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Racemization, chiral stability and weak interactions

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Abstract

We study, in the framework of the Schrödinger's equation, the effect of intermolecular interactions on tunneling racemization of the active 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 active molecule is assumed to be embedded in a gas, liquid or solid, submitted to a perturbing potential U created by the molecules of the sample. In our model we take into account the difference of energy (ε) between the left (L) and right (R) configurations due to the weak interactions. We show that when $\varepsilon = 0$ and the perturbing potential U is due to random binary collisions, the optically active system inevitably racemizes. However, when $\varepsilon \neq 0$ there is chiral stability when $\varepsilon \gg \delta$, where δ is the difference of energy, between left and right configurations, due to the natural tunneling effect. On the other hand, when $\varepsilon \neq 0$ and U is created by a cooperative effect between the interacting molecules we show that there is no racemization but it is possible to have chiral stability. This occurs when the heterochiral interaction (U_{LR}) and δ are much smaller than ε. According to our estimates the stability occurs, for typical molecular parameters, only for fundamental harmonic oscillator frequencies $\omega > 5.2 \times 10^{13}$ rad/s, that is, in the infrared and far-infrared regions. In our approach the weak interaction, which is responsible for the left–right symmetry breaking, plays a fundamental role in the optical stability.

Keywords: Optical activity; Racemization; Weak interactions

1. Introduction

As is well known [1,2], 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. Many approaches have been proposed to describe the racemization [3].

Optical activity occurs [1,2] 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

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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_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, $|L>$ and $|R>$ are eigenstates of H_0, i.e., $<L|H_0|L> = <R|H_0|R> = E_0$ and there is a small overlap of these states inside the barrier $V_0(x)$ so that, $<L|V_0|R> = <R|V_0|L> = \delta$.

Let us assume that the double-bottomed potential well has the shape of two overlapping harmonic potentials. 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]:

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

The left and right configurations states of the active molecule will be written in a Born–Oppenheimer approximation (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 these conditions, $\delta = <L|V_0(x)|R> = <R|V_0(x)|L>$ is given by[4]

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

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 1970s, 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, $<L|H_0|L> = E_L = E_0 - \varepsilon$ and $<R|H_0|R> = E_R = E_0 + \varepsilon$, where 2ε is the difference of energy between the left and right configurations due to the parity-violating interaction. According to recent calculations [7–13], 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.

In Section 2 we show how to calculate, within the framework of the Schrödinger's equation, the racemization when the active molecule is submitted to a generic perturbing potential $U(t)$.

In Section 3, using the general expressions deduced in Section 2, the racemization is calculated when $\varepsilon = 0$ and $U(t)$ is due to binary, independent and random collisions. It is shown that in these conditions the optically active system inevitably racemizes.

In Section 4, the racemization is calculated assuming that $\varepsilon \neq 0$ and that the interaction potential U is due a cooperative effect between the active and the perturbing molecules. This cooperative interaction will be understood as a self-consistent Hartree field and its effect is evaluated in the framework of Schrödinger's equation. We show that the optical stability can be obtained only when the heterochiral energy $<L|U|R>$ and δ are much smaller than ε.

In Section 5 we show how to estimate the racemization and the chiral stability when $\varepsilon \neq 0$ and $U(t)$ is due to binary random collisions.

In Section 6 we present a summary of our approach where the weak interaction, which is responsible for the left–right symmetry breaking, plays a fundamental role in the optical stability. We also comment the adoption of nonlinear Schrödinger's equations to study the chiral stability.