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Abstract

A two-level quantum mechanical approach is developed in order to explain how the racemization depends on the interaction of the active molecule with the environment. All relevant physical parameters of the molecules and of the optically active sample are explicitly defined in our calculations. Our general predictions are applied to study two particular cases: (a) dilute gases and (b) dense gases, liquids and solids.

1. Introduction

As well known,[1] the optical activity of an optically active material change with time. The sample, containing predominatly one stereoisomer, will become a mixture of equal amounts of each isomer. We investigate how this relaxation process, named racemization, depends on the interaction of the active molecule with the environment.

Many approaches, dynamical and static ones, have been proposed to describe the interaction of an active molecule with the enviroment as one can see, discussed in details, in the paper of Claverie and Jona-Lasinio.[2] As pointed out by them,[2] these models are not completely satisfactory because they involve some phenomenological parameters whose identification is not immediate. Claverie and Jona-Lasinio[2] have developed a static approach that would be able to explain the fact that active molecules exhibiting symmetric configurations could be localized in one of them.

In this paper, assuming that an active molecule changes its handedness only by tunnelling, a two-level quantum mechanical formalism will be developed in order to explain the effect of the environment in the racemization process. Our approach can be applied when the active molecule is embedded in a gas, liquid, solid or submitted to a generic external field.[2] All relevant physical parameters of the molecules and of the optically active sample are explicitely defined in our calculations. Since the asymmetries in the spectra and in the optical activity induced by the weak interaction seem to be small,[1-3] only electromagnetic forces will be taken into account in our model.

Our general predictions are applied to study racemization of samples in two limiting cases: (a) dilute gases and (b) dense gases, liquids and solids.

2. Perturbed Active Molecule

Optical activity occurs[1] when the molecule has two distinct left and right configurations, $|L\rangle$ and $|R\rangle$, which are degenerate by the parity operation, that is,

$P|L\rangle = |R\rangle$ and $P|R\rangle = |L\rangle$. Left-right isomerism can be viewed in terms of a double bottomed potential well[4,5] and the states $|L\rangle$ and $|R\rangle$ may be pictured as molecular configurations that are concentrated in the left or right potential well. The coordinate x involved in the parity operation P, connecting the two potential minima, may represent the position of an atom, the rotation of a group around a bond, some other coordinate or collective coordinate of the molecule.

Let us indicate by H_0 the hamiltonian of each side of the double well and by $V_0(x)$ the potential barrier separating the two minima of the double well. In this picture $|L\rangle$ and $|R\rangle$ are eigenstates of H_0, that is, $\langle L|H_0|L\rangle = \langle R|H_0|R\rangle = E_0$ and will have a small overlap inside the barrier $V_0(x)$ so that $\langle L|V_0|R\rangle = \langle R|V_0|L\rangle = \delta$.

We develop now a theory to explain the racemization of an optically active sample assuming that th · relaxation process is produced essentially by transitions between the two vibrational states $|L\rangle$ and $|R\rangle$.

The interaction potential of the active molecule with the environment will be represented by $U(t)$. First, let us assume that $V_0(x)$ and $U(t)$ are, in principle, equally relevant for transitions between $|L\rangle$ and $|R\rangle$ configurations. In this case the state function $|\psi(t)\rangle$ of the active molecule will be represented by

$$|\psi(t)\rangle = e^{-iE_0 t/\hbar}[a_L(t)|L\rangle + a_R(t)|R\rangle] . \tag{2.1}$$

obeying the equation $i\hbar\partial|\psi(t)\rangle/\partial t = [H_0 + V(x,t)]|\psi(t)\rangle$, where $V(x,t) = V_0(x) + U(t)$. Thus, $a_L(t)$ and $a_R(t)$ are governed by the following differential equations

$$\dot{a}_L(t) = (-i/\hbar)[a_L(t)\,V_{LL} + a_R(t)\,V_{LR}] , $$
$$\dot{a}_R(t) = (-i/\hbar)[a_R(t)\,V_{RR} + a_L(t)\,V_{RL}] . \tag{2.2}$$

where the matrix elements V_{nk}, with $n,k = L$ and R, are real functions given by $V_{nk} = \langle n|V(x,t)|k\rangle$. Due to left and right symmetry, $V_{LR} = V_{RL}$ and $V_{LL} = V_{RR}$.

Solving Eqs. (2.2) we get

$$a_L(t) = e^{-i\theta_{LL}(t)}[a\,e^{-i\theta_{LR}(t)} + b\,e^{i\theta_{LR}(t)}]/2 , $$
$$a_R(t) = e^{-i\theta_{LL}(t)}[a\,e^{-i\theta_{LR}(t)} - b\,e^{i\theta_{LR}(t)}]/2 , \tag{2.3}$$

where a and b are constants determined by the initial conditions and $\theta_{nk}(t) = \int_0^t V_{nk}\,dt/\hbar$.

If at $t = 0$ the active molecule is prepared so that $|\psi(0)\rangle = [|R\rangle + |L\rangle]/\sqrt{2}$, we have, from Eqs. (2.1) and (2.3), $a = \sqrt{2}$ and $b = 0$. So, in these conditions, the molecular state will be described by the state function $|\psi_+(t)\rangle$ written as $|\psi_+(t)\rangle = e^{-i\alpha_+(t)}|\phi_+(t)\rangle = e^{-i\alpha_+(t)} e^{-iE_+t/\hbar}|+\rangle$, where $\alpha_+(t) = \int_0^t [U_{LL}(t) + U_{LR}(t)]dt/\hbar$, $|+\rangle = [|R\rangle + |L\rangle]/\sqrt{2}$ and $E_+ = E_0 + \delta$. On the other hand, if $|\psi(0)\rangle = [|R\rangle - |L\rangle]/\sqrt{2}$, we see that $a = 0$ and $b = \sqrt{2}$, resulting the molecular state $|\psi_-(t)\rangle$: $|\psi_-(t)\rangle = e^{-i\alpha_-(t)}|\phi_-(t)\rangle = e^{-i\alpha_-(t)}e^{-iE_-t/\hbar}|-\rangle$, where $\alpha_-(t) = \int_0^t [U_{LL}(t) - U_{LR}(t)]\,dt/\hbar$, $|-\rangle = [|R\rangle - |L\rangle]/\sqrt{2}$ and $E_- = E_0 - \delta$. These states, with $+$ and $-$ partities, respectively, are eigenstates of $H = H_0 + V_0(x)$, that is, $H|\psi_\pm(t)\rangle = E_\pm|\psi_\pm(t)\rangle$.

Molecules prepared at $+$ and $-$ parity states give a net contribution equal to zero to the chirality of the sample. Since the initial left-right symmetry of these $+$ and $-$ states is not modified by $U(t)$, no alteration of the chirality of the system is produced by the external potential.

Let us study now the case when the active molecule is prepared at $t = 0$ at left or right configuration. We will see that only in this case $U(t)$ can contribute to the racemization process. Thus, solving Eqs. (2.2) assuming, for instance, that $|\psi(0)\rangle = |L\rangle$, we get from Eqs. (2.1) and (2.3), $a_L(0) = 1$, $a_R(0) = 0$ and $a = b = 1$. Consequently, $a_L(t)$ and $a_R(t)$ are given by

$$a_L(t) = e^{-i\theta_{LL}(t)} \cos(\theta_{LR}(t)) , $$
$$a_R(t) = -i\,e^{-i\theta_{LL}(t)} \sin(\theta_{LR}(t)) . \tag{2.4}$$

Using Eqs.(2.1) and (2.4), the state function of the active molecule, initially in a left configuration, will be written as

$$|\psi_L(t)\rangle = e^{-i(\theta_{LL}(t) + E_0 t/\hbar)} [\cos(\theta_{LR}(t))|L\rangle - i\sin(\theta_{LR}(t))|R\rangle] . \tag{2.5}$$

The racemization is described by $r(t)$ that is defined by

$$r(t) = |\langle R|\psi_L(t)\rangle|^2 = \sin^2(\theta_{LR}(t)) , \tag{2.6}$$

where $\theta_{LR}(t) = \int_0^t \langle L|V_0(x) + U(t)|R \rangle \, dt/\hbar$.

First, let us show that the well known quantum mechanical description of $|\psi_L(t)\rangle$ for an isolated molecule is obtained putting $U(t) = 0$ in Eq.(2.5). Indeed, in this case, Eq.(2.5) becomes

$$|\psi_L(t)\rangle = e^{-iE_0 t/\hbar} [\cos(\delta t/\hbar)|L\rangle - i \sin(\delta t/\hbar)|R\rangle] \; , \qquad (2.7)$$

and, consequently, $r(t) = \sin^2(\delta t/\hbar)$. According to Eq.(2.7), the molecule prepared left-handed at $t = 0$ will oscillate back and forth between left and right forms with frequency $\omega = \delta/\hbar$. The quantum oscillation time $\tau = 2\pi/\omega$ can be estimated in terms of the tunnelling rate through the barrier $V_0(x)$.[4] Taking into account the range of molecular parameters,[1] we see that it would exist τ of seconds, minutes, hours, years up to billions of years. For alanine, for instance, $\tau \sim 10^9$ years, according to Hund[6] estimates.

Now, using our general predictions, given by Eq.(2.6), we will investigate the effect of the perturbation $U(t)$ on the chirality of the system in two limiting cases: (a) Dilute Gases and (b) Dense Gases, Liquids and Solids.

(a) Dilute Gases

By dilute gas we mean[5] that the dynamics of interactions of active molecule is expressed in terms of binary collisions with the perturbing molecules of the sample, the duration of which are very short compared to all other time scales, in particular the tunnelling time. In other words, molecular interactions can be treated in the "impact approximation".[7]

Thus, let us see how to estimate $\theta_{LR}(t)$ in the impact approximation. According to Eq.(2.6) we see that $\theta_{LR}(t) = \delta t/\hbar + \int_0^t U_{LR}(t) \, dt/\hbar$. So, if the collision times are much smaller than the tunnelling time and during the time interval t there is a large number of collisions between the active and perturbing molecules, the tunnelling effect becomes negligible compared with the collision effects. Calculating now the collision effects, using the well known impact approximation formalism,[7] we see that

$r(t) = e^{-\lambda t}$, where the transition probability per unit of time λ is given by[8]

$$\lambda = 2\pi N^{(2)} \int_0^\infty b \, db \int_0^\infty v \, P(v) \, dv \, \langle \sin^2(\theta_{LR}) \rangle \; , \qquad (2.8)$$

where $N^{(2)}$ is the density of perturbing molecules, b the impact parameter of the colliding particles, v the relative velocity between them, $P(v)$ the Maxwell-Boltzmann velocity distribution, the brackets $\langle \cdots \rangle$ mean an average over internal states of the colliding particles and finally,

$$\theta_{LR} = \theta_{LR}(t = +\infty) = \int_0^\infty u_{LR}(t) \, dt/\hbar = \int_0^\infty \langle L|u(t)|R \rangle \, dt/\hbar \; ,$$

$u(t)$ being the interacting potential between active and perturbing molecules.

The racemization factor λ, defined by Eq.(2.8), could be calculated in details[8] taking into account all relevant parameters of the optically active sample. However, we intend to obtain here only the main features of the relaxation phenomenum. In this way, let us indicate the interaction potential $u(t)$ simply by $u(t) = \gamma/R(t)^p$, where γ represent the force constants of the interacting particles,[9,10] $R(t)$ the distance between colliding molecules and and p is equal to $3, 4, 5, \ldots$, if the interaction is dipole-dipole, dipole-quadrupole, quadrupole-quadrupole and so on. Since for the active molecule, the dipole matrix element $\langle L|\hat{d}|R \rangle = 0$, we see that $p > 3$. Thus, using this simplified potential and Eq.(2.8), λ will be given by[8,11]

$$\lambda \simeq (\gamma/\hbar)^{2/(p-1)} N^{(2)} (kT/m)^{(p-3)/(2p-2)} \; , \qquad (2.9)$$

where k is the Boltzamnn constant, T the absolute temperature of the system and m the reduced mass of the colliding particles. We see, from Eq.(2.9), that the racemization increases as the temperature increases.[5] We must note, however, that Eq.(2.9) can be applied only when the impact approximation is valid, that is, when $\tau > 1/\lambda$. This implies that, when a dilute gas approximation is satisfied, collisions would always destroy rather than stabilize the handedness of the sample.[5]

(b) Dense Gases, Liquids and Solids

In dense gases and liquids multiple interactions dominate binary ones. To a first approximation in dense gases and liquids, as in solids, the active molecule will be assumed to be inside a small cavity surrounded by perturbing molecules regarded as at rest. In these conditions, the interaction potentials created by the perturbing molecules inside this cavity will be taken as static and equal to $U_1(x)$ in the region of the double well potential. Thus, instead of $V_0(x)$, the potential barrier would be given by the effective potential $V_{\text{eff}}(x) = V_0(x) + U_1(x)$. Defining $\delta_{\text{eff}} = \langle L|V_{\text{eff}}(x)|R\rangle = \langle L|V_0(x)+U_1(x)|R\rangle$ and using Eq.(2.6) we get $\theta_{LR}(t) = \delta_{\text{eff}}\,t/\hbar$ and, consequently,

$$r(t) = \sin^2(\delta_{\text{eff}}\,t/\hbar) \ . \tag{2.10}$$

Eq.(2.10) shows that the racemization time is given by an effective time $\tau_{\text{eff}} = h/\delta_{\text{eff}}$. Depending on the perturbative potential $U_1(x)$ the effective racemization time τ_{eff} can be larger or smaller than the natural tunnelling time τ.

Claverie and Jona-Lasinio[2] have considered in their paper a perturbative potential $U_1(x)$ which is concentrated in a small space region compared with the size of the double well. They have shown that this kind of perturbation would be able, in principle, to stabilize molecules in a given, left or right, configuration. Numerical estimates for this localization have been performed for dipolar molecules (NH_3, AsH_3 and PH_3) in a gaseous state. The potential $U_1(x)$ was taken as the following: once a molecule is in a given, left and right, configuration, its dipole moment $\vec{d_1}$ locally polarizes the surrounding which, in turn, creates, at the position of $\vec{d_1}$, as so called reaction field $\vec{E_r}$,[12] which is collinear with $\vec{d_1}$. This U_1 would be given by $U_1 = -(\varepsilon - 1)d_1^2/(2\varepsilon + 1)a^3$, where ε is the dieletric constant of the medium and a the radius of the cavity where the molecule is embedded. As U_1 is negative it tends to stabilize the configuration by lowering the potential energy of the localized, $|L\rangle$ or $|R\rangle$, state.

Finally, let us study the effect of $U(t)$ on active molecules prepared at $+$ and $-$ parity states. In this case, as shown before, the energy difference $E_+ - E_- = 2\delta$ and the left-right oscillation frequency $\omega = \delta/\hbar$, depend only on the internal structure of the molecule. In these conditions, as well known,[8,13] the state function $|\psi(t)\rangle$ of the active molecule can be represented in terms of the two eigenstates, $|\phi_+(t)\rangle$ and $|\phi_-(t)\rangle$, of the operator $H = H_0 + V_0(x)$, that is

$$|\psi(t)\rangle = a_+(t)|\phi_+(t)\rangle + a_-(t)|\phi_-(t)\rangle \ ,$$

where $|\phi_\pm(t)\rangle = |\pm\rangle\,e^{-iE_\pm t/\hbar}$, $|\pm\rangle = (|R\rangle \pm |L\rangle)/\sqrt{2}$, $E_\pm = E_0 \pm \delta$, and $H|\phi_\pm(t)\rangle = E_\pm|\phi_\pm(t)\rangle$. In this context, $|\psi(t)\rangle$ obeys the equation $i\hbar\partial|\psi(t)\rangle/\partial t = [H + U(t)]|\psi(t)\rangle$.

In these conditions, as shown in Appendix, the net contribution of $U(t)$ to the chirality of the sample is equal to zero, independently of the initial state $|\psi(0)\rangle$.

APPENDIX

We calculate here the racemization produced by $U(t)$ when the active molecules are prepared at the $+$ and $-$ parity states. In these conditions, as pointed out in section 2, the active molecule state function would be represented by[8,13]

$$|\psi(t)\rangle = a_+(t)|\phi_+(t)\rangle + a_-(t)|\phi_-(t)\rangle \ , \qquad (A.1)$$

where $|\phi_\pm(t)\rangle = |\pm\rangle \, e^{-iEt/\hbar}$, with $|\pm\rangle = (|R\rangle \pm |L\rangle)/\sqrt{2}$ and $E_\pm = E_0 \pm \delta$, are eigenstates of $H = H_0 + V_0(x)$, that is, $H|\phi_\pm(t)\rangle = E_\pm|\phi_\pm(t)\rangle$. Since $|\psi(t)\rangle$ obeys the equation $i\hbar\partial|\psi(t)\rangle/\partial t = [H + U(t)]|\psi(t)\rangle$, $a_+(t)$ and $a_-(t)$ obey the following differential equations

$$\dot{a}_+(t) = (-i/\hbar)[a_+(t)\,U_{++}(t) + a_-(t)\,U_{+-}(t)\,e^{-2i\delta t/\hbar}] \ .$$
$$\dot{a}_-(t) = (-i/\hbar)[a_-(t)\,U_{--}(t) + a_+(t)\,U_{-+}(t)\,e^{2i\delta t/\hbar}] \ , \qquad (A.2)$$

where the real matrix elements U_{nk}, with $n, k = +$ and $-$, are given by $\langle n|U(t)|k\rangle$. Due to left and right symmetry, $U_{++} = U_{--}$ and $U_{+-} = U_{-+}$.

As one can easily verify,[8,13] Eqs.(A.2) can be solved, in a good approximation, taking $\delta = 0$. In this case we obtain

$$a_+(t) = e^{-i\theta_{++}(t)}\,[a\,e^{-i\theta_{+-}(t)} + b\,e^{i\theta_{+-}(t)}]/2 \ .$$
$$a_-(t) = e^{-i\theta_{++}(t)}\,[a\,e^{-i\theta_{+-}(t)} - b\,e^{i\theta_{+-}(t)}]/2 \ . \qquad (A.3)$$

where the constants a and b are determined by the inital conditions and $\theta_{nk}(t) = \int_0^t \langle n|U(t)|k\rangle \, dt/\hbar$.

Assuming, for instance, that $|\psi(0)\rangle = |+\rangle$ we get, from Eqs.(A.1) and (A.3), $a = b = 1$, resulting

$$a_+(t) = e^{-i\theta_{++}(t)}\cos(\theta_{+-}(t)) \ ,$$
$$a_-(t) = -i\,e^{-i\theta_{++}(t)}\sin(\theta_{+-}(t)) \ . \qquad (A.4)$$

Using Eqs.(A.1) and (A.4) we write $|\phi(t)\rangle$ as

$$|\psi(t)\rangle = e^{-i\theta_{++}(t)}\,[\cos(\theta_{+-}(t))|\phi_+(t)\rangle - i\,\sin(\theta_{+-}(t))|\phi_-(t)\rangle] \ . \qquad (A.5)$$

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We are now in conditions to calculate the racemization produced by $U(t)$, that will be given by the transition probabilities between $|\psi(t)\rangle$ and the $|L\rangle$ and $|R\rangle$ states. Using Eq.(A.5) we see that left and right configurations appear with the same probability, that is

$$|\langle L|\psi(t)\rangle|^2 = |\langle R|\psi(t)\rangle|^2 = [1 - \cos(\theta_{+-}(t))\,\sin(\theta_{+-}(t))\,\sin(2\delta t/\hbar)]/2 \ .$$

This implies that the net racemization produced by $U(t)$ is equal to zero.

Assuming now that $|\psi(0)\rangle = |L\rangle$ we get, from (A.1) and (A.3), $a = 0$ and $b = \sqrt{2}$, resulting $a_+(t) = -a_-(t) = e^{-i\theta(t)}\sqrt{2}/2$, where $\theta(t) = \theta_{++}(t) - \theta_{+-}(t)$. Consequently, we obtain from Eq. (A.1),

$$|\psi(t)\rangle = e^{-i\theta(t)}\,e^{-iE_0t/\hbar}\,[\cos(\delta t/\hbar)|L\rangle - i\sin(\delta t/\hbar)|R\rangle] \ .$$

showing that the racemization independs of the perturbation $U(t)$.

We have shown for two particular initial states, $|\psi(0)\rangle = |+\rangle$ and $|\psi(0)\rangle = |L\rangle$, that the perturbative $U(t)$ is not able to change the chirality of the sample, however, as can be easily verified, this result is the same for any $|\psi(0)\rangle$.

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