REduced Equations of Motion for Collision-Induced Intersystem Crossing

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A model is proposed for collision-induced intersystem crossing in "intermediate case" and small molecules. The collisions are assumed to cause dephasing ($T_2$) among the zero order singlet and triplet molecular states. The combined effect of the intramolecular spin—orbit coupling ($\mu$) and the collisional dephasing, results in the experimentally observable relaxation of populations ($T_1$). The basic assumption of the present model is that the duration of a collision $\tau_0$ is short compared to the intramolecular coupling ($\mu \tau_0 < 1$). Reduced equations of motion for the molecular density matrix are derived and conditions for observing nonexponential relaxations are discussed. The model demonstrates the equivalence of $T_1$ and $T_2$ processes, depending on our choice of a basis set.

1. Introduction

Collisional induced electronic to vibrational intramolecular relaxation plays an important role in the dynamics of small and "intermediate case" molecules, whereby the density of molecular states is insufficient to induce an irreversible relaxation in the isolated molecule [1]. Collisions of electronically excited intermediate molecules with inert molecules (e.g., inert gas atoms) result in collisionally induced intersystem crossing (CISC) which causes the quenching of the fluorescence and enhancement of phosphorescence. Some of the molecules which have been studied in the low pressure gas phase and which exhibit CISC are methylene [2], glyoxal [3], biacetyl [4], pyrazine [5], CO [6,7], formaldehyde [8], and benzophenone [9].

Gelbart and Freed [10,11] have developed a model for CISC, assuming that the collision does not directly couple the zero order (singlet and triplet) molecular states but rather causes rotational relaxation within the triplet and singlet manifolds. The combined effects of the rotational relaxation and the intramolecular spin—orbit coupling result in a CISC rate of $\Gamma_{\text{rot}} \beta^2$ where $\Gamma_{\text{rot}}$ is a cross section for rotational relaxation and $\beta$ is the intramolecular mixing parameter between the singlet and triplet states. This model is capable of predicting magnitudes of quenching rates and their variation with the perturbers. The proportionality of the rate to $\beta^2$ results from a perturbative solution of the equation of motion and has been proven recently to fail for large mixing, where the intersystem crossing rate saturates with $\beta$ [12]. To account for that, Grimbert et al. [12] and Freed and Tric [13] have solved semiclassically the collisional problem in the presence of the intramolecular coupling and were able to account for the observed saturation.

In this paper we derive the reduced equations of motion (REM) for the molecular density matrix in the presence of collisions. The basic assumption is that the duration of a collision ($\tau_0$) is short compared to the inverse intramolecular spin—orbit coupling $\hbar/\mu$. Using this assumption, we need not solve for the collision in the presence of $\mu$. The collisions cause a dephasing (i.e., they destroy the phase coherence between the singlet and triplet zero order states, produced by the intramolecular coupling). The combined effect of the intramolecular spin—orbit coupling and the dephasing result in a CISC. Formally, the present model is analogous to the Lorentz model of pressure broadening of spectral lines [14] where the interaction with an external electromagnetic field takes the place of the intramolecular coupling. The present model and the resulting reduced equations of motion enable us to discuss
under what conditions will the molecular time evolution exhibit nonexponential behavior [15]. The reduced equations may be solved nonperturbatively without going into the fine details of the collision, and the experimentally observed saturation arises naturally from our analysis. In addition, the model demonstrates the equivalence of dephasing processes \( T_2 \) and relaxations of population \( T_1 \), depending on our choice of a basis set [16].

2. The model

Consider a two-level molecular system consisting of a singlet \( |S\rangle \) and a triplet state \( |T\rangle \). The molecular hamiltonian is

\[
H_M = \frac{1}{2}\Delta (|S\rangle\langle S| - |T\rangle\langle T|) + \mu(|S\rangle\langle T| + |T\rangle\langle S|). 
\]

(1)

Here \( \Delta \) is the energy splitting between the two states and \( \mu \) is the spin–orbit coupling.

Our molecular system is assumed to suffer collisions with inert molecules. The collisional coupling \( V \) is taken to be diagonal within the \( |S\rangle, |T\rangle \) representation (i.e., collisions do not directly couple \( |S\rangle \) and \( |T\rangle \)). We thus write

\[
V = |S\rangle V_{SS}(R) |S\rangle + |T\rangle V_{TT}(R) |T\rangle,
\]

(2)

where \( R \) is the internuclear separation between our molecule and the perturber. The selection rule (2) (i.e., that the collisions do not couple \( |S\rangle \) and \( |T\rangle \) directly) has been suggested by Freed and Gelbart [10,11].

If the duration of a collision \( (\tau_c) \) is short enough compared to the intramolecular coupling \( \mu^{-1} \), i.e.,

\[
\mu \tau_c \ll 1,
\]

(3)

we may ignore the effects of \( \mu \) during a single collision. In this case the collisions can only destroy the phase coherence between the \( |S\rangle \) and \( |T\rangle \) states and cannot induce transitions of population between \( |S\rangle \) and \( |T\rangle \). Thus the effect of collisions is properly incorporated by adding a dephasing \( T_2 \) relaxation term into the equations of motion for the molecular density matrix [14,17]. Note that the condition \( \mu \tau_c \ll 1 \) is different from the condition for weak mixing \( (\mu/\Delta \ll 1) \) which results in a perturbative expression for the relaxation rate [10,11].

We shall now write the equations of motion for the molecular density matrix

\[
d\rho/dt = -i[H_M, \rho] + \text{collisional relaxation}
\]

(4)
as follows:

\[
\frac{d\rho_{SS}}{dt} = -i\mu(\sigma_{TS} - \sigma_{ST}), \quad \frac{d\rho_{TT}}{dt} = i\mu(\sigma_{TS} - \sigma_{ST}),
\]

\[
\frac{d\rho_{ST}}{dt} = -i\Delta \sigma_{ST} - i\mu(\sigma_{TT} - \sigma_{SS}) - \Gamma \sigma_{ST}, \quad \frac{d\sigma_{TS}}{dt} = i\Delta \sigma_{TS} + i\mu(\sigma_{TT} - \sigma_{SS}) - \Gamma \sigma_{TS},
\]

(5)

where \( \Gamma \) is the collisional dephasing term. \( \Gamma \) may be evaluated from the coupling (2) using semiclassical theory [18] or the more complete Anderson formulation [19]. For the purpose of the present work, however, it is sufficient to note that using assumption (3), \( \Gamma \) is independent of \( \mu \) and is proportional to the pressure.

Let us consider now the true molecular states \( |\tilde{S}\rangle \) and \( |\tilde{T}\rangle \) which are the eigenstates of \( H_M \). \( |\tilde{S}\rangle \) and \( |\tilde{T}\rangle \) reduce to \( |S\rangle \) and \( |T\rangle \), respectively, as \( \mu \to 0 \). From eq. (1) we immediately have:

\[
\begin{pmatrix}
|\tilde{S}\rangle \\
|\tilde{T}\rangle
\end{pmatrix} = \begin{pmatrix}
\cos \phi & \sin \phi \\
-\sin \phi & \cos \phi
\end{pmatrix} \begin{pmatrix}
|S\rangle \\
|T\rangle
\end{pmatrix},
\]

(6)

where

\[
\sin \phi = 2\mu(\Delta^2 + 8\mu^2)^{1/2}, \quad \cos \phi = [(\Delta^2 + 4\mu^2)/(\Delta^2 + 8\mu^2)]^{1/2}.
\]

(7a)

The corresponding eigenvalues are:
\[ E\left(\hat{S}\right) = \frac{1}{2} (\Delta^2 + 4\mu^2)^{1/2} \equiv \frac{1}{2} \Delta^2, \quad E\left(\hat{T}\right) = -\Delta^2 + 4\mu^2)^{1/2} \equiv -\frac{1}{2} \Delta^2. \] (7b)

We shall assume an ideal experimental set-up in which the frequency resolution satisfies \( \Delta \nu_{\text{exp}} \ll (\Delta^2 + 4\mu^2)^{1/2} \) and the excitation is made with a light pulse of a very short duration so that at time \( t = 0 \) we prepare the state \( |\hat{S}\rangle \). We further assume that we are detecting only \( |\hat{S}\rangle \) (the lifetimes of \( |\hat{S}\rangle \) and \( |\hat{T}\rangle \) are sufficiently separated). It will be thus more convenient to transform eq. (5) to the \( |\hat{S}\rangle \), \( |\hat{T}\rangle \) representation. Furthermore, in this basis set \( H_M \) is diagonal. \( \Gamma \) however becomes more complicated. In order to transform \( \Gamma \), let us adopt the double bracket notation [20] and note that the relaxation part of eq. (5) has the form: \( \Gamma\left(|ST\rangle\langle ST| + |TS\rangle\langle TS|\right) \). Here \( |ij\rangle \) is the tetradic vector corresponding to \( |i\rangle\langle j| \). Making use of the transformation (6), we have

\[ |ST\rangle\langle ST| = (\cos \phi |\hat{S}\rangle - \sin \phi |\hat{T}\rangle)(\sin \phi |\hat{S}\rangle + \cos \phi |\hat{T}\rangle). \] (8)

Rewriting eq. (8) in the double bracket notation, we get

\[ |ST\rangle\langle ST| = \cos \phi \sin \phi (|\hat{S}\hat{S}\rangle - |\hat{T}\hat{T}\rangle) + \cos^2 \phi |\hat{S}\hat{T}\rangle - \sin^2 \phi |\hat{T}\hat{S}\rangle. \] (9)

Thus, in the molecular basis set we have:

\[ |ST\rangle\langle ST| = \begin{pmatrix}
\cos \phi \sin \phi \\
-\cos \phi \sin \phi \\
\cos^2 \phi \\
\sin^2 \phi
\end{pmatrix}
\begin{pmatrix}
\cos \phi \sin \phi, -\cos \phi \sin \phi, \cos^2 \phi, \sin^2 \phi
\end{pmatrix}
\]

\[ = \begin{pmatrix}
\cos^2 \phi \sin^2 \phi & -\cos^2 \phi \sin^2 \phi & \cos^3 \phi \sin \phi & -\sin^3 \phi \cos \phi \\
-\cos^2 \phi \sin^2 \phi & \cos^2 \phi \sin^2 \phi & \cos^3 \phi \sin \phi & \sin^3 \phi \cos \phi \\
\cos^3 \phi \sin \phi & -\cos^3 \phi \sin \phi & \cos^4 \phi & -\sin^2 \phi \cos^2 \phi \\
-\sin^3 \phi \cos \phi & \sin^3 \phi \cos \phi & -\sin^2 \phi \cos^2 \phi & \sin^4 \phi
\end{pmatrix}. \] (10)

Similar matrix is obtained for \( |TS\rangle\langle TS| \) by the substitution \( \sin \phi \rightarrow -\cos \phi, \cos \phi \rightarrow \sin \phi \).

Combining eqs. (5) and (10), we get, after some algebraic manipulations

\[ \frac{d}{dt}\begin{pmatrix}
\sigma_{\hat{S}\hat{S}} \\
\sigma_{\hat{S}\hat{T}} \\
\sigma_{\hat{T}\hat{S}} \\
\sigma_{\hat{T}\hat{T}}
\end{pmatrix} = -\Gamma\begin{pmatrix}
\eta & -\eta & \xi & \xi \\
-\eta & \eta & -\xi & -\xi \\
\xi & -\xi & 1 - \eta - \frac{1}{2} i \Delta / \Gamma & -\eta \\
\xi & -\xi & -\eta & 1 - \eta + \frac{1}{2} i \Delta / \Gamma
\end{pmatrix}\begin{pmatrix}
\sigma_{\hat{S}\hat{S}} \\
\sigma_{\hat{S}\hat{T}} \\
\sigma_{\hat{T}\hat{S}} \\
\sigma_{\hat{T}\hat{T}}
\end{pmatrix}. \] (11)

where

\[ \eta = \frac{1}{2} \sin^2 2\phi, \quad \xi = \frac{1}{2} \sin 2\phi \cos 2\phi. \] (11a)

Eq. (11) may be written in the matrix form

\[ \frac{d \sigma}{dt} = A \cdot \sigma. \] (12)

3. Discussion

Eq. (11) is our most general result. In general, the time evolution of \( |\hat{S}\rangle \) is not a simple exponential but rather given by
\[ \langle \vec{S}(0) | \vec{S}(t) \rangle = \sum_{j=1}^{4} \langle \vec{j} | A | \vec{j} \rangle \exp(\lambda_j t) , \]  
(13)

where |j\rangle and |\vec{j}\rangle are the four right and left eigenvectors of the A matrix; i.e., A |j\rangle = \lambda_j |j\rangle and \langle \vec{j} | A = \lambda_j |\vec{j}\rangle. \lambda_j are, in general, complex. The observed fluorescence,

\[ I_F(t) \propto |\langle \vec{S}(0) | \vec{S}(t) \rangle|^2 \]  
(14)

is thus, in general, nonexponential and may exhibit also an oscillatory temporal behavior (quantum beats) [15].

For weak mixing (\phi \to 0) we have \eta \approx 2\phi^2 and \xi \approx \phi. We thus see that the largest damping term in eq. (11) is the pure dephasing \Gamma(1 - \eta) = \Gamma(1 - \phi), whereas all other damping terms are \mathcal{O}(\Gamma\phi^2) or \mathcal{O}(\Gamma\phi). It is thus reasonable that on a time scale (\Gamma\phi)^{-1} \gtrsim t > \Gamma^{-1} we may assume \sigma_{\vec{F}\vec{F}}, \sigma_{\vec{F}\vec{S}} to be in steady state, i.e., \frac{d\sigma_{\vec{F}\vec{F}}}{dt} = \frac{d\sigma_{\vec{F}\vec{S}}}{dt} = 0. With this assumption, we may solve for \sigma_{\vec{F}\vec{F}}, \sigma_{\vec{F}\vec{S}} and substitute back into eq. (11) so that we get a closed equation for the populations (\sigma_{\vec{S}\vec{S}}, \sigma_{\vec{F}\vec{F}}) only. Solving for \sigma_{\vec{F}\vec{F}} results in

\[ \sigma_{\vec{F}\vec{F}} = \frac{\xi(\sigma_{\vec{F}\vec{F}} - \sigma_{\vec{S}\vec{S}})}{\Gamma(1 - 2\eta) + \Delta^2/4\Gamma}, \quad \sigma_{\vec{F}\vec{S}} = \sigma_{\vec{S}\vec{F}}. \]  
(15)

Substituting (15) in the first two equations (11) results in

\[ \frac{d(\sigma_{\vec{S}\vec{S}} - \sigma_{\vec{F}\vec{F}})}{dt} = -\frac{\Gamma\Delta^2 \sin^2 2\phi}{\Delta^2 + 4\Gamma^2 \cos^2 2\phi} (\sigma_{\vec{S}\vec{S}} - \sigma_{\vec{F}\vec{F}}). \]  
(16)

The quenching rate of the fluorescence is thus

\[ \gamma = \Gamma\Delta^2 \sin^2 2\phi / (\Delta^2 + 4\Gamma^2 \cos^2 2\phi). \]  
(17)

Introducing the mixing parameter \beta = \sin \phi, we have

\[ \gamma = 4\Gamma\Delta^2 \beta^2 (1 - \beta^2) / (\Delta^2 + 4\Gamma^2 (1 - 2\beta^2)) \]  
(18)

and for \Delta \gg \Gamma we get

\[ \gamma = 4\Gamma\beta^2 (1 - \beta^2). \]  
(19)

We note that for strong mixing (large \beta), the separation of the time scales of coherences and populations (and hence the steady-state assumption) no longer hold, and the time evolution (13) may become nonexponential. However, other factors (interference between many states, finite temporal resolution) may still result in an apparent exponential behavior.

In conclusion, we note the following:

1. The present model demonstrates the interrelation between dephasing (T_2) and relaxation of population (T_1) processes, depending on the choice of a basis set. Previous works [10–13] have used the molecular basis set (|\vec{S}\rangle, |\vec{T}\rangle) and calculated the T_1 induced directly by the collisions. In the present work, we assumed that the collisions cause pure dephasing (T_2) within the zero order basis set (|\vec{S}\rangle, |\vec{T}\rangle). The two approaches are not identical since, strictly speaking, in both basis sets collisions cause T_1 and T_2 so that different terms are neglected in the two approaches. We note, however, that for weak mixing we recover the results of Freed (\gamma = 4\Gamma\beta^2).

2. Since the present solution is not perturbative in \beta, we get the saturation of \gamma with \beta^2 [eq. (19)] in a straightforward way without having to solve for the detailed dynamics of the collision. This saturation is in accord with recent experimental observations [12].

3. If each |\vec{S}\rangle and |\vec{T}\rangle levels is a set of unresolved rotational states exhibiting similar couplings and rauative lifetimes, then the rotational relaxation within |\vec{S}\rangle or |\vec{T}\rangle will be easily incorporated in the present formulation by an additional contribution to the dephasing rate \Gamma [21]. In general, \Gamma arises due to our reduced description of the molecular dynamics [16]. The reduction can be over the unresolved rotational or over the translational degrees of freedom (where the effects of modifying E_{\vec{S}} and E_{\vec{T}} during the collision due to the diagonal coupling (2) contribute to \Gamma).
(4) For the sake of simplicity we did not include explicitly the radiative lifetimes in our REM (11). We thus assume that they are sufficiently long compared to the other processes so that the spontaneous emission serves as a probe for the molecular dynamics. Addition of \( T_1 \) terms into our REM is, however, straightforward and will not change our basic conclusions.

(5) The present REM enable us to examine the detailed time evolution of the system (which will be, in general, nonexponential) and see clearly the conditions under which it becomes purely exponential corresponding to completely incoherent time evolution.

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References