Stabilization of Chiral Molecules by Weak Interactions: a Simple Double-Bottomed Harmonic Model

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Abstract.
We present a simple theoretical approach within the framework of a linear Schrödinger´s equation to show that it is possible to explain the stabilization of chiral molecules due to the effect of weak interactions. The chiral molecule is taken as a two-level system where the left-right isomerism is viewed in terms of double-bottomed harmonic potential well.
Keywords: *optical activity; weak interactions; chiral stability*

(1)Introduction.

Recently, using Schrödinger´s formalism, we have published some preliminary results[1] showing that chiral stability could be generated by weak interactions. In these papers the main hypothesis of our approach are well defined and the calculations have been correctly done. However, in spite of this, we verified that it would be necessary to enhance and analyze more carefully some aspects and results of these works. The present paper was written with this intention. We will study, using the linear Schrödinger equation, the optical activity of a chiral molecule immersed in a thermal bath submitted to intermolecular interactions U and also taking into account the effects of weak forces possibly inherent in the molecular structure. Our intention is only to propose a simple model to study these competitive effects. So, the chiral molecule is assumed as a two-level system where 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. The difference of energy due to *weak interactions* between the L and R is indicated by ε. At this point it is necessary to emphasize three important points of our approach: (1)the electric dipole moment **d** of chiral molecule can be equal to zero or not. If $\mathbf{d} \neq 0$ it can be invariant or not by a parity operation; (2)the chiral molecule can have any geometry. It is not necessary to have, for instance, a pyramidal form;[1] (3)the interactions U of the chiral molecule with the thermal bath can be generated by chiral or non-chiral molecules. In Section (A) we present the Basic Equations involving U, δ and ε. Finally, it is important to note that in our approach *no linear effects are taken into account*.

(A) *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.

(A.1) *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 $P(x) | R > = | L >$. 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 the superposition of the odd and even parity eigenstates of the double well localized around the potential minima, $x = - a$ and $x = a$. The coordinate x involved in the parity operation $P = P(x)$ 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 H_o, 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, $< L | V_o | R > = < R |V_o | L > = \delta$.[4]

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]

$$| \Phi_L(x) > = (\mu\omega/\pi\hbar)^{1/4} \exp[-(\mu\omega/2\hbar)(x - a)^2],$$
$$(1.1)$$
$$| \Phi_R(x) > = (\mu\omega/\pi\hbar)^{1/4} \exp[-(\mu\omega/2\hbar)(x + a)^2].$$

The left and right configurations states of the active molecule will be written in a Born−Oppenheimer approximation[1] (adiabatic approximation) as $| L > = | \psi_L > | \Phi_L(x) >$ and $| R > = | \psi_R> | \Phi_R(x) >$, where $| \psi >$ describes all internal degrees of freedom of the active molecule except x .

In this way, $\delta = < L | V_o(x) | R > = < R | V_o(x) | L >$ is given by:[4]

$$\delta = (h\omega/\pi^{3/2}) (\mu \omega a^2/\hbar)^{1/2} \exp(-\mu \omega a^2/\hbar) \qquad (1.2),$$

that gives the natural tunneling frequency $f = \delta/h$ of the transition between the L and R configurations.[4]

In general case, if at the instant of time t the state molecule is represented by$| \Psi(t) >$ and at t = 0 it was prepared at the state $| L >$ or $| R >$ we define the “racemization” function r(t) as follows:

$$r(t) = | < Q | \Psi(t) > |^2 \qquad (1.3),$$

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

$$O_p(t) = 1 - 2 r(t) \qquad (1.4).$$

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

In this paper in order to simplify our analysis it will be assumed in what follows that the chiral molecule is initially in the left state $|L >$. So, r(t) will written as

$$r(t) = | < L | \Psi(t) > |^2 \qquad (1.5).$$

So, if in the final state $| \Psi(t) > = [| L > + | R >]/\sqrt{2}$ we get r(t) = ½ and, consequently, the optical activity according to (1.4) is $O_p(t) = 0$, that is, there is a *complete racemization*. On the other hand, if in the final state we have $| \Psi(t) > = | L >$ we get r(t) = 1 and, consequently, $O_p(t) = -1$. That is, we have a “*chiral stability*” or “*optical stability*”.

Some 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, $< L \mid H_o \mid L > = E_L = E_o - \varepsilon$ and $< R \mid H_o \mid R > = E_R = E_o + \varepsilon$, where 2ε is the difference of energy between the left and right configurations due to the parity-violating interaction. According to 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] More recent results on these subjects can be seen, for instance, in the papers of M.Quack et al.[14], I.Gonzalo and P.Bargueño[15] and P.Bargueño et al.[16] and references therein.

(A.2) *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). It will be also assumed that the racemization is produced *essentially* by transitions between the two vibrational states $\mid L >$ and $\mid R >$. In this way, the state function $\mid \Psi(t) >$ of the active molecule, is represented by

$$\mid \Psi(t) > = a_L(t) \mid L > + a_R(t) \mid R > , \tag{1.6}$$

which obeys the Schrödinger´s equation

$$i \hbar \, \partial \mid \Psi(t) > / \partial t = [H_o + V_o(x) + U(t)] \mid \Psi(t) > \tag{1.7}$$

So, $a_L(t)$ and $a_R(t)$ are governed[1] by the following differential equations:

$$\begin{aligned} da_L(t)/dt &= -(i/\hbar)[a_L(t)\,(E_o - \varepsilon + U_{LL}(t)) + a_R(t)\,(\delta + U_{LR}(t))], \\ da_R(t)/dt &= -(i/\hbar)[a_R(t)\,(E_o + \varepsilon + U_{RR}(t)) + a_L(t)\,(\delta + U_{RL}(t))], \end{aligned} \tag{1.8}$$

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

Since the homochiral and heterochiral interactions are equal,[17] we define $u(t) = U(t)_{LL} = U(t)_{RR}$ and $\varphi(t) = U(t)_{LR} = U(t)_{RL}$. In this way Eq.(1.8) are written as:

$$da_L(t)/dt = -(i/\hbar)[a_L(t)\,(E_o - \varepsilon + u(t)) + a_R(t)\,(\delta + \varphi(t))],$$

$$da_R(t)/dt = -(i/\hbar)[a_R(t)\,(E_o + \varepsilon + u(t)) + a_L(t)\,(\delta + \varphi(t))] \qquad (1.9).$$

These general equations (1.9) 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 static interaction and when they are isolated. Depending on U, ε and δ occurs racemization, chiral stability and cases when the "optical activity" or "optical rotation" (O_p) can assume any value in the range $-1 \leq O_p \leq 1$. In Section 6 we present the Conclusions and in Section 7 we present the final Comments.

(2) Active Molecule Submitted to Binary Random Collisions and ε = 0.

In this section we assume that ε = 0 and that the active molecule is embedded, for instance, in a dilute and compressed gases or liquid where the potential U(t) is due to binary collisions[18-21] 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 $N \sim 10^{17}/\text{cm}^3$. The molecular collisions induce transitions between L and R configurations, described by $\varphi(t) = U(t)_{LR}$. The spontaneous transitions between L and R are described by δ given by (1.2). Putting ε = 0 into (1.9), these equations can be solved exactly. As pointed out in Section 1 it is assumed that the chiral molecule at t = 0 is at initial state $|\Psi(0)\rangle = |L\rangle$.

The interaction U(t) is written as a sum of binary interactions given simply by[19] $u(t) = \gamma_p/R(t)^p$, where γ_p represents the force constant for the interacting particles, R(t) the distance between them as a function of the time t and p is equal to p = 3,4,5,..if the interaction is dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and son on. Note that in our approach it is not necessary to assume that the dipole moment **d**(x) of the chiral molecule is parity invariant, that is, we can have both possibilities, P(x)**d**(x) = ± **d**(x).

(2.a) *Dilute gases*.

In the case of dilute gases, treating the binary collisions in the *impact approximation*, we obtain[18–21]

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

where $\lambda_p = (\gamma_p/\hbar)^{2/(p-1)} N(kT/m)^{(p-3)/(2p-2)} C_p$, N the density of perturbing molecules, k the Boltzmann constant, T the absolute temperature of the system, m the reduced mass of the colliding particles and C_p is a numerical factor which depends on p that is shown explicitly elsewhere.[18]

(2.b) *Compressed gases and liquids.*

For compressed gases or liquid, where collisions are *quasi-static*, we see that[18-21]

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

where

$$\lambda_p^* = (8\pi/p)N(\gamma_p/2\hbar)^{3/p} \int_0^\infty x^{-(p+3)/p} \sin^2 x \, dx.$$

(2.c) Conclusions.

Taking into account (2.1) and (2.2) we verify that when $\varepsilon = 0$, in gases and liquids, binary random collisions between active and perturbing molecules *always produce a complete racemization* of the sample. That is, for sufficiently large times t so that $\exp(-\lambda_p t) \to 0$ and $\exp(-\lambda_p^* \, t^{3/p}) \to 0$ we have, respectively, $r_1(t) \to 1/2$ and $r_2(t) \to 1/2$.

In Appendix A are performed numerical estimations of $r_1(t)$ and $r_2(t)$ considering typical molecular parameters.

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

Let us assume that $\varepsilon \neq 0$ and that the active molecule is embedded in a dense gas, liquid or solid, where multiple interactions dominate over binary interactions creating a cooperative effect between the interacting molecules. Due to this collective behavior each molecule will be subjected to a mean field which is a result of combined interactions of all molecules in the system. This mean field is understood as a self-consistent Hartree field.

Let us assume that this cooperative effect generates a *time independent* interaction potential $U_o(x)$. Thus, replacing in equations (1.9) the function $\varphi(t)$ by $\phi_o = \langle L|U_o(x)|R\rangle = \langle R|U_o(x)|L\rangle$ these equations can be exactly solved.[21-23] If at t = 0 the initial state molecule is $|\,\Psi(0)\rangle = |\,L\,\rangle$, we obtain[21-23]

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

where Θ is the “r(t) amplitude” given by

$$\Theta = (\delta + \phi_o)^2/[\varepsilon^2 + (\delta + \phi_o)^2]. \qquad (3.2)$$

According to (3.1) and (3.2) the optical activity $O_p(t)=1 - 2\,r(t)$ oscillates with period $T = 2\pi\hbar/[\varepsilon^2 + (\delta + \phi_o)^2]^{1/2}$ around the average value $< O_p > = 1 - \Theta/2$. So, to have chiral stability $< O_p > = 1$, we must have $\Theta << 1$, that is, the condition $\varepsilon >> (\delta + \phi_o)$ must be obeyed. That is, when the difference of energy ε is sufficiently large to block the L−R transitions induced simultaneously by the spontaneous tunneling and by the cooperative potential $U_o(x)$.

Let us assume that the average distance between the chiral molecule and the neighbors is equal to R. If U_o is due to dipole-dipole interactions[24] we see that $U_o(d\text{-}d) \sim d^2/R^3$.However, if U_o is due to dipole-quadrupole interactions we have $U_o(d\text{-}Q) \sim dQ/R^4$. For typical molecular parameters $d \approx 10^{-18}$ e.s.u., $Q = \theta \approx 10^{-26}$ e.s.u. (see Appendix A) for $R \sim 10^{-8}$ cm $U_o(d\text{-}d)$ and $U_o(d\text{-}Q)$ are of the same order of magnitude, that is, $U_o(d\text{-}Q) \approx U_o(d\text{-}Q) \approx 10^{-12}$ e.s.u. So, using the same approximation adopted in Appendix A it will be assumed that U_o is created by dipole-quadrupole interactions. Consequently (see Appendix A), ϕ_o/h will be written as

$$\phi_o/h = (\theta d/hR^4) \exp(-\mu\omega a^2/\hbar). \qquad (3.3).$$

Putting $\omega = A\ 10^{13}$ rad/s, $d = 10^{-8}$e.s.u, $\theta = 10^{-26}$e.s.u. and $R = 3\ 10^{-8}$ cm we have $\delta/h=5.54\ 10^{12} A^{3/2} \exp(-9.52A)$ Hz and $\phi_o/h = 1.51\ 10^{12} \exp(-9.52\ A)$ Hz.

In Figure 1 the amplitudes Θ(A), for $\varepsilon/h = 10^{-3}$ Hz and $\varepsilon/h = 10^{-6}$ Hz, are plotted as a function of the parameter A.

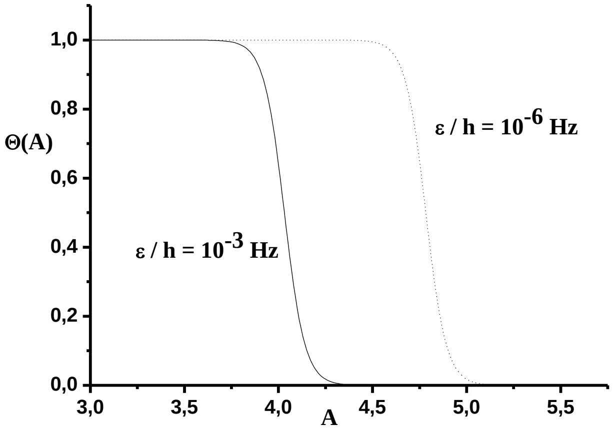

Figure 1. *The amplitude Θ(A), defined by (3.2), plotted as a function of the parameter A, defined by the equation* $\omega = A\ 10^{13}$ *rad/s. Two limiting cases have been considered:* $\varepsilon/h = 10^{-3}$ *Hz (vibrational and rotational transitions) and* $\varepsilon/h = 10^{-6}$ *Hz (nuclear magnetic transitions).*

(3.a) When $\varepsilon/h = 10^{-3}$ Hz (rotational and vibrational transitions) we can have optical stabilization, that is, $\Theta \to 0$, $r \to 0$ and $O_p \to 1$, only for frequencies $\omega > 4{,}5\ 10^{13}$ rad/s found, for instance, in infrared harmonic vibrations.

(3.b) When $\varepsilon/h = 10^{-6}$ Hz (nuclear magnetic transitions) we can have chiral stability only for frequencies $\omega > 5 \sim 5.5\ 10^{13}$ rad/s.

Thus, for frequencies $\omega > 5.5\ 10^{13}$ rad/s the weak energy ε produces chiral stability, that is, $\Theta \to 0$, $r \to 0$ and $O_p \to 1$, because, for these frequencies, ε becomes much larger than δ and ϕ_o.

(4) Isolated Molecule when ε = 0 and ε ≠ 0.

When chiral molecule is isolated U = 0. So, we can put $\varphi(t) = u(t) = 0$ in (1.9) and, consequently, put $\phi_o = 0$ in (3.1) and (3.2). Thus, we obtain, writing $\Theta^* = \delta^2/(\varepsilon^2 + \delta^2)$:

$$r(t) = \Theta^* \sin^2\{(\varepsilon^2 + \delta^2)^{1/2} t/\hbar\} \qquad (4.1).$$

(4.a) If ε = 0 from (4.1) we get,

$$r(t) = \sin^2(2\delta t/\hbar) \qquad (4.2),$$

showing L-R oscillations with the spontaneous tunneling period $T = \pi\hbar/\delta$.

(4.b) If $\varepsilon >> \delta$ we verify, using (4.1), that chiral stability can be obtained since $\Theta \rightarrow 0$, $r \rightarrow 0$ and $O_p \rightarrow 1$. According to Fig.3 this occurs for $\omega > 5{\sim}5.5\ 10^{13}$ rad/s. If, for instance, $\varepsilon/h = 10^{-3}$ Hz there is practically chiral stability because $\Theta = 1.6\ 10^{-12}$.

This shows that in the case of an isolated chiral molecule, the blocking effect due to the weak interactions occurs when $\varepsilon >> \delta$. This 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 spontaneous L-R transitions are allowed only when $\Delta E \sim \delta \geq \varepsilon$. On the other side, the transitions are prohibited when $\varepsilon >> \delta$. In the presence of the potential energy ϕ_o (see Section 3) using the same reasoning, the L−R transitions will be blocked when $\varepsilon >> \delta + \phi_o$.

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

In Section 2 r(t) was calculated assuming that $\varepsilon = 0$ and that the chiral molecule is submitted to a time dependent potential U(t) due to random binary collisions. In Section 3, r(t) was determined for $\varepsilon \neq 0$ and taking U as a time independent interaction potential U_o. In both cases (1.9) were exactly solved.

On the other side, when $\varepsilon \neq 0$ and $U = U(t)$ equations (1.9) cannot be exactly solved. However, an approximate solution $r_4(t)$ for (1.9) is given by:

$$r_4(t) \approx (\delta/\Delta_o)^2\ [\ 1 - \cos(2\Delta_o t/\hbar)\ \exp(-f_p(t))]/2 \qquad (5.1),$$

where $\Delta_o = (\varepsilon^2 + \delta^2)^{1/2}$; $f_p(t) = \lambda_p t$, for dilute gases and $f_p(t) = \lambda_p{}^* t^{3/p}$ for compressed gases and liquids, according to Section 2.

(5.a) When $\varepsilon \rightarrow 0$ from (5.1) we get $r_1(t)$ and $r_2(t)$ given by (2.1) and (2.2), respectively.

(5.b) When $\varepsilon >> \delta$ we see from (5.1) that $r_4(t) \rightarrow 0$, $\Theta \rightarrow 0$ and $O_p \rightarrow 1$ which is the condition for chiral stability, according to Section 4.

(5.c) If $U = 0$, that is, when the chiral molecule is isolated we get

$$r_4(t) = (\delta/\Delta_o)^2 \sin^2(\Delta_o t/\hbar) \qquad (5.2),$$

which is exactly equation (4.1) valid for an isolated chiral molecule.

(5.d) Intermediates situations, different from (a), (b) and (c) analyzed above.

Defining $r_{max} = (\delta/\Delta_o)^2/2$ we verify from (5.1) that the optical activity O_p varies in the range $1-2\, r_{max} \leq O_p \leq 1$. Thus, for very long times, that is, for $f_p(t) >> 1$, $r(t) \rightarrow r_{max}$. So, only when $\delta >> \varepsilon$ occurs racemization, that is, $r_{max} \rightarrow ½$ and $O_p \rightarrow 0$. On the other hand, when $\varepsilon >> \delta$ 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 $\omega = A\ 10^{13}$ rad/s. For frequencies in the interval $4\ 10^{13} < \omega < 5.2\ 10^{13}$ 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 2, $r_4(t)$, defined by (5.1), is shown as a function of t for dilute gases for $\varepsilon = 10^{-3}$ and A = 4.5, that is, $\omega = 4.5\ 10^{13}$ rad/s. According to this figure $r_4(t)$ oscillates between 0 and 0.21 and stabilizes with $r_{max} \approx 0.11$ for t > 10 months, giving an asymptotic optical activity $O_p \rightarrow 0.78$.

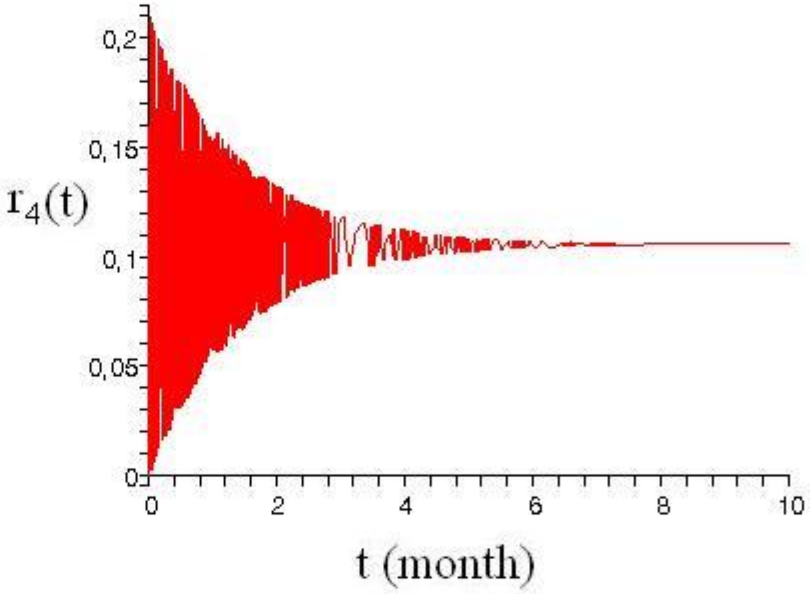

Figure 2. *$r_4(t)$ given by (5.1) as function of the time t measured in years, for $\varepsilon/h = 10^{-3}$ and $A = 4.5$, that is, $\omega = 4.5\ 10^{13}$ rad/s.*

(6)Conclusions.

From the analysis performed above, within the framework of Schrödinger´s equation and using a double bottomed harmonic model, we can conclude that:

(6.1) If $\varepsilon \neq 0$ and the if chiral molecule is submitted to a collective *time independent* potential $U_o(x)$ we can have chiral stability, that is, $<O_p> \rightarrow 1$ only when $\varepsilon >> \delta + \phi_o$, where $\phi_o = <L|U_o(x)|R> = <R|U_o(x)|L>$. That is, when the difference of energy ε is sufficiently large to block the L-R transitions induced simultaneously by the spontaneous tunneling and by the cooperative potential $U_o(x)$.

(6.2) If $\varepsilon \neq 0$ and chiral molecules are free or perturbed by binary, additive, independent and random collisions to get chiral stability it is necessary to have $\varepsilon >> \delta$. The chiral stability can be total $<O_p> \rightarrow 1$ or partial, that is, $<O_p>$ smaller than 1

(6.3) If $\varepsilon = 0$ it is impossible for any interaction potential U to have optical stability. The system always racemizes, that is, $r(t) \rightarrow ½$ and $<O_p> \rightarrow 1$.

(7) Final Comments.

Many papers have been written using linear and non-linear quantum effects to explain the chiral stability (see, for instance, references 1,14-34 and references there in). Since these papers are very numerous and it is not a review article they will not be analyzed here.

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.[35] In our works these processes have not been considered.

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Appendix A

To perform a simple estimate of the racemization functions $r_1(t)$ and $r_2(t)$ of Section 2 let us assume that there is *only* a dipole-quadrupole (p=4) interaction between the molecules of the sample: the perturbing molecules with dipoles and chiral molecules with quadrupoles. In this case,[20-23] using (2.1) we have $\gamma_4 = d < L|\ Q(x)\ | R > = d\ \theta\ \exp(-\mu\omega a^2/\hbar)$, λ_4 and $\lambda_4^*$are given, respectively, by

$$\lambda_4 = 13.0\ N\ (kT/m)^{1/6}\ (\theta d/\hbar)^{2/3}\ \exp(-2\mu\omega a^2/3\hbar)\ , \qquad (A.1)$$

and

$$\lambda_4^* = 2.86\pi\ N(\theta d/2\hbar)^{3/4}\ \exp(-3\mu\omega a^2/4\hbar). \qquad (A.2).$$

Numerical estimations of $r_1(t)$ and $r_2(t)$ will be done here 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 $N = 10^{17}/\text{cm}^3$.

Putting $\omega = A\ 10^{13}$ rad/s we obtain, respectively, measuring the time t in years, using (1.2), (2.3) and (2.4):

$$\delta/\hbar = 1.10\ 10^{21}\ A^{3/2}\ \exp(-9.52\ A)\ y^{-1}.$$

$$\lambda_4 = 5.03\ 10^{15} \exp(-6.35\ A)\ y^{-1} \qquad (A.3),$$

and $$\lambda_4^* = 2.90\ 10^{12}\ \exp(-7.14\ A)\ y^{-1}.$$

When fundamental harmonic frequencies ω are in the infrared region $10^{12} < \omega < 10^{15}$ rad/s the parameter A varies in the interval $0.1< A< 10^2$.

In Figures (A.1) and (A.2) are shown $r_1(t)$ and $r_2(t)$, respectively, as a function of the time t, measured in years, for A = 4.5. For a *dilute gas* (see Figure (A.1)) the racemization occurs for t > 1 day. The factor $r_1(t)$ slowly oscillates around 0.5, assuming rapidly this value. The complete racemization occurs after a time interval ~ 10 month.

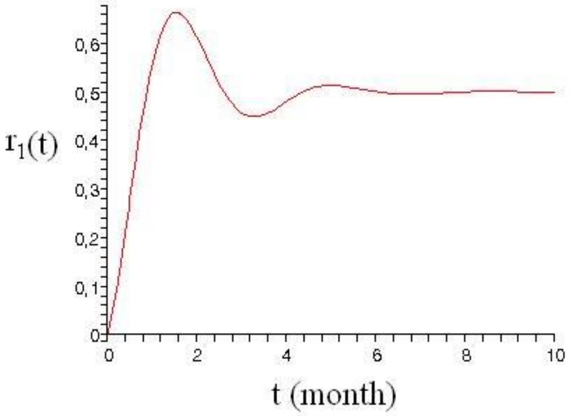

Figure (A.1). *$r_1(t)$ for dilute gases, defined by (2.1), shown as a function of the time t, measured in months. The racemization was calculated taking the harmonic oscillation frequency $\omega = 4.5\ 10^{13}$ rad/s*

For compressed gases or liquids (see Fig.(A.2)), when collisions are quasi static $r_2(t)$ we see that the system would be racemized only for $t > 2\ 10^5$ y. In addition, since the tunneling frequency $\delta/\hbar \sim 2600\ y^{-1}$ is very big the time average the function $r_2(t)$, defined by (2.2), is $<r_2(t)> \approx ½$. Thus, from the beginning, practically there is no chiral stability.

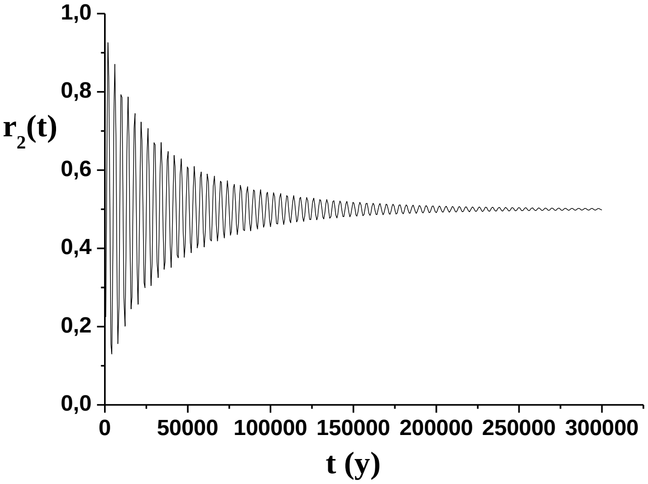

Figure (A.2). *$r_2(t)$ for dense gases and liquids, defined by (2.2), shown as a function of the time t, measured in years. The racemization was calculated taking the harmonic oscillation frequency $\omega = 4.5\ 10^{13}$ rad/s.*

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