Min et al.,³ studies on the enantiomeric purity of substances is very important not only to investigate the origins of life but also to improve methods for the production of chiral molecules, necessary for pharmacology and medicine, in laboratories and on industrial scale.⁷ Since light and electric fields also "feel" a molecule's handedness, single-handed products of enantiochemistry could lead to new materials for optical and optoelectronic technologies.⁸

With the discovery of parity violation in weak interactions many attempts have been made to show the interrelation of this effect with the homochiral dominance in biochemistry. Amazing results have been obtained by Kondepudi and Nelson^{9,10} considering the parity violation effect in open nonequilibrium model chemical systems. It was demonstrated that the very small neutral weak currents (WNC) suffices to break the chiral symmetry of racemic reaction sequences in an open nonequilibrium system (see also Cattani and Tomé¹¹). It was shown¹⁰ that if these reactions occur in a system where the net effect of random fluctuations can be taken as very small perturbations, the production of L-enantiomers will be enhanced since the weak forces favor the left-handed enantiomers. Thus, chirally asymmetric life could evolve in these chemical systems.

Absolute asymmetric synthesis (AAS) denotes an enantioselective synthesis from a chiral starting material without the help of chiral reagents. In 1975 Gerike¹² intro-

duced a new AAS carrying out reactions in electric fields to which parallel, or orthogonal constant or alternating magnetic fields were superimposed. In 1978 the effects of magnetic and electric fields on prochiral chemical reactions was estimated theoretically by Rhodes and Dougherty.¹³ Recently, Breitmaier et al.¹⁴ applying only a static magnetic field, of between 1.2 and 2.1 tesla, to the reaction solution obtained a virtually pure single enantiomer product. Up to now we have no clear idea why the electric and magnetic technique works.¹⁵ In this paper a very simple two-level approach will be developed in order to help us to understand a little better these AAS processes.

In section 2 we study optical active molecules, taken as two-level systems, placed in parallel magnetic and electric static fields. Since we intend only to investigate the essential aspects of the phenomenon, we assume that the magnetic and electric dipoles of the active molecules are only those that are responsible for the optical activity in the molecules. In these conditions we verify that a chiral symmetry breaking occurs in the optical system. In section 3 we see how this symmetry breaking can be used to amplify the production of one enantiomer in chemical systems.

2. OPTICAL ACTIVE MOLECULES PLACED IN MAGNETIC AND ELECTRIC STATIC FIELDS

Optical activity occurs¹ when the molecule has two distinct left and right configurations, $|L\rangle$ and $|R\rangle$, which are degenerate for a parity operation, i.e., $P|L\rangle = |R\rangle$ and $P|R\rangle = |L\rangle$. Left-right isomerism can be viewed in terms of a double-bottomed potential well^{16,17} and the states $|L\rangle$ and $|R\rangle$ may be pictured as molecular configurations that are concentrated in the left or right potential well. Let us indicate by x the coordinate involved in the parity operation P connecting the two potential minima. It may represent the position of an atom, the rotation of a group around a bond, some other coordinate, or a collective coordinate of the molecule.

We will assume¹⁸ that the double bottomed well has the shape of two overlapping

harmonic potentials with the minima at the points $x = -a$ and $x = a$. Indicating by ω the fundamental frequency of each harmonic oscillator and by μ the reduced mass of the vibrating particles between $x = -a$ and $x = a$, the natural tunnelling frequency Λ is written as¹⁸

$$\Lambda = \left(2/\pi^{3/2}\right) \omega (\mu\omega a^2/\hbar)^{1/2} \exp(-\mu\omega a^2/\hbar) \quad (2.1)$$

Since in our analysis it is necessary to consider somewhat stable molecules, we will take $\Lambda = 10^{-9} s^{-1}$, which corresponds to a lifetime around 100 years. By using typical molecular parameters, $a = 10^{-8}$ cm and $\mu = 10^{-23}$ g, we see that the fundamental frequency $\omega \cong 5.5 \cdot 10^{13}$ rad/s, in the infrared region.

Now, as we intend to study only the essential aspects of the problem, we adopt a very simple model, that is, we assume that the magnetic and electric dipoles of the active molecules are only those that are responsible for the optical activity in the molecule. Let us indicate by $d_L = \langle L|\hat{d}|L\rangle = d$, $d_R = \langle R|\hat{d}|R\rangle$, $\mu_L = \langle L|\hat{\mu}|L\rangle = \mu$ and $\mu_R = \langle R|\hat{\mu}|R\rangle$ the electric and magnetic dipole, respectively, of the active molecule in the left and right configurations. Since the left and right configurations are degenerate for a parity operation we must have¹⁹ $d_L = -d_R$ and $\mu_L = \mu_R$. The electric and magnetic dipole moments for the L-enantiomer will be taken as parallel and equal to d and μ and for D-enantiomer as antiparallel, equal to $-d$ and μ .

Now, we will analyse an optically active system, gas or liquid, when it is in a electric and magnetic fields which are static and parallel. Also we will assume that these fields are weak do not affecting appreciably the geometry of the molecule and, therefore, do not affecting the frequency for the natural tunneling Λ .

Defining H as the Hamiltonian of the double well which includes the electric and magnetic dipole interactions with the static and parallel fields \mathbf{E} and \mathbf{B} , we have $\langle L|H|L\rangle = E_L = E_0 - d \cdot \mathbf{E} - \mu \cdot \mathbf{B}$, $\langle R|H|R\rangle = E_R = E_0 + d \cdot \mathbf{E} - \mu \cdot \mathbf{B}$ and $\langle L|H|R\rangle = \langle R|H|L\rangle = \delta$, where E_0 is the energy of the fundamental left and right states and $\delta = \hbar\Lambda$.^{18,20} Now, let us choice the fields \mathbf{E} and \mathbf{B} so that $\langle d \cdot \mathbf{E} \rangle = \langle \mu \cdot \mathbf{B} \rangle = \epsilon$, where the brackets mean an average value. With this simplifying hypothesis, that

will not modify the essential points of our analysis, we get $E_L = E_0 - 2\epsilon$ and $E_R = E_0$. In these conditions, assuming that the molecular interactions in the active sample are negligible, the state function $|\psi(t)\rangle$ of the active molecule will be represented by

$$|\psi(t)\rangle = a_L(t)|L\rangle e^{-iE_L t/\hbar} + a_R(t)|R\rangle e^{-iE_R t/\hbar}, \quad (2.2)$$

obeying the equation $i\hbar\partial|\psi(t)\rangle/\partial t = H|\psi(t)\rangle$. Thus, $a_L(t)$ and $a_R(t)$ are governed by the following differential equations:²⁰

$$\begin{aligned} \dot{a}_L(t) &= -(i/\hbar) [a_L(t) E_L + a_R(t)\delta], \\ \dot{a}_R(t) &= -(i/\hbar) [a_R(t) E_R + a_L(t)\delta]. \end{aligned} \quad (2.3)$$

We verify that the general solution of Eqs. (2.3) is given by,

$$\begin{aligned} a_L(t) &= a \cos \phi e^{-iE_1 t/\hbar} + b \sin \phi e^{-iE_2 t/\hbar}, \\ a_R(t) &= -a \sin \phi e^{iE_1 t/\hbar} + b \cos \phi e^{-iE_2 t/\hbar}, \end{aligned} \quad (2.4)$$

where $\cot 2\phi = \epsilon/\delta$, $E_1 = E_0^* - \Delta$, $E_2 = E_0^* + \Delta$, $E_0^* = E_0 - \epsilon$ and $\Delta = (\epsilon^2 + \delta^2)^{1/2}$.

If at $t = 0$ the active molecule is prepared at $|\psi(0)\rangle = |L\rangle$, we have, from Eqs. (2.2) and (2.3), $a = \cos \phi$ and $b = \sin \phi$. Therefore, $|\psi(t)\rangle$ will be described by

$$|\psi(t)\rangle = e^{-iE_0^* t/\hbar} \left[\left(\cos^2 \phi e^{i\Delta t/\hbar} + \sin^2 \phi e^{-i\Delta t/\hbar} \right) |L\rangle - i \sin 2\phi \sin(\Delta t/\hbar) |R\rangle \right]. \quad (2.5)$$

Since $\sin 2\phi = \delta/\Delta$, the racemization rate $r(t)$ will be given by²⁰

$$r(t) = |\langle R|\psi(t)\rangle|^2 = (\delta/\Delta)^2 \sin^2(\Delta t/\hbar), \quad (2.6)$$

and the optical rotation will be proportional to $\theta(t)$, defined as¹⁶

$$\theta(t) = |\langle L|\psi(t)\rangle|^2 - |\langle R|\psi(t)\rangle|^2 = 1 - (\delta/\Delta)^2 \sin^2(\Delta t/\hbar). \quad (2.7)$$

Thus, by Eqs. (2.6) and (2.7), we verify that, due to the left-right symmetry breaking produced by \mathbf{E} and \mathbf{B} , the racemization is never complete and the optical rotation oscillates around a non-zero value that is proportional to $1 - (\delta/\Delta)^2$. We note that similar results are obtained when $|\psi(0)\rangle = |R\rangle$.

By using Eqs. (2.6) and (2.7) we can determine the physical conditions so that the applied fields contribute to stabilize the active molecules at the left or right configurations.²¹ Indeed, $r(t) \cong 0$ and $\theta(t) \cong 1$ when $\epsilon = \langle \boldsymbol{\mu} \cdot \mathbf{B} \rangle \gg \delta$. If this condition is not satisfied the applied fields would contribute to the racemization of the sample, becoming difficult an enantiomeric selection. As will be seen in next section, where the possibility of an asymmetric synthesis is investigated, this stabilization condition is obeyed.

3. CHIRAL SYMMETRY BREAKING IN CHEMICAL SYSTEMS

In the preceding section we have shown that occurs a chiral symmetry breaking when the active sample is placed in a parallel electric and magnetic fields. The energy of the fundamental left configuration is equal to $E_L = E_0 - 2\epsilon$, where $\epsilon = \langle \boldsymbol{\mu} \cdot \mathbf{B} \rangle$, and the energy of the right one is $E_R = E_0$. For paramagnetic gases and liquids we get, for $kT \gg \mu B$, $\epsilon_P \cong (\mu B)^2/3kT$. For liquid crystals where strong cooperative magnetic effects can occur, we have $\epsilon_c \cong \mu B$. Let us estimate the parameter ϵ taking $\mu \cong 10^{-20}$ cgs, $T = 300K$ and B that goes from 0.5 gauss (Earth's magnetic fields) up to 10^4 gauss. In these conditions ϵ_P goes from $2.0 \cdot 10^{-28}$ erg up to $8.0 \cdot 10^{-20}$ erg and ϵ_c from $5 \cdot 10^{-21}$ erg up to 10^{-16} erg. We verify that, for all these cases, the condition $\epsilon \gg \delta = \hbar\Lambda = 10^{-36}$ erg, according to Eq. (2.1), which means that the applied fields contribute to stabilize the active molecules at the left or right configurations.

Now, let us consider chemical systems where substrate molecules A and B, which have no chirality, submitted to the parallel fields \mathbf{E} and \mathbf{B} , combine to produce chiral X_L (left-handed) and X_D (right-handed) molecules.^{5-11,22,23} If K_L and K_D are the reaction rates so that $A + B \xrightarrow{K_L} X_L$ and $A + B \xrightarrow{K_D} X_D$, we can expect that during the synthesis of X_L and X_D they go through intermediate states⁹ with an energy difference $\Delta E = 2\epsilon = E_R - E_L$. Then, in accordance with Arrhenius kinetics we have $K_L/K_D \cong 1 + g$, where $g = \Delta E/kT$. For paramagnetic substances at Earth's magnetic field, $g \cong 10^{-14}$. Since this g is very small (similar to that produced by the

WNC⁹⁻¹¹) it would be necessary to expect a very long time¹⁰ to have a considerable excess of L-enantiomers. For $B = 10^4$ gauss, since $g \simeq 2.0 \cdot 10^{-6}$, a small asymmetric synthesis is expected.¹³ However, in a somewhat short period of time a reasonable excess of X_L could be produced and this excess could be amplified by the action of catalytic and autocatalytic reactions.^{5,14,22,23} Of course, the L-enantiomeric amplification would be much more efficient in systems like liquid crystals, since for $B = 10^4$ gauss we have $g \simeq 5.0 \cdot 10^{-3}$.

If the chemical system is composed by a gaseous racemic mixture of X_L and X_D the separation of L-enantiomers could be performed by nonuniform electric and magnetic fields. This method would be similar to that used to separate the ammonia molecules, in up and down states, in the ammonia masers.

Finally, we must note that with our simple model we cannot explain the recent results of Breitmaier et al.,¹⁴ where the reaction solution is submitted only to a static magnetic field. However, we believe that the electric field could be created by a polarization effect. Indeed, the applied magnetic field aligning the large molecules of the starting material,^{14,15} would align their electric dipoles, creating, in this way, an electric polarization and, consequently, an electric field in the medium.²¹ This is a possibility that we intend to analyse in a forthcoming paper.

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REFERENCES

- [1] S.F. Mason, *Molecular Optical Activity and the Chiral Discriminations*, Cambridge, Univ. Press. Cambridge, U.K. (1982)
- [2] S.F. Mason, *Nature* **311**, 19 (1984)
- [3] W.A. Bonner, *Origins of Life* **21**, 59 (1991)
- [4] S.F. Mason, *Chirality* **1**, 183 (1989)
- [5] M. De Min, G. Levy and J.C. Micheau, *J. Chim. Phys.* **85**, 603 (1988)
- [6] V.V. Avetisov and V.I. Goldanski, *Biosystems* **25**, 141 (1991)
- [7] T. Bushe, D. Lavabre, J.C. Micheau and W. Thiemann, *Chirality* **5**, 341 (1993)
- [8] I. Amato, *Science* **156**, 964 (1992)
- [9] D.K. Kondepudi and G.W. Nelson, *Physica* **125A**, 465 (1984)
- [10] D.K. Kondepudi and G.W. Nelson, *Nature* **314**, 438 (1985)
- [11] M. Cattani and T. Tomé, *Origins of Life* **23**, 125 (1993)
- [12] P. Gerike, *Naturwissenschaften* **62**, 38 (1975)
- [13] W. Rhodes and R.C. Dougherty, *J. Am. Chem. Soc.* **100**, 6247 (1978)
- [14] G. Zadel, C. Eisenbraun, G. Joachim Wolff and E. Breitmaier, *Angew. Chem. Int. Ed. Engl.* **33**, 454 (1994)
- [15] D. Bradley, *Science* **264**, 908 (1994)
- [16] R.A. Harris and L. Stodolsky, *Phys. Lett.* **B78**, 313 (1978)
- [17] R.A. Harris and L. Stodolsky, *J. Chim. Phys.* **74**, 2145 (1981)
- [18] M. Cattani, *JQSRT* **49**, 325 (1993)
- [19] E.U. Condon, *Rev. Mod. Phys.* **9**, 432 (1937)
- [20] M. Cattani, *JQSRT* **46**, 507 (1991)
- [21] P. Claverie and G. Jona-Lasinio, *Phys. Rev.* **33A**, 2245 (1986)
- [22] K. Tennakone, *Chem. Phys. Lett.* **105**, 444 (1984)
- [23] K. Tennakone, *Origins of Life* **20**, 515 (1991)