Photoisomerization in a Dissipative Environment

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We investigate photoisomerization (PI), the shape change of a molecule upon photoabsorption, in a dissipative environment using a simple spin-boson model. We identify two classes of environment depending on whether it “entangles” with the molecule. In the absence of entanglement, the environment merely causes a blue shift of the required photon frequency and reduces the quantum efficiency of PI. With entanglement the molecule can undergo a quantum phase transition between a state that photoisomerizes to a state that does not.

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Photoisomerization (PI) is a phenomenon where a molecule absorbs a photon and changes its shape (conformation) [1, 2, 3, 4, 5]. This important phenomenon is relevant to vision and other biological processes. Recently it has been proposed that molecules which photoisomerize (the “PI molecules”) can be used as light sensitive molecular switches [6, 7] and optomechanical devices [8, 9]. A good example of PI molecule is the “azobenzene” [10]. It switches between two isomers, the trans and cis configurations upon absorbing light.

For microscopic systems, environment usually plays a critical role in affecting their quantum mechanical behavior. PI of molecules is not an exception. The goal of this paper is to study PI in the presence of an environment. Although the rest of the discussions are coined in terms of PI, our theory should be applicable to a variety of situations. Examples include Jahn-Teller distortion in an environment and quantum bit in an environment.

The physical mechanism of PI has attracted a lot of interests in the past two decades. In this work we present a simple theory for it. Our theory differs from those in the literature in that we emphasize the importance of the environment. Specifically, we suggest the existence of two types of environment, depending on whether it “entangles” with the PI molecule. Without entanglement the environment merely causes a blue shift in the photon frequency necessary to induce PI and reduces the quantum efficiency. With entanglement the molecule can undergo a quantum phase transition between a state that photoisomerizes to a state that does not. Our investigation of the environmental effects on PI is stimulated by a very recent scan tunneling microscopy experiment [11] which reported the loss of PI functionality when azobenzene is in close contact with a metallic (gold) surface, and the regaining of the PI functionality as the molecules are elevated sufficiently far from the surface.

The irreducible ingredients of a PI molecule are (1) two electronic states [10] and (2) a structure degree of freedom, and (3) a strong coupling between the two. We model (1) by a quantum bit (or a quantum spin) where the up and down states correspond to the two electronic states in question, and (2) by a simple harmonic oscillator. The coupling between the two sets of freedom is described by the following Hamiltonian

$$H_{\text{mol}} = t_0 \sigma_z + g' \sigma_z x + \frac{k}{2} x^2 + \frac{p^2}{2m}. \quad (1)$$

Here $x$ and $p$ are the dynamic variables of the harmonic oscillator, $\sigma_z$ is the third Pauli matrix, and $2t_0$ describes the energy difference between the two electronic states. It is instructive to first analyze Eq. (1) in the limit $m \to \infty$ where the harmonic oscillator is classical. In this limit, depending on the value of $\sigma_z (\pm 1)$, the energy landscape for the structural degree of freedom ($U(x)$) takes on different shapes. This is shown as the red and green curves in Fig. 1(a). In conventional picture of PI, the system jumps vertically from the minimum of the red (green) curve to the green (red) curve upon absorbing a photon. Subsequently the structure relaxes until $x$ reaches the minimum of the green (red) curve. The two minima of the green and red curves, situated at $x = \pm g'/k$, correspond to the two relevant molecular structures. We note that by setting $t_0$ to zero Eq. (1) describes the physics of Jahn-Teller effect where the structure distortion (i.e., $x = 0 \to x \neq 0$) spontaneously sets in to split the electronic degeneracy and lower the total energy.

The above intuitive picture for PI leaves unclear an important question: since electronic transition often proceeds at a faster rate than structural relaxation, what holds the molecule from de-exciting back to the original electronic state during structural relaxation? We begin our discussions by first addressing this question.

Restoring the full quantum mechanical nature of the harmonic oscillator and introducing creation ($a^\dagger$) and annihilation ($a$) operators, we replace the 2nd to 4th terms of Eq. (1) by $g \sigma_z (a^\dagger + a) + \omega a^\dagger a$. This simple model can be solved exactly to yield the following eigen-states...
and eigen-energies
\[ |s, n\rangle = \frac{e^{-a_c^2/2}}{\sqrt{n!}} (\hat{a}^\dagger + s a_c)^n e^{-s a_c \hat{a}^\dagger} |s, 0\rangle, \]
\[ E_{s,n} = n\omega_0 + s t_0 - \frac{g_0^2}{\omega_0}. \] (2)

Here \( a_c \equiv g_0/\omega_0, s = \pm 1 \) (which labels the two electronic states), and \( n \) are non-negative integers. The state \( |s, 0\rangle \) satisfies \( \hat{a}|s, 0\rangle = 0 \) and \( \sigma_z |s, 0\rangle = s |s, 0\rangle \). It is simple to show that regardless of the value for \( n \), we have \( \pm 1, n \) states, \( \pm 2a_c \) implying the presence of two structural conformations with the associated quantum structural fluctuations. For \( t_0 > 0 \), the ground state is \( | -1, 0\rangle \) with \( \langle x \rangle = 2a_c \). After absorbing a photon the molecule makes a transition from \( | -1, 0\rangle \) to \( | +1, n\rangle \). When that happens the structure changes from that corresponding to \( \langle x \rangle = +2a_c \) to that corresponding to \( \langle x \rangle = -2a_c \).

If we model the electric dipole operator as \( \sigma_x \), the optical absorption spectrum is given by
\[ \sigma(\varepsilon) = \sum_{n=0}^{\infty} |\langle +1, n|\sigma_x| -1, 0\rangle|^2 \delta(\varepsilon - E_{+1,n} + E_{-1,0}). \] (3)

Substituting Eq. (2) into Eq. (3) we obtain
\[ \sigma(\varepsilon) = \sum_{n=0}^{\infty} f_n(a_c) \delta(\varepsilon - n\omega_0 - 2t_0), \]
where \( f_n(a_c) = (4a_c^2)^n e^{-4a_c^2/n} \) is the Franck-Condon factor between the initial \( | -1, 0\rangle \) and final \( | +1, n\rangle \) states. The red curve in Fig. 1(b) shows \( \sigma(\varepsilon) \) for a specific choice of parameters. The closely spaced peaks originate from the excited states of the harmonic oscillator. The envelope of the red absorption curve is determined by the Franck-Condon factor \( f_n(a_c) \). As shown in Fig. 1(b) the absorption practically vanishes for \( (\varepsilon - 2t_0)/\omega_0 \lesssim 10 \). This is due to the suppression of the optical transition matrix element by \( f_n(a_c) \). Likewise, the envelope peaks at the energy where the Frank-Condon factor reaches maximum. At this peak frequency the incident photon has the highest quantum efficiency in inducing isomerization. Due to the strong suppression of the optical matrix element, the molecule will cease to spontaneous emit once its energy has descended below certain energy

\[ \sim 10\omega_0 \text{ in Fig. 1(b)}. \] This result suggests the presence of two time scales \( T_{1,2} \). \( T_1 \) is the time it takes for structural relaxation to bring the molecule’s energy outside the absorption peak, and \( T_2 \) is the time for it to bring the molecule to the isomerized ground state. During \( t = 0 \rightarrow T_1 \) the molecule relaxes both structurally and electronically (by spontaneous emission). During \( t = T_1 \rightarrow T_2 \) the molecule can only relax structurally because spontaneous emission is strongly suppressed. Thus once the photo-excited molecule survives through \( T_1 \) it can relax to the isomerized ground state without further interruption from spontaneous emission. This answers the earlier posed question, and at the same time predicts that the quantum efficiency of PI is determined by the probability for the molecule to survive through \( T_1 \). The existence of time regimes with different relaxation dynamics is consistent with the experimental results for azobenzene.[11] Moreover, due to the energy difference \( 2t_0 \), the peak photon frequency for the \( \langle x \rangle = +2a_c \rightarrow (x) = -2a_c \) conversion will be different from the \( \langle x \rangle = -2a_c \rightarrow (x) = +2a_c \) one. This is also consistent with experiments.[11]

Next we consider the effects of the environment. Following Calderia and Leggett[12] we model the environment by a continuum of harmonic oscillators. These oscillators couple to the PI molecule via the Hamiltonian
\[ H_{env} = \sum \alpha g_\alpha (\hat{a}_\alpha^\dagger + a_\alpha) \sigma_\mu + \sum \alpha \omega_\alpha a_\alpha^\dagger a_\alpha. \] (4)

Here \( \alpha \) labels the environment oscillators and \( \mu = x \) or \( y \) or \( z \) depending on the nature of molecule-environment coupling. Clearly when \( \mu = z \) we have \( [H_{mol}, H_{env}] = 0 \), which implies the absence of “entanglement” between the molecule and the environment (see later). On the other hand, for \( \mu = x \) or \( y \) \( H_{mol} \) and \( H_{env} \) do not commute and the environment entangles with the molecule. As we shall show that these two types of environment have fundamentally different effects on PI.

Let us begin with the unentangled environment (i.e. \( \mu = z \)). In this case the eigenstates of the molecule plus the environment are the following direct products (hence no entanglement) \( |s, n\rangle \otimes |s, \{n_\alpha\}\rangle \). Here \( |s, n\rangle \) is given in Eq. (2) and \( |s, \{n_\alpha\}\rangle \) is given by
\[ |s, \{n_\alpha\}\rangle = \prod_\alpha \frac{e^{-a_c^2/2}}{\sqrt{n_\alpha!}} (\hat{a}_\alpha^\dagger + s a_c)^{n_\alpha} e^{-s a_c \hat{a}_\alpha^\dagger} |s, 0\rangle \] (5)
with \( a_c^\alpha \equiv g_\alpha/\omega_\alpha \). In this case the environment has no effect on the structure, i.e., \( \langle x \rangle \), of the molecule. It merely modifies the absorption spectrum to
\[ \sigma(\varepsilon) = \sum_{n=0}^{\infty} f_n(a_c) D(\varepsilon - n\omega_0 - 2t_0), \] (6)

where
\[ D(\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t + 4K(t)}, \]
\[ K(t) = \int_0^{\infty} \frac{d\omega}{2\pi} J(\omega)(e^{i\omega t} - 1), \] and \( J(\omega) = \sum_\alpha g_\alpha^2 \delta(\omega - \omega_\alpha) \). In the
case where the environmental dissipation is Ohmic we have $J(\omega) = A_0 \omega e^{-\omega/\omega_c}$, where $A_0$ reflects the molecule-environment coupling strength, and $\omega_c$ is a cut-off frequency. For, e.g., $A_0 = 3$ and $\omega_c/\omega_0 = 3$ the absorption spectrum is shown as the blue curve in Fig. 1(b). It is blue-shifted relative to the red curve, and the peak intensity is greatly reduced reflecting a considerable reduction of the quantum efficiency of PI. Moreover, the sharp phonon peaks in the red curve is now smoothened.

Next, we consider the more interesting case where the environmental entanglements with the molecule. Such an environment can be simulated by putting $\mu = x$ in Eq. (4), which results in the non-commutivity between $H_{\text{mol}}$ and $H_{\text{env}}$. Physically this type of environment induces transition between the electronic states (or flips the spin). When resent alone, the ground state of $H_{\text{mol}}$ and $H_{\text{env}}$ is the eigenstate of $\sigma_z$ and $\sigma_x$ respectively. When present together the spin is subjected to the conflicting quantum noise exerted by the structure degree of freedom and the environment. If we choose the eigenstate of, say, $\sigma_x$ to describe the spin, the dynamics dictated by $H_{\text{mol}} + H_{\text{env}}$ causes the spin to flip as a function of time. The primary effect of the environment is to induce correlation between spin-flipping events. In the following we use a well-established formulation, which translates above physical picture into precise mathematical languages. Technically we employ the imaginary-time path integral representation of the quantum partition function of the molecule plus the environment. We then “integrate out” the environmental degrees of freedom and obtain the following effective partition function for the molecule

$$Z = \sum_{n=0}^{\infty} \int_0^\beta d\tau_2 n \int_0^{\tau_2 - \tau_0} d\tau_{2n-1} \cdots \int_0^{\tau_2 - \tau_0} d\tau_1 \int D[x(\tau)] \prod_{i=1}^{2n} [t_0 + g' x(\tau_i)] e^{-S[x(\tau), Q(\tau_i)]},$$

(7)

where $2n$ counts the number of $\sigma_x \rightarrow -\sigma_x$ spin flips between $\tau = 0$ and $\tau = \beta$, the imaginary time integral is subjected to the constraint $\tau_1 < \tau_2 < \cdots < \tau_{2n}$, $x(\tau)$ specifies the history of the molecular oscillator, and $\tau_0 = 1/\omega_c$. The quantity $Q(\tau_i)$ is an alternating sequence of $\pm 1$ (+1 for down $\rightarrow$ up flip and -1 for up $\rightarrow$ down flip respectively) at $t_1, \ldots, t_{2n}$. The action $S[x(\tau), Q(\tau_i)]$ in Eq. (7) is given by

$$S = \int_0^\beta d\tau H(\tau) - \sum_{i \neq j} Q(\tau_i) V(\tau_i - \tau_j) Q(\tau_j),$$

(8)

where $V(\tau_i - \tau_j)$ given by Eq. (9) the result of such calculation gives the following recursion relations

$$\frac{dV}{dt} = -2A(t^2 + g^2 e^{-\omega t}), \quad \frac{dV}{dt} = (1 - A/2)t, \quad \frac{dV}{dt} = (1 - A/2)g, \quad \frac{dV}{dt} = \omega,$$

here $l$ is the logarithm of the time separation of the farthest spin flip pair integrated out so far divided by $\tau_0$, and $A$, $t$, $g$, and $\omega$ are all dimensionless quantities.

They are function of $l$ satisfying the initial conditions $A(0) = A_0$, $t(0) = t_0 \tau_0$, $g(0) = g_0 \tau_0$, $\omega(0) = \omega_0 \tau_0$. These recursion relations can be solved numerically to obtain the phase diagram for the zero temperature ($\beta \rightarrow \infty$) state of the PI molecule as a function of the initial $t_0 \tau_0$ and $A_0$ for different $g_0/t_0$ and $\omega_0 \tau_0$. In Fig. 2 we present the phase boundary between the “instanton metal” where the spin flips are uncorrelated (aside from the global constraint of alternating up and down spin flips), and the “instanton insulator” where up and down spin flips are correlated so that they form bound pairs in time, for several different values of $\omega_0 \tau_0$ at a fixed $g_0/t_0$.

To obtain information about the molecular structure in these two phases we compute the correlation function

$$\Gamma_{xx}(\tau_a - \tau_b) = \langle x(\tau_a) x(\tau_b) \rangle.$$

It can be shown that

$$\Gamma_{xx}(\tau_a - \tau_b) = G_0(\tau_a - \tau_b) + g'^2 \int d\tau_1 d\tau_2 G_0(\tau_1 - \tau_a) G_0(\tau_2 - \tau_b) C(\tau_1, \tau_2),$$

(10)

where $G_0(\tau_2 - \tau_1) = e^{-\omega_0 |\tau_2 - \tau_1|}/(2m\omega_0)$ and $C(\tau_1, \tau_2) = e^{-\Delta S(\tau_1, \tau_2)}$ with $\Delta S$ the action change due to the insertion of two instantons at $\tau_1$ and $\tau_2$. In the two different instanton (IST) phases

$$\Delta S(\tau_1, \tau_2) = \begin{cases} c_1 + c_2 \ln \frac{|\tau_2 - \tau_1|}{\tau_0} + e^{-\frac{|\tau_2 - \tau_1|}{\tau_0}} & \text{IST metal} \\ c_3 \ln \frac{|\tau_2 - \tau_1|}{\tau_0} & \text{IST insulator} \end{cases},$$

where $\tau_a$ is an instanton “screening length”, and $c_1, c_2, c_3$ are positive constants, implying

$$C(\tau_1, \tau_2) \left(\frac{\tau_2 - \tau_1}{\tau_0}\right)^{+\infty} \begin{cases} e^{-c_1} & \text{IST metal} \\ 0 & \text{IST insulator} \end{cases}.$$
Substituting the above asymptotic behavior of $C(\tau_1, \tau_2)$ into Eq. (10) and noting the exponential decaying nature of $G_0(\tau_1 - \tau_2)$, we conclude that the molecule has a long/short range to instanton insulator (lower right) phases for $\omega_0\tau_0 = 0.3, 0.6$, and $\omega_0\tau_0 \to \infty$, respectively.

This suggests that in the instanton metal phase the molecule essentially behaves as if it is in isolation (i.e., the electronic eigenstates are eigenstates of $\sigma_z$ and the structure degrees of freedom shows non-zero $\langle x \rangle$). In contrast, in the instanton insulator phase the coupling between the electronic state and the environment dominates. As a result, the electronic eigenstates are essentially the eigenstates of $\sigma_x$ and the two distinct molecular structures are averaged out. In the former case the molecule retains its PI functionality, while in the latter case the functionality is lost. This phase transition can be realized by, e.g., tuning the strength of the molecule-environment coupling ($A_0$ in Fig. 2).

The transition between these two cases will be manifested as a quantum phase transition at absolute zero temperature. This phase transition can be detected via optical absorption spectrum. To compute such spectrum we note that in the two different instanton phases the spin-spin correlation function behaves

$$
\Gamma_{ss}(\tau) \mid_{\tau \to \infty} \begin{cases} 
a_1(\tau) e^{-\tau/\tau_s} & \text{IST metal} \\
a_2 + a_3(\tau) e^{-\tau/\tau_s} & \text{IST insulator} \end{cases}
$$

Since $\Gamma_{ss}(\tau)$ is the Laplace transform of the optical absorption spectrum, i.e., $\Gamma_{ss}(\tau) \equiv \int_0^\infty \sigma(\omega)e^{-\tau\omega}d\omega$, Eq. (11) implies

$$\sigma(\omega) = a_2\delta(\omega) + a_3\theta(\omega - \Delta)(\omega - \Delta)^{\alpha - 1},$$

where $\Delta = 1/\tau_s$, the zero-frequency delta-function weight $a_2$ is nonzero only in the instanton insulator phase, and $a_4$ is a constant proportional to $a_1$ or $a_3$ depending on whether the system is in the instanton metal or insulator phase. At the quantum critical point $\tau_s$ diverges and the optical absorption gap closes. As the molecule loses the PI functionality a zero frequency peak should appear in the optical absorption spectrum. These features can in principle be detected optically. At non-zero temperatures, the quantum phase transition will be smeared out. In the $A_0 - T$ plane (assuming we reach the phase transition by tuning $A_0$) there will be a region in which $k_BT > 1/\tau_s(T)$ where the molecule exhibit quantum critical characteristics.

So far we have discussed the simplest model for PI. In reality there could be more than one structural modes that couple to the electronic optical transition. We have investigated a two-oscillator model and reach the conclusion that so long as the two structure oscillator are non-degenerate, the results discussed above remain qualitatively unchanged.

In conclusion we have presented a theory of photoisomerization in an environment. It points to the crucial role the environment plays in this fascinating molecular quantum mechanics.

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