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ON THE STABILITY OF OPTICAL ISOMERS

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Abstract

We improve our two-level approach developed to explain the racemization produced by the interaction of the active molecule with the environment. Assuming that left and right enantiomeric configurations are not equally perturbed by the external potential we see that the stability of optical activity can occur.

1 Introduction

As is well known,¹ 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, is due to the interaction of the active molecule with the environment. This interaction can be with the remaining molecules of the sample or with an external field. Many dynamic and static approaches have been proposed to describe the interaction of an active molecule with the environment, as is shown in details in recent papers.²⁻⁵ However, these models are not completely satisfactory because they involve some phenomenological parameters whose identification and quantification is not immediate.² In preceding papers,⁶⁻¹⁰ we developed a two-level formalism to explain the environment racemization process when the active molecule is embedded in a gas, liquid or solid. In our approach all relevant physical parameters for the molecules of the active sample are clearly defined. Detailed calculations were performed for optically active dilute gases.⁷⁻¹⁰ However, in our first and basic paper,⁶ we assumed that left and right enantiomeric configurations were equally perturbed by the external potential. This was done in order to integrate exactly our differential equations. In the present paper we improve our theoretical predictions do not using this simplifying hypothesis. We verify

that the optical activity can be stabilized when left and right enantiomeric configurations are not equally perturbed by the external potential.

2 The two-level approach

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 $P|R\rangle = |L\rangle$. Since asymmetries in the spectra and in the optical activity induced by weak interactions are small,¹¹⁻¹⁴ only electromagnetic forces will be taken in our model. Left-right isomerism can be viewed in terms of a double-bottomed potential well¹⁵⁻¹⁷ and the states $|L\rangle$ and $|R\rangle$ may be pictured as molecular configurations that are concentrated in the left and right potential well. The coordinate x , involved in the parity operation P 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.

We define H_0 as the Hamiltonian of each side of the double well and $V_0(x)$ as the potential barrier separating the two minima of the double well. In this picture, the $|L\rangle$ and $|R\rangle$ are eigenstates of H_0 , i.e., $\langle L|H_0|L\rangle = \langle R|H_0|R\rangle = E_0$ and we 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 now develop a theory to explain the racemization of an optically-active sample assuming that relaxation process is produced essen-

tially by transitions between the two fundamental vibration states $|L\rangle$ and $|R\rangle$.¹⁰ The interaction potential of the active molecule with the environment will be represented by $U(t)$. It is assumed that $U(t)$ is weak, not affecting appreciably the geometry of the molecule and, therefore, not affecting the frequency for the natural tunneling. So, the state function $|\Psi(t)\rangle$ of the active molecule will be represented by

$$|\Psi(t)\rangle = e^{-iE_0t/\hbar} [a_L(t)|L\rangle + a_R(t)|R\rangle] \quad (1)$$

and will obey 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:

$$\begin{aligned} \dot{a}_L(t) &= (-i/\hbar) [a_L(t)(\delta + U_{LL}(t)) + a_R(t)U_{LR}(t)] \\ \dot{a}_R(t) &= (-i/\hbar) [a_R(t)(\delta + U_{RR}(t)) + a_L(t)U_{LR}(t)] \end{aligned} \quad (2)$$

where $\delta = \langle L|V_0(x)|R\rangle$, $\langle L|V_0(x)|L\rangle = \langle R|V_0(x)|R\rangle = 0$ and, due to the left-right symmetry, $\langle L|U(t)|R\rangle = U_{LR}(t) = \langle R|U(t)|L\rangle$. In the preceding paper⁶ we assumed that $U_{LL}(t) = U_{RR}(t)$, that is, left and right configurations are equally perturbed by $U(t)$. In these conditions Eqs.(2) could be exactly solved and we have shown that the racemization $r(t)$ is described by

$$r(t) = \sin^2 \Theta_{LR}(t) \quad (3)$$

where $\Theta_{LR}(t) = \delta t/\hbar + \int_0^t U_{LR}(t)dt/\hbar$, showing that only the $U_{LR}(t)$ matrix element of the external potential would contribute to the racemization of the

sample. It is interesting to remark that the same results for the racemization $r(t)$ are obtained representing the molecular state function $|\Psi(t)\rangle$ by⁶

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

where $|\phi_{\pm}(t)\rangle$ are eigenstates of $H = H_0 + V_0(x)$, with eigenstates $E_{\pm} = E_0 \pm \delta$.

Now, let us see how to estimated by $U(t)$, that is, when $U_{LL}(t) \neq U_{RR}(t)$. With this intention, defining $b_n(t) = a_n(t) \exp(i\alpha_n(t))$, $\alpha_n(t) = \int_0^t U_{nn}(t) dt/\hbar$, with $n = L, R$ and $\varphi(t) = \int_0^t [U_{LL}(t) - U_{RR}(t)] dt/\hbar$, Eqs.(2) are written as,

$$\begin{aligned} \dot{b}_L(t) &= (-i/\hbar) b_R(t) (\delta + U_{LR}(t)) \exp(i\varphi(t)) \\ \dot{b}_R(t) &= (-i/\hbar) b_L(t) (\delta + U_{LR}(t)) \exp(-i\varphi(t)), \end{aligned} \quad (4)$$

where we see that the effects due to $U_{LL}(t) \neq U_{RR}(t)$ are given by $\varphi(t)$ in the exponential term $\exp(\pm i\varphi(t))$.

It is important to note that, since Eqs(4) cannot be exactly integrated in the general case, it is not possible to determine the exact contribution of $\varphi(t)$ to the racemization. However, this contribution can be reasonably well estimated, as will be done in what follows. First, we observe that, according to Eqs(4), the main contributions to the racemization are given by δ and $U_{LR}(t)$; indeed, $r(t) = 0$ when $\delta = U_{LR}(t) = 0$. Second, based on studies performed in a preceding paper,⁸ where differential equations similar to Eqs.(4) have been analysed, we see that $\varphi(t)$ would be essentially responsible for the isomeric stability. Indeed, to show this, let us assume that the $U_{LL}(t) - U_{RR}(t)$ average value is given by $\langle U_{LL}(t) - U_{RR}(t) \rangle = -2\epsilon$. So, $\varphi(t)$ is written as

$\varphi(t) \cong -2\epsilon t$. In these conditions Eqs.(4) can be exactly integrated⁸ giving:

$$\begin{aligned} b_L(t) &= a \cos \phi \exp [(i/\hbar) (\Delta t + \Theta_1(t) - \epsilon t)] + \\ &\quad b \sin \phi \exp [(-i/\hbar) (\Delta t + \Theta_2(t) + \epsilon t)] , \\ b_R(t) &= a \sin \phi \exp [(i/\hbar) (\Delta t + \Theta_1(t) + \epsilon t)] + \\ &\quad b \cos \phi \exp [(-i/\hbar) (\Delta t + \Theta_2(t) - \epsilon t)] , \end{aligned} \quad (5)$$

where a and b are constants to be determined by the initial conditions,

$$\begin{aligned} \Delta^2 &= \epsilon^2 + \delta^2, \quad \sin(2\phi) = \delta/\Delta, \quad \cos(2\phi) = \epsilon/\Delta , \\ \Theta_1(t) &= \tan(\phi) \int_0^t U_{LR}(t) dt \quad \text{and} \quad \Theta_2(t) = \cot(\phi) \int_0^t U_{LR}(t) dt . \end{aligned}$$

Assuming that $|\Psi(0)\rangle = |L\rangle$ we can easily show, using Eq.(1) and Eq.(5), that $r(t) = |\langle R|\Psi(t)\rangle|^2$ is given by:

$$r(t) = (\delta/\Delta)^2 \left\{ 1 - \cos \left[(2\Delta t)/\hbar + (2\Delta/\delta) \int_0^t U_{LR}(t) dt/\hbar \right] \right\} . \quad (6)$$

that, for $\epsilon = 0$, coincides with $r(t)$ described by Eq.(3).

On the other hand, when $\epsilon \gg \delta$, we get $r(t) \cong (\delta/\epsilon)^2 \ll 1$, showing that, in these conditions, the interaction of the active molecule with the environment would be able to induce the stability of optical isomers.

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