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Chiral Stability Generated by Weak Interactions

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Abstract
  We present a brief review of our preceding theoretical predictions where is shown that the weak interaction which is responsible for the left-right chiral symmetry breaking can generate chiral stability.
Keywords: *optical activity; weak interactions; chiral stability*

(I)**Introduction**
  In a recent paper[1] we have presented a detailed study, in the framework of the Schrödinger`s equation, of the effect of the intermolecular interactions U on tunneling racemization of an optical active chiral molecule. This molecule is assumed as a two−level system and the left−right isomerism is viewed in terms of a double−bottomed harmonic potential well. The difference of energy due to the spontaneous tunneling between left(L) and right(R) configurations is indicated by δ. In our model we take into account the difference of energy (ε) between the L and R configurations due to the weak interactions. In Section 1 we present the basic equations involving these parameters. In Section 2 we assume that the perturbing potential U is due to random binary collisions and in Section 3 that U is created by a cooperative effect between the interacting molecules. Depending on the parameters ε, δ and φ there is racemization, chiral stability and intermediate cases when the "optical activity" or "optical rotation" (O_p) can assume any value in the range $-1 \le O_p \le 1$.

(1) Basic Equations

As is well known [1−3] the optical activity of an optically active material changes with time. The sample, containing predominantly one stereoisomer, will become a mixture of equal amounts of each isomer. This relaxation process, which is called racemization, occurs spontaneously or is due to the interaction of the active molecule with the environment.

(1.A) *Intrinsic Properties of the Chiral Molecule*

Optical activity occurs when the molecule has two distinct left and right configurations, $| L >$ and $| R >$, which are degenerate for a parity operations, i.e., $P(x)| L > = | R >$ and $P | R > = | L >$. Left − right isomerism can be viewed in terms of a double − bottomed potential well and the states $| L >$ and $| R >$ may be pictured as molecular configurations that are concentrated in the left or right potential well. The two enantiomers of a chiral molecule are described by superpositions of the odd and even parity eigenstates of the double well localized around the potential minima, $x = a$ and $x = -a$. The coordinate x is involved in the parity operation $P = P(x)$ and connects 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.

Let us define by H_o the Hamiltonian of each side of the double well and by $V_o(x)$ the potential barrier separating the two minima of the double well. In this picture, $| L >$ and $| R >$ are eigenstates of Ho, i.e., $< L | H_o | L > = < R| H_o | R > = E_o$ and there is a small overlap of these states inside the barrier $V_o(x)$ so that , $< L | V_o | R > = < R |V_o | L > = \delta$.

Let us assume that the double−bottomed potential well has the shape of two overlapping harmonic potentials.[4] Indicating by ω the fundamental frequency of each harmonic oscillator and by μ the reduced mass of the particles vibrating between $x = a$ and $x = - a$, the fundamental vibrational states $| \Phi(x) >$ of the left and right harmonic oscillators are written, respectively, as: [4]

$$\left| \Phi_L(x) > = (\mu\omega/\pi\hbar)^{1/4} \exp[-(\mu\omega/2\hbar)(x + a)^2],\right.$$

$$(A.1)$$

$$\left| \Phi_R(x) > = (\mu\omega/\pi\hbar)^{1/4} \exp[-(\mu\omega/2\hbar)(x - a)^2].\right.$$

The left and right configurations states of the active molecule will be written in a Born−Oppenheimer approximation (adiabatic approximation)

as $|L\rangle = |\psi_L\rangle |\Phi_L(x)\rangle$ and $|R\rangle = |\psi_R\rangle |\Phi_R(x)\rangle$, where $|\psi\rangle$ describes all internal degrees of freedom of the active molecule except x .

In these conditions, $\delta = \langle L | V_o(x) | R \rangle = \langle R | V_o(x) | L \rangle$ is given by:[4]

$$\delta = (h\omega/\pi^{3/2})\ (\mu\ \omega\ a^2/\hbar)^{1/2}\ \exp(-\mu\ \omega\ a^2/\hbar) \qquad (A.2),$$

that gives the natural tunneling frequency δ/h of the transition between the L and $|R\rangle$ configurations.[4]

In general case, if at a time t the state molecule is $|\Psi(t)\rangle$ and at t = 0 it was prepared at the state $|L\rangle$ or $|R\rangle$ we define a function r(t) named "racemization" by

$$r(t) = |\langle Q | \Psi(t) \rangle|^2 \qquad (A.3),$$

where Q = L or R. The "optical activity" or "optical rotation" $O_p(t)$ of the molecule is defined by the function

$$O_p(t) = 1 - 2\ r(t) \qquad (A.4).$$

Since $r(t) \leq 1$ we see that $O_p(t)$ values are is in the interval $-1 \leq O_p(t) \leq 1$.

Recent optical experiments[5,6] have demonstrated cases in which mirror symmetry in stable atoms is broken during absorption of light. These results support the theory of unification of the electromagnetic and weak forces. The discovery of parity violation in an atomic process was the outcome of many years of experimental effort. After the emergence of unified theories in the early 1970´s, many experiments were designed to test the new theories, to choose between them, and to measure the fundamental constants involved.[5]

If weak interaction effects are present, parity is violated and the left and right sides of the double-bottomed potential are no longer symmetrical. In this way, $\langle L | H_o | L \rangle = E_L = E_o - \varepsilon$ and $\langle R | H_o | R \rangle = E_R = E_o + \varepsilon$, where 2ε is the difference of energy between the left and right configurations due to the parity-violating interaction. According to recent calculations performed by Di Giacomo et al.[7], ε/h is typically of the order of 10^{-3} Hz for rotational and vibrational transitions and of the order of 10^{-6} Hz for nuclear magnetic transitions.[8–13]

(1.B) *Chiral Molecule Interacting with the Environment.*

Let us assume now that the chiral molecule is embedded in a gas, liquid or solid where it is submitted to a generic external field U(t). In our approach we have assumed that the racemization is produced essentially by transitions

between the two vibrational states $| L >$ and $| R >$. In this way, the state function $| \Psi(t) >$ of the active molecule, is represented by

$$| \Psi(t) > = a_L(t) | L > \; + \; a_R(t) | R > , \qquad (B.1)$$

and obey the Schrödinger´s equation

$$i \hbar \, \partial | \Psi(t) >/\partial \, t = [H_o + V_o(x) + U(t)] \, | \Psi(t) >. \qquad (B.2)$$

So, $a_L(t)$ and $a_R(t)$ are governed by the following differential equations:

$$da_L(t)/dt = -(i/\hbar)[a_L(t) \, (E_o - \; \varepsilon + U_{LL}) + a_R(t) \, (\delta + U_{LR})],$$
$$\qquad (B.2)$$
$$da_R(t)/dt = -(i/\hbar)[a_R(t) \, (E_o + \varepsilon + U_{RR}) + a_L(t) \, (\delta + U_{RL})],$$

where the matrix elements U_{nk}, with n, k = L and R , are given by $U_{nk} = < n \, | \, U(t) \, | \, k >$.

Since the homochiral and heterochiral interactions are equal,[14] we define $u = U_{LL} = U_{RR}$ and $\varphi = U_{LR} = U_{RL}$. In this way Eq.(B.2) are written as:

$$da_L(t)/dt = -(i/\hbar)[a_L(t) \, (E_o - \varepsilon + \; u) + a_R(t) \, (\delta + \varphi)],$$
$$\qquad (B.3).$$
$$da_R(t)/dt = -(i/\hbar)[a_R(t) \, (E_o + \varepsilon \; + u) + a_L(t) \, (\delta + \varphi)]$$

These general equations (B.3) will be used in Sections 2, 3, 4 and 5 to calculate the racemization r(t) and the optical stability $O_p(t)$ of active molecules embedded in a medium submitted to random collisions, in a dense medium submitted to a collective interaction and isolated. In section 6 we present the Conclusions and Discussions.

(2) Active Molecule Submitted to Binary Random Collisions and $\varepsilon = 0$.
In this section we assume that $\varepsilon = 0$ and that the active molecule is embedded, for instance, in a dilute and compressed gas or liquid where the potential U(t) is due to binary collisions[15,16] between molecules of the sample that are taken as additive, independent and at random. In dilute gases the collisions have very short duration (around 10^{-11}s for a system at room temperature) but with a very high collision frequency, for molecular densities $N \sim 10^{17}/cm^3$. The molecular collisions induce transitions between L and R

configurations, described by $\varphi = U_{LR}$. The spontaneous transitions between L and R are described by δ given by (A.2). Putting $\varepsilon = 0$ into (5), these equations can be solved exactly. It is assumed that the molecule at t = 0 is at initial state $|\Psi(0)> = |L>$.

The interaction U(t) is written as a sum of binary interactions given simply by $u(t) = \gamma/R(t)^p$, where γ represents the force constant for the interacting particles, R(t) the distance between them as a function of the time t, p = 4,5,…if the interaction is dipole-quadrupole, quadrupole-quadrupole, and son on.

In the case of a dilute gas, treating the binary collisions in the *impact approximation*, we have shown that[17−19]

$$r_1(t) = [\,1 - \cos(2\delta t/\hbar)\,\exp(-\lambda t)]/2, \qquad (2.1)$$

where $\lambda = (\gamma/\hbar)^{2/(p-1)}\,N(kT/m)^{(p-3)/(2p-2)}$, N the density of perturbing molecules, k the Boltzmann constant, T the absolute temperature of the system and m the reduced mass of the colliding particles.

For a compressed gas or liquid, where collisions are *quasi-static*, we have shown that:[17,19]

$$r_2(t) = [\,1 - \cos(2\delta t/\hbar)\,\exp(-\lambda^* t^{3/p})]/2 \;, \qquad (2.2)$$

where

$$\lambda^* = (8\pi/p)N(\gamma/2\hbar)^{3/p} \int\limits_0^\infty x^{-(p+3)/p}\,\sin^2 x\,dx.$$

Taking into account (2.1) and (2.2) we verify that, in gases and liquids, when $\varepsilon = 0$, binary random collisions between active and perturbing molecules produce the racemization of the sample. Comparing $r_1(t)$ and $r_2(t)$ we verify that $r_1(t)$, in dilute gases, decays in time as $\exp(-\lambda t)$ and in dense gases and liquids $r_2(t)$ more slowly, as $\exp(-\lambda^* t^{3/p})$, since p = 4,5,…and so on.

In order to estimate $r_1(t)$ and $r_2(t)$ we will assume that there is only a dipole−quadrupole (p=4) interaction between active and perturbing molecules. In this case [20] since $\gamma = d <L|\,Q(x)\,|R> = d\,\theta\,\exp(-\mu\omega a^2/\hbar)$, λ is given by :

$$\lambda = 13.0\,N\,(kT/m)^{1/6}\,(\theta d/\hbar)^{2/3}\,\exp(-2\mu\omega a^2/3\hbar) \;, \qquad (2.3)$$

where d is the electric dipole of the perturbing molecule and θ quadrupole matrix element of the active molecule between left and right configurations. Similarly, λ^* is written as:

$$\lambda^* = 2.86\pi \, N(\theta d/2\hbar)^{3/4} \exp(-3\mu\omega a^2/4\hbar). \tag{2.4}$$

A numerical estimation of $r_1(t)$ and $r_2(t)$ will be done considering the following typical molecular parameters: $a = 10^{-8}$ cm, $\mu = 10^{-23}$g, $m = 10^{-22}$ g , $d = 10^{-18}$ e.s.u., $\theta = 10^{-26}$ e.s.u., $T = 300$ K and $N = 10^{17}$/cm^3 .The frequencies ω will written as $\omega = A \, 10^{13}$ rad/s. Taking into account these values we verify that $\delta/\hbar$, λ and λ^*, defined by (A.2), (2.3) and (2.4) are is given by $\delta/\hbar = 1.10 \, 10^{21} \, A^{3/2} \exp(-9.52 \, A)$ y^{-1}, $\lambda = 5.03 \, 10^{15} \exp(-6.35 \, A)$ y^{-1} and $\lambda^* = 2.90 \, 10^{12} \exp(-7.14 \, A)$ y^{-1}, respectively, measuring the time t in years.

In Figures 1 and 2 are shown $r_1(t)$ and $r_2(t)$, respectively, as a function of t, measured in years, for $A = 4.5$. For a dilute gas, according to Figure 2, the racemization occurs for $t > 1$ day. The factor $r_1(t)$ slowly oscillates around 0.5, assuming rapidly this value. The case of compressed gases or liquids, where the collisions are quasi static, is shown in Fig.3. We see that $r_2(t)$ oscillates for a long period ($0 < t < 10^5$ y) around 0.5 assuming asymptotically this value only for $t > 2 \, 10^5$ y. These results show that racemization mechanism due to binary collisions in dilute gases (*impact approximation*), is much more efficient than that produced by the *quasi static interactions* in compressed gases and liquids.

In conclusion, when $\varepsilon = 0$ and U(t) is created by binary random collisions the optically active system inevitably racemizes, that is, for long times $r(t) \to 0.5$ and, consequently, $O_p(t) = 1 - 2 \, r(t) \to 0$.
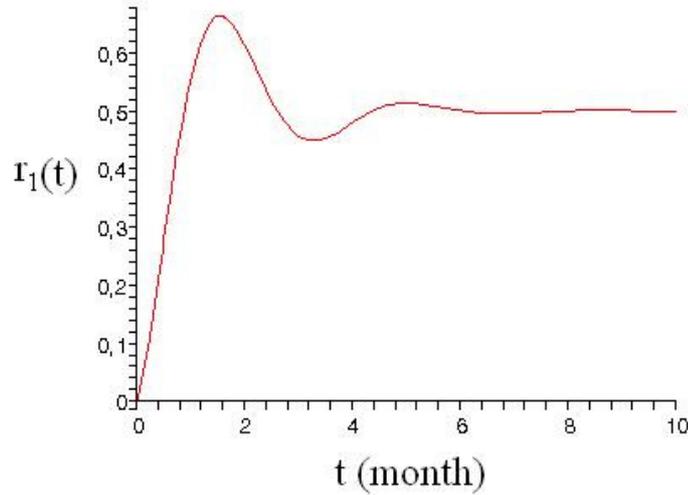

Figure 1. *$r_1(t)$ for dilute gases, defined by (2.1), shown as a function of the time t, measured in months. The racemization was calculated taking the harmonic oscillation frequency $\omega = 4.5 \, 10^{13}$ rad/s.*
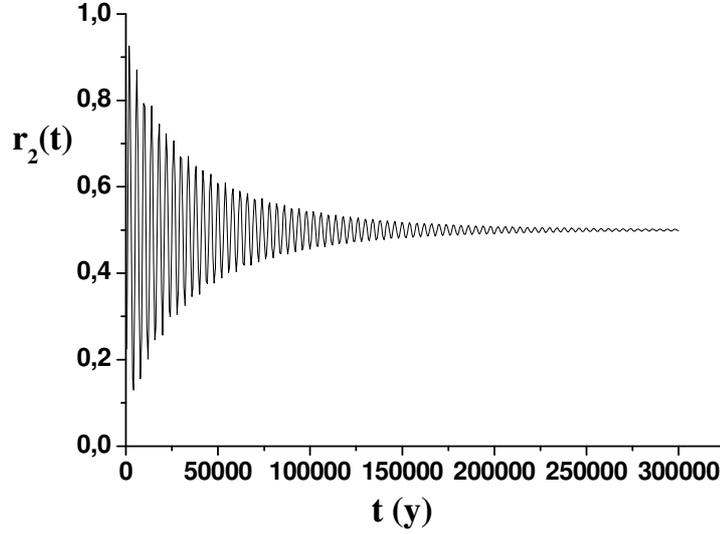
Figure 2. *$r_2(t)$ for dense gases and liquids, defined by (2.2), shown as a function of the time t, measured in years. The racemization was calculated taking the harmonic oscillation frequency $\omega = 4.5 \ 10^{13}$ rad/s.*

(3)Chiral Molecule Submitted to a Collective Interaction when $\varepsilon \neq 0$.

Let us consider now the case when $\varepsilon \neq 0$ and the active molecule is embedded in a dense gas, liquid or solid, where multiple interactions dominate over binary interactions and that there is a cooperative effect between the interacting molecules. Due to this collective behavior we will assume that each molecule is subjected to a mean field resulting from these combined interactions of all other molecules in the system. This mean field is understood as a self−consistent Hartree field.

The cooperative interaction potential, that will be indicated by U(x), will be considered in the framework of Schrödinger`s equation simultaneously with the weak interaction. Consequently, taking into account that U(x) is static (B.3) can be exactly solved. In this way, if at t = 0 the active molecule is prepared so that $| \Psi(0) > = | L >$, we get [20]

$$r(t) = |< R \mid \Psi(t) >|^2 = \Theta \sin^2\{[\varepsilon^2 + (\delta + \varphi)^2]^{1/2} t/\hbar\} \qquad (3.1),$$

where Θ is the "r(t) amplitude" given by $\Theta = (\delta + \varphi)^2 / [\varepsilon^2 + (\delta + \varphi)^2]$. So, when U is static, according to (3.1) there is no racemization and the optical activity $O_p(t)$ oscillates with a period $T = 2\pi\hbar / [\varepsilon^2 + (\delta + \varphi)^2]^{1/2}$ around the average value $<O_p> = 1 - \Theta/2$.

In this way, that to get chiral stability, that is $<O_p> = 1$, it is necessary that $\Theta << 1$. Thus, when there is a cooperative interaction U(x) between the molecules of the sample, optical stability occurs only when $\varepsilon >> (\varphi + \delta)$.

Let us consider the particular case of dense gases and liquids composed by dipolar molecules. This is a special case because a cooperative interaction mechanism appears between the molecules of the sample and U(x) can be easily calculated.[22] In the dielectric medium[22−24] appears a *reaction field* $\mathbf{E_r}$ given by $\mathbf{E_r} = 2(\varepsilon - 1)\mathbf{d}/(2\varepsilon + 1)R^3$, where ε is the dielectric constant of the medium, $\mathbf{d}$ the average dipole moment of the active molecule and R the radius of the cavity where $\mathbf{d}$ is embedded. In this way, the interaction potential between $\mathbf{E_r}$ and the active molecule is given by $U(x) = -\mathbf{d}\cdot\mathbf{E_r}$ Since the dipole matrix element of the active molecule between $| L >$ and $| R >$ is zero, the heterochiral interaction $< L |U(x)| R> = \varphi$ of this molecule with $\mathbf{E_r}$ will calculated taking into account the quadrupole moment Q(x) of the active molecule. So, φ will be given by $\varphi \approx d <L|Q(x)|R>/R^4$. As shown elsewhere,[20] $< L|Q(x)|R> = \theta \exp(-\mu\omega a^2/\hbar)$, where θ is the quadrupole matrix element of the active molecule between L and R configurations. In this way, φ is given by

$$\varphi \approx (\theta d/R^4) \exp(-\mu\omega a^2/\hbar) \tag{3.2}.$$

Now, let us estimate the amplitude $\Theta = (\delta + \varphi)^2 / [\varepsilon^2 + (\delta + \varphi)^2]$, defined by (3.1), taking into account that δ/h and φ/h are given, respectively, by $\delta/h = (2\omega/\pi^{3/2}) (\mu\omega a^2/\hbar)^{1/2} \exp(-\omega a^2/\hbar)$ and $\varphi/h = (\theta d/hR^4) \exp(-\mu\omega a^2/\hbar)$, according to (A.2) and (3.2). These two factors, using the molecular parameters defined in Section 2, taking $R \approx 3 \ 10^{-8}$ cm and putting $\omega = A \ 10^{13}$ rad/s, become $\delta/h = 5.54 \ 10^{12} \ A^{3/2} \exp(-9.52 \ A)$ Hz and $\varphi/h = 1.51 \ 10^{12} \exp(-9.52 \ A)$ Hz. In Fig (3) the amplitudes $\Theta(A)$, for $\varepsilon/h = 10^{-3}$ Hz and $\varepsilon/h = 10^{-6}$ Hz, are plotted as a function of the parameter A.
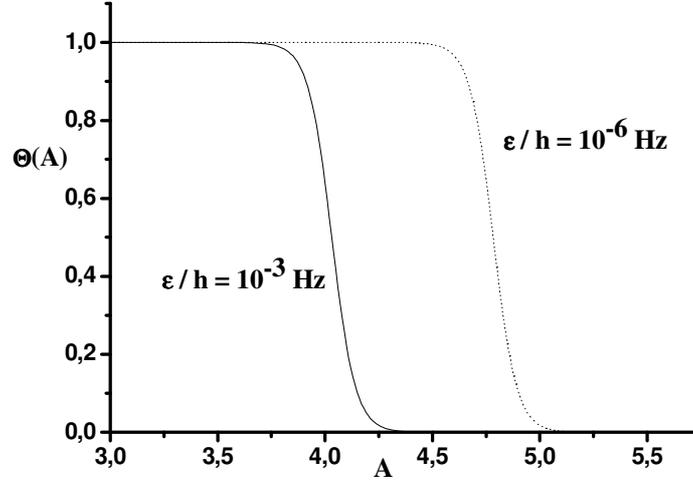
Figure 3. *The amplitude $\Theta(A)$, defined by (3.1), plotted as a function of the parameter A, defined by the equation $\omega = A\ 10^{13}$ rad/s. Two limiting cases have been considered: $\varepsilon/h = 10^{-3}$ Hz (vibrational and rotational transitions) and $\varepsilon/h = 10^{-6}$ Hz (nuclear magnetic transitions).*

From Figure 3 we see that the amplitude Θ decreases very rapidly for frequencies $\omega > 4\ 10^{13}$ rad/s. When $\varepsilon/h = 10^{-3}$ Hz (rotational and vibrational transitions) Θ is in the interval $1.82\ 10^{-8} \le \Theta \le 1.67\ 10^{-13}$, for frequencies ω in the range $5\ 10^{13} \le \omega \le 6\ 10^{13}$ rad/s. These results show that it is possible to get optical stabilization for frequencies $\omega > 5\ 10^{13}$ rad/s. When $\varepsilon/h = 10^{-6}$ Hz (nuclear magnetic transitions) stability conditions are found for $\omega > 5 \sim 5.5$ 10^{13} rad/s. These results show that for frequencies $\omega > 5.5\ 10^{13}$ rad/s the weak force energy ε produces a chiral stability because, for these frequencies, ε becomes much larger than δ and φ. In these conditions the optical activity becomes equal to one.

(4) Isolated Molecule when $\varepsilon \neq 0$ and $\varepsilon = 0$.
To analyze the case of an isolated chiral molecule we put $\varphi = 0$ in (3.1). Consequently, the amplitude Θ is given by $\Theta = \delta^2/(\varepsilon^2 + \delta^2)$, showing that chiral stability is obtained when $\varepsilon \gg \delta$. According to Fig.3 this occurs for $\omega > 5 \sim 5.5\ 10^{13}$ rad/s. If $\varepsilon = 0$, r(t) is given by $r(t) = \sin^2(2\delta t/\hbar)$, showing that it would have a L−R oscillation with a period $T = \pi\hbar/\delta$. As $\delta/h = 5.54\ 10^{12}\ A^{3/2}$ exp(−9.52 A) Hz, according to Section 3. Taking, for instance, A = 5 we obtain $T \approx 43$ days. On the other hand, if $\varepsilon/h = 10^{-3}$ Hz it would have chiral stability since the parameter Θ is given by $\Theta = 1.6\ 10^{-12}$.

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In the case of an isolated active molecule, the blocking effect of the weak interactions in the L–R oscillations, which occurs when $\varepsilon \gg \delta$, can be explained using the energy uncertainty relation $\Delta E \, \Delta t \sim \hbar$. Indeed, since the spontaneous oscillation time between the L and R configurations is $\Delta t = T = \pi\hbar/\delta$ the energy uncertainty is given by $\Delta E \sim \delta$. In this way, if there is a difference of energy ε between L and R, the natural L–R transitions are allowed only when $\Delta E \sim \delta \geq \varepsilon$. On the other side, the transitions will be prohibited when $\varepsilon \gg \delta$. In the presence of the potential interaction energy φ, using the same reasoning, the L–R transitions are blocked when the condition $\varepsilon \gg \delta + \varphi$ is obeyed.

(5) Active Molecule Submitted to Binary Random Collisions when $\varepsilon \neq 0$.

In Section 2 we have calculated r(t) for an active molecule assuming that $\varepsilon = 0$ and that it is submitted to a time dependent potential U(t) due to random binary collisions. In Section 3, we have determined r(t) assuming that $\varepsilon \neq 0$ and that U(x) is a static interaction potential due to a cooperative effect between the interacting molecules.

In these two cases (B.3) could be exactly solved. In the first case (Section 3) we have $\varepsilon = 0$ and U(t) depending on the time. In the second case (Section 4), $\varepsilon \neq 0$ and U independent of the time. On the other side, when $\varepsilon \neq 0$ and U = U(t) the (B.3) cannot be exactly solved. In these conditions, we verify that r(t), in the case of binary random collisions, is given by

$$r(t) \approx (\delta/\Delta_o)^2 \, [\, 1 - \cos(2\Delta_o t/\hbar) \, \exp(-f(t))]/2, \qquad (5.1)$$

where $\Delta_o = (\varepsilon^2 + \delta^2)^{1/2}$, $f(t) = \lambda t$, for dilute gases in the impact approximation, and $f(t) = \lambda * t^{3/p}$ for compressed gases and liquids, in a quasi–static approximation, according to Section 2.

Let us consider three particular cases of (5.1). When $\varepsilon = 0$ we obtain $r_1(t)$ and $r_2(t)$ given by (2.1) and (2.2), respectively, that describe the racemization of the sample. When $\varepsilon \gg \delta$ we see that r(t) = 0, which is the condition for chiral stability. Finally, when U = 0, $r(t) = (\delta/\Delta_o)^2 \, \sin^2(\Delta_o t/\hbar)$ which is the case of an isolated molecule analyzed in Section 4.

Defining $r_{max} = (\delta/\Delta_o)^2/2$ we verify from (5.1) that the optical activity O_p varies in the range $1 - 2\,r_{max} \leq O_p \leq 1$. We see that for very long times, that is, for f(t) $\gg$ 1, r(t) $\rightarrow r_{max}$. So, only when $\delta \gg \varepsilon$ occurs racemization, that is, $r_{max} \rightarrow \frac{1}{2}$ and $O_p \rightarrow 0$. On the other hand, when $\varepsilon \gg \delta$ there is chiral stability, that is, $r_{max} \rightarrow 0$ and $O_p \rightarrow 1$. When, for instance, $\varepsilon/h = 10^{-3}$ Hz we verify that this last condition is satisfied only for $\omega > 5.2 \, 10^{13}$ rad/s considering that $\delta/h =$

5.54 10^{12} $A^{3/2}$ exp(–9.52 A) Hz and remembering that ω = A 10^{13} rad/s. For frequencies in the interval 4 10^{13} < ω < 5.2 10^{13} rad/s r(t) oscillates and decreases as the time increases tending asymptotically to r_{max} which is in the range 0 < r_{max} < ½.

In Figure 4, $r_4(t)$, defined by (5.1), is shown as a function of t for dilute gases for ε = 10^{-3} and A = 4.5, that is, ω = 4.5 10^{13} rad/s. According to this figure r(t) oscillates between 0 and 0.21 and stabilizes with $r_{max} \approx 0.11$ for t > 10 months, giving an asymptotic optical activity $O_p \rightarrow 0.78$.
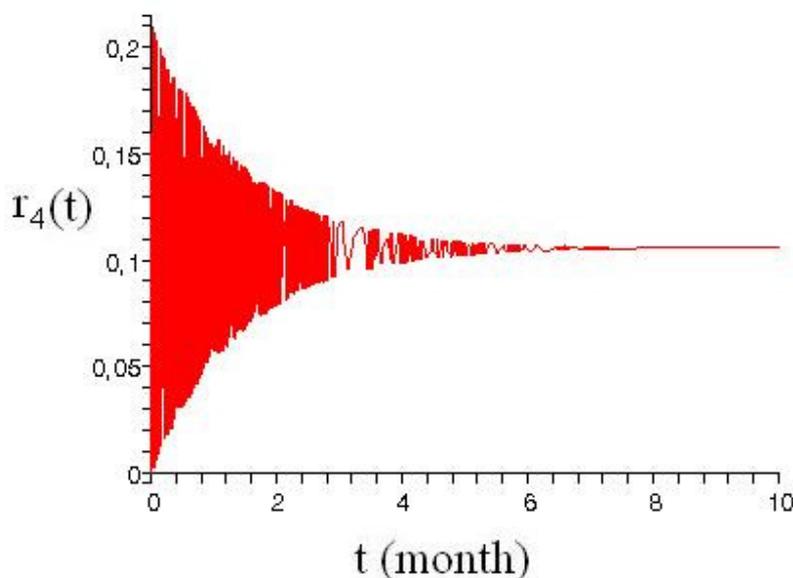

Figure 4. $r_4(t)$ given by (5.1) as function of the time t measured in years, for $\varepsilon/h = 10^{-3}$ and A = 4.5, that is, ω = 4.5 10^{13} rad/s.

(6)Conclusions and Discussions.

Taking into account the analysis performed above in the framework of our double bottomed harmonic model we can conclude that:

(1)When ε = 0 it is impossible, in all cases, to have optical stability. The system always racemizes, that is, r(t) $\rightarrow$ ½ and <O_p > $\rightarrow$ 1

(2)When chiral molecules are free or perturbed by binary, additive, independent and random collisions to get chiral stability it is necessary and sufficient to have ε >> δ. The chiral stability can be total <O_p > $\rightarrow$ 1 or partial, that is, smaller than 1.

(3)In a dense medium when U = U(x) is due to a cooperative effect between the interacting molecules of medium there is chiral stability <O_p > $\rightarrow$ 1 only when ε >> δ + φ, where φ is the heterochiral interaction φ = < L |U(x)| R>.

That is, when the difference of energy ε is sufficiently large to block the L−R transitions induced simultaneously by the natural tunneling and by the cooperative potential.

Taking into account that $\varepsilon/h = 10^{-3}$ Hz and the molecular parameters values adopted in Section 2−5 we verify that the condition $\varepsilon \gg \delta + \varphi$ is satisfied for $\omega > 4.2\ 10^{13}$ rad/s. These frequencies are found, for instance, in harmonic vibrations in the infrared region.

In a recent approach[25] proposed to study the chiral stability, the self-consistent field has two components: U_{hom} and U_{het} emanating from the homochiral and heterochiral interactions, respectively. These components have been introduced in a nonlinear Schrödinger equation in order to give the time evolution of the active system. They have shown that when U_{hom} interactions are energetically favorable to U_{het} interactions, spontaneous left-right symmetry breaking may amplify the optical activity of a nearly racemic mixture.

Nonlinear quantum mechanics have been used [25,26] to explain the chiral stability. This seems to be a plausible attempt because the stationary states of a nonlinear Schrödinger`s equation[26,27] need not to be eigenstates of the operators that correspond to the symmetry group of the potential. So, the nonlinear term introduces a spontaneous symmetry breaking [27,28]hich favors the localization in one of the wells. However, realistic nonlinear Schrödinger`s equations must be deduced taking into account cooperative effects in the many-body interactions in the sample.[28−31] This algorithm would permit us to obtain a faithful nonlinear equation to study the optical stability. The nonlinear equations adopted by Vardi[25] and Koschany et al.[26] have not been obtained in this way. They have proposed, somewhat arbitrarily, equations following generic nonlinear models adopted in the literature.[31] In addition, we know that nonlinear equations exhibit a large number of rich and complex solutions depending on the magnitude of the nonlinear parameters. So, from the analysis of Vardi[25] and Koschany et al.,[26] it is difficult to conclude that the nonlinear effects are, or are not, effective mechanisms responsible for the chiral stability.

Finally, it is important to remark that our conclusions regarding the stabilization of enantiomers are limited to those molecules that principally racemizes through simple inversion alone. As is well known, there are many other different racemization mechanisms.[32] In our works these processes have not been considered.

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