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Microwave Induced Time Dependent Effects in

Triplet Phosphorescence

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Abstract

The changes in the polarization and intensity of phosphorescent

emission from triplet states induced by a resonant time dependent

microwave field coupling magnetic sublevels is described in the

absence of spin lattice relaxation. Specifically, the microwave

field can be used to amplitude modulate the polarization and intensity

of phosphorescence from organic molecules or to rotate the polarization

vector of phosphorescence. In addition, "optical phase precession,"

a phenomena closely resembling quantum beats, is predicted. Finally

the use of adiabatic inversion of the magnetic sublevel populations

to directly measure intersystem crossing is demonstrated.

Introduction

The optical detection of a radio frequency resonance in atoms and molecules is an area of considerable importance. From the first experiments of Fermi and Rasetti,[1] and Breit and Ellett[2] who observed changes in the polarization of mercury vapor fluorescence under the influence of an applied alternating magnetic field to the first successful optical pumping experiments by Brossel and Bitter,[3] and Kastler,[4] the method continued to provide experimental results on a wide variety of problems. With the development of microwave and radio frequency spectroscopy, methods for determining electronic structure parameters such as the g-factor, nuclear-electron hyperfine, nuclear quadrupole interaction, etc., of molecules in the ground state became common place. Hutchinson,[5] in a fundamental experiment, successfully detected the electron spin resonance (ESR) in an excited triplet state of an organic molecule; thus, provided chemists with a method for determing excited state properties of an important class of compounds. Later, Geschwind[6] in a series of experiments _optically_ detected the ESR of excited state species in the solid state.

Recently, the optical detection of magnetic resonance (ODMR) and its accompanying ENDOR in zeeman fields and in zero field of organic molecules in excited triplet states has been successfully observed by Sharnoff,[7] Kwiram,[8] van der Waals, _et al._,[9] and Harris, _et al._[10] It is generally recognized as a powerful method for obtaining zero-field splittings, nuclear-electron hyperfine, and nuclear quadrupole interactions of phosphorescent triplet states.

ODMR may appear, at first sight, to be more sensitive than conventional ESR since the detection of photons requires only $\sim 10^8$ molecules while the detection of magnetization requires $\sim 10^{13}$ molecules. However, in principle, this need not be the case. It will be shown that certain intrinsic properties of phosphorescence may severely restrict the sensitivity of ODMR, even to the extent that the effect vanishes. Specifically, the differences in ODMR and EPR arise because different components of the excited triplet state are being detected in each method. EPR measures the magnetization of the electrons magnetic dipole moment precessing at the Larmor frequency while ODMR measures changes in the polarization and/or intensity of phosphorescence induced by the time dependent radio frequency magnetic field. Since changes in phosphorescence are being detected in the ODMR, proper consideration of the phenomenon must address itself to the electric dipole transition moment between the excited triplet state and the ground singlet state or a vibration in the ground state singlet manifold.

Two questions immediately arise. (1) To what extent is the polarization and/or intensity of phosphorescence modulated when the magnetic sublevels of the triplet state are subject to a time dependent oscillating magnetic field? (2) Is the polarization and/or intensity of phosphorescence modulated at the Larmor frequency? The following discussion will be restricted to ODMR in zero field. It is the purpose of the paper to show in a simple way what explicit features of the phosphorescence are changed by a time dependent r-f field and under what conditions interference effects are manifested in the phosphorescence.

Discussion

In general, the effects of first and second order mixing of the
singlet and triplet states of a molecule via spin-orbit and vibronic-
spin-orbit coupling are specific for the individual magnetic sublevels
of the triplet states. Thus, each of three magnetic sublevels can be
represented by a wavefunction, ϕ_i , composed of linear combinations of
a triplet, T, and singlet states, S^J. By defining the polarization, J,
of a singlet state as the polarization of the transition moment
between an excited singlet state and the ground state singlet, S_0,
or a vibration of the singlet manifold, (i.e., $< S^J \mid \mu_e \cdot R(J) \mid S_0 > \neq 0$;
$\mu_e \cdot R(J)$ is the electric dipole operator), the magnetic sublevels
of the triplet can be represented simply as:

$$\phi_i = T_i + \sum_{J=x,\ y,\ z} c_i^J\ S^J \qquad (i = x,\ y,\ z) \quad (1)$$

where c_i^J is the mixing coefficient of singlet states of J polarization
in the ith magnetic sublevel. The coefficients are in general the sum
of the coefficients of different singlet states of the same polarization.

Because of spin-orbit and electron dipole-dipole interactions,
the ϕ_i's will have different energies, E_i, in zero field. It is
assumed that the molecules are "isolated" and translationally equivalent.
Naturally translational nonequivalence and solid state effects will
mix the ϕ_i's. With these preliminaries the energies and wavefunctions
in the lowest excited triplet state and the population, N_i, under
steady state conditions in the individual magnetic sublevels are,

$$E_x \; : \; \phi_x = T_x + C_x^x \, S^x + C_x^y \, S^y + C_x^z \, S^z \; : \; N_x \qquad (2)$$

$$E_y \; : \; \phi_y = T_y + C_y^x \, S^x + C_y^y \, S^y + C_y^z \, S^z \; : \; N_y \qquad (3)$$

$$E_z \; : \; \phi_z = T_z + C_z^x \, S^x + C_z^y \, S^y + C_z^z \, S^z \; : \; N_z \qquad (4)$$

It should be noted that the processes of intersystem crossing, internal conversion and particularly phosphorescence depend upon the C_i^J's. Thus, they determine, in the absence of spin-lattice relaxation,[11] the alignment of the lowest triplet state, (i.e., the number of molecules, N_i, in each of the magnetic sublevels). Although the phosphorescent polarization and radiative lifetime of the individual magnetic sublevels are determined by the C_i^J's, the intensity of phosphorescence depends additionally upon proper consideration of spin-lattice relaxation and radiationless processes. It will be assumed that the phosphorescence lifetimes from the individual sublevels, τ_p^i, where $1/\tau_p^i \sim \sum_J (C_J^i)^2$, are much shorter than the spin-lattice relaxation time, T_1, and that radiationless transitions are absent. The condition $\tau_p^i < T_1$ can, in most molecular crystals, be satisfied by low temperatures, i.e. < 4.2 K.

Considering only two levels, say ϕ_x and ϕ_y, the time _independent_ phosphorescence with J polarization and intensity I(J), is simply related to the electric dipole transition matrix element between the states ϕ_x and ϕ_y and the ground state singlet, S_0.

$$I(J) \sim N_x \, | < \phi_x \, | \, \mu_e \cdot R(J) \, | \, S_0 > |^2 + N_y \, | < \phi_y \, | \, \mu_e \cdot R(J) \, | \, S_0 > |^2 \qquad (5)$$

The total phosphorescence intensity from ϕ_x and ϕ_y is simply Π, where

$$\Pi = \sum_{J=x, y, z} I(J) \qquad (6)$$

J in all cases represents the polarization of the transition moments.

The effect of a time-dependent oscillating magnetic field, $\mathcal{H}(t) = 2\gamma \hbar H_1 \hat{S}_z \cos \omega_0 t$, where $\hat{S}_z$ is the electron dipole transition moment operator. at a frequency $\hbar \omega_0 = E_x - E_y$ can be easily solved in the absence of spin-lattice relaxation. The result is to produce time <u>dependent</u> functions $\phi_x(t)$ and $\phi_y(t)$;

$$\phi_x(t) = \phi_x \cos \gamma H_1 t \, e^{i/\hbar \, E_x t} + i \, \phi_y \sin \gamma H_1 t \, e^{i/\hbar \, E_y t} \qquad (7)$$

$$\phi_y(t) = \phi_y \cos \gamma H_1 t \, e^{i/\hbar \, E_y t} + i \, \phi_x \sin \gamma H_1 t \, e^{i/\hbar \, E_x t} \qquad (8)$$

where γH_1 is a power factor (γ is magnetogyric ratio of an electron, H_1 is the magnitude of the rotating rf field) and t is time.

Generally speaking EPR treats the magnetic component,[12] T_i, of only one time dependent function, say $\phi_x(t)$, and measures the magnetization along the x-axis in the laboratory frame. ODMR, on the other hand, must consider the singlet character of $\phi_i(t)$. When emission from ϕ_x and ϕ_y cannot be optically resolved, both components $\phi_x(t)$ and $\phi_y(t)$, must be considered together. The time <u>dependent</u> phosphorescent intensity of J polarization is simply

$$I(J, t) \sim N_x \, | < \phi_x(t) \, | \, \mu_e \cdot R(J) \, | \, S_0 > |^2 + N_y \, | < \phi_y(t) \, | \, \mu_e \cdot R(J) \, | \, S_0 > |^2 \qquad (9)$$

and the total time dependent phosphorescence intensity $\Pi(t)$ is simply:

$$\Pi(t) = \sum_{J=x,\ y,\ z} I(J,t) \tag{10}$$

Thus, the effect of a time dependent oscillating magnetic field is to produce a change in the phosphorescence polarization, $\Delta I(J, t)$, and total intensity, $\Delta \Pi(t)$, given by

$$\Delta I(J,t) = I(J,t) - I(J) \tag{11b}$$

$$\Delta \Pi(t) = \Pi(t) - \Pi \tag{11b}$$

The phosphorescent intensity must be thought of in terms of its polarized components to properly consider the "phase" factor introduced by $\hbar\omega_0 = E_x - E_y$. In terms of the singlet mixing coefficients, c_i^J, and populations, N_i, equation (11a) can be written as:

$$\Delta I(J,t) = \left\{ N_x (c_x^J)^2 + N_y (c_y^J)^2 \right\} (\cos^2 \gamma H_1 t - 1) +$$
$$\left\{ N_x (c_y^J)^2 + N_y (c_x^J)^2 \right\} \sin^2 \gamma H_1 t) + \tag{12}$$
$$\left\{ N_x - N_y \right\} c_x^J c_y^J \sin 2\gamma H_1 t \sin \omega_0 t$$

It has been assumed that the spin-spin relaxation time, T_2, between the electron spin states ϕ_x and ϕ_y is long compared to the power factor $\gamma H_1 t$ (i.e., high microwave power and short times). One can, under pulsed H_1 fields, properly consider T_2 relaxation phenomenon[13] and incorporate them into equation (12).

Results

Many features of the effect of the $\mathcal{H}(t)$ field upon the phosphorescence can be seen from this simplified[14] approach to $\Delta I(J, t)$.

(1) No change can occur in the phosphorescent emission if $N_x = N_y$ (i.e., fast T_1 processes or no selective intersystem crossing). Naturally, N_x and N_y can, at worst, be Boltzmann in ordinary circumstances.

At this point it is instructive to consider qualitatively the effects of spin-lattice relaxation in ODMR. If the spin lattice relaxation time, T_1, between sublevels becomes competitive with the phosphorescent lifetime, τ_p^i, and radiationless transition from the triplet are small, one expects the change in population dN_x/dt and dN_y/dt in ϕ_x and ϕ_y from depletion processes to be

$$- \frac{dN_x}{dt} \approx \left(\frac{1}{T_1} + \frac{1}{\tau_p^x} \right) N_x \tag{13}$$

$$- \frac{dN_y}{dt} \approx \left(\frac{1}{T_1} + \frac{1}{\tau_p^y} \right) N_y \tag{14}$$

From equation (13) and (14) when $T_1 > \tau_p^i$ spin alignment is maintained and the time averaged (i.e., $< \cos^2 \gamma H_1 t > = < \sin^2 \gamma H_1 t > = 1/2$, $< \sin \omega_0 t > = 0$) change in intensity $< \Delta \Pi >$ is large,

$$< \Delta \Pi > = \left(\frac{N_y - N_x}{2} \right) \left(\frac{1}{\tau_p^x} - \frac{1}{\tau_p^y} \right) \tag{15}$$

On the other hand, when the populations become controlled

by T_1 via $T_1 < \tau_p^i$, a Boltzmann distribution between ϕ_x and ϕ_y

is rapidly established. In this limit, if the sublevels are

saturated by the application of the microwave field, $< \Delta \Pi >$ is only:

$$< \Delta \Pi > = \frac{N_y}{2} (1 - e^{-\Delta E/kT}) \left(\frac{1}{\tau_p^x} - \frac{1}{\tau_p^y} \right) \tag{16}$$

It is clear that very low temperatures are needed to achieve any

appreciable change in the phosphorescence.

It might appear from equation (16) that a small population

difference determined by Boltzmann conditions would always prevail

when $T_1 < \tau_p^i$ and therefore, provided τ_p^x were different from τ_p^y

either in polarization or magnitude, the ODMR effect would always

be observable although comparatively weak. Indeed this is true provided

the T_1 process is associated with a thermalization of ϕ_x and ϕ_y

by phonon interactions such as Raman,[15] Orbach[16] processes or

even spontaneous emission[17] between ϕ_x and ϕ_y. However, if a fast

effective T_1 occurs via a nonthermalization process such as exiton

hopping in molecular exiton bands one can conceive of an equal population

distribution. Consider the case of phosphorescence from an triplet

exiton band where the phonon contributions to T_1 were long compared

to τ_p^i . If the exiton exchange were associated with the translationally

equivalent molecules in the crystal, spin alignment would be maintained

in the exiton band since the exchange interaction, $(1/r_{ij})$, is totally

symmetric. If however, exiton exchange were associated with the

translationally nonequivalent molecules in the crystal, the spin state

of molecule i would be redistributed to other spin states of molecule j

depending upon the relative orientation of i and j when triplet

exiton exchange occurs between the two molecules. Consequently, on the

time scale of an rf or microwave frequency the population N_x and N_y could appear equal even with exchange interaction as small as $\sim 1 \text{ cm}^{-1}$. Under these conditions neither ODMR nor ESR would be detectable and it would be necessary to raise the temperature ($> 2 - 4.2$ K) to ensure that the Orbach[15] or Raman[16] relaxation processes were faster than the τ_p^i's.

Finally, it is interesting to note that even in doped molecular crystals or in trapping sites of "pure" molecular crystals N_x may approach N_y if energy is transferred from the host to the guest via host exiton bands.[18] Naturally, exactly equal populations requires rather specific orientations between molecules in the exiton band. In this case the alignment ratio N_x/N_y would be concentration dependent. Specifically N_x/N_y would approach unity as the guest concentration is decreased. Whether ESR or ODMR would be more sensitive in detecting exiton interactions would then depend upon the τ_p^i's. Differences in the magnitude and polarization between the τ_p^i's and short phosphorescent lifetimes would favor ODMR while equal τ_p^i's and long lifetimes would favor ESR.

(2) No change in the total phosphorescence, $\Delta \Pi(t)$, is predicted if $\sum_J (c_x^J)^2 = \sum_J (c_y^J)^2$. Another way of expressing this is to say: when the rate constants for phosphorescence from ϕ_x and ϕ_y are equal, no change in the total phosphorescent intensity is expected under $\mathcal{H}(t)$. The vanishing time averaged intensity, $< \Delta \Pi >$ is given in equation (15).

Although there may be no change in the total emission, it is still possible to see changes in the polarized components if the polarization of ϕ_x is different from ϕ_y. Indeed, in many cases, greater sensitivity in ODMR can be expected if changes in the polarized components of the phosphorescences are detected from an oriented singlet crystal.

(3) In the limit of high spin alignment (i.e., $N_y > N_x$, three interesting phenomenon are predicted. (a) In the approximation that c_x^J equals zero for all polarizations (i.e., no phosphorescence from the ϕ_x sublevel), the phosphorescence from ϕ_y would be amplitude modulated as $\cos^2 \gamma H_1 t$.[19] If in addition the light were J polarized from ϕ_y, then plane polarized phosphorescence would be amplitude modulated by $\cos^2 \gamma H_1 t$. It should be noted that the power factor γH_1 is an experimentally adjustable field; thus, the frequency of modulation could be varied. (b) If $c_x^J = c_y^{J'}$ ($J' \neq J$) and $c_x^{J''} = c_y^{J''} = 0$ ($J' \neq J$, J')(i.e., phosphorescence from ϕ_x and ϕ_y has J and J' polarization respectively and the τ_p's from ϕ_x and ϕ_y are equal), then the plane of polarization in phosphorescence is rotated at a frequency γH_1. (c) Intermediate cases between (a) and (b) result in ellipitical components of light rotating at γH_1.

(4) No modulation effect at the Larmor frequency, ω_0, is predicted unless singlet states of the same polarization are mixed into both magnetic sublevels ϕ_x and ϕ_y. If singlet states of the same polarization are mixed into both ϕ_x and ϕ_y and $N_x \neq N_y$, an "optical phase precession" occurs. Under pulsed H_1 fields and "optical phase free induction decay" and an "optical phase echo" are predicted at a frequency ω_0. Both of these phenomena have analogies in other areas. In magnetic resonance free induction decay[20] and spin echo's[21] are well known to result from a dephasing and rephasing of the magnetization. In optical spectroscopy a "photon echo" has been observed and explained[22] in terms of the oscillating electric dipole's phase coherence associated with optical exitations. The phenomenon "optical phase precession" is different in so far as it results from the constructive and destructive interference of the admixed sin s

polarization at a frequency $(E_x - E_y)/\hbar$. In this respect it is

analogous to quantum beat experiments in fluorescence[23] and the

fluorescent modulation induced in the Hg atomic emission[24] by

$\mathcal{H}(t)$ fields.

(5) No change in the time averaged intensity of a polarized

component J occurs if $c_x^J = c_y^J$. This is the case where singlet

states of the same polarization are admixed equally into ϕ_x and ϕ_y .

Under these conditions equal phosphorescent rate constants of the same

polarization from these levels would result, and only the "optical

phase precession" would be detectable.

(6) Adiabatic inversion of the population N_x and N_y between

levels ϕ_x and ϕ_y is predicted if the power factor γH_1 and the

time duration of the applied field, t , are adjusted such that

$2 \gamma H_1 t = \pi$. In magnetic resonance this is commonly referred to as

adiabatic inversion with a 180° pulse.[25] In a zeeman spin system

when a short intense rf pulse is applied, a necessary condition for

inversion is that H_1 greatly exceeds the local dipolar field.

This insures that all spin in the ensemble are prepared identically

in the time duration of the pulse. In zero magnetic field, an

integer spin system such as triplet states experience "spin-quenching".[26]

In other words the magnetic dipole-dipole coupling of foreign spins

with the ensemble of zero field triplet states is reduced in much the

same way as electron orbital angular momentum is quenched in

paramagnetic ions.[27] The result is that the triplet state molecules

see a greatly reduced local dipole field, the line width in the zero

field EPR transitions are relatively narrow; consequently, adiabatic

inversion of the zero field levels can be accomplished with smaller H_1

fields. An additional and less restrictive way of producing adiabatic

inversion is the rapid fast passage method.[25,28,29] It is known that the zero

field Hamiltonian can be transformed to effective zeeman Hamiltonian

in a frame of reference termed the "interaction representation."[30]

In this representation a magnetization is definable and it corresponds

to the alignment of the spin state in the laboratory frame. Inversion

of the magnetization in the interaction representation is analogous

to population inversion in the laboratory frame. The condition for

inversion is that the time derivative of the effective magnetic field

be less than (γH_1^2) and that γH_1 be sufficiently large that

inversion occurs faster than spin lattice relaxation[25] i.e.,

$$| dH_{eff}/dt | \ll \gamma H_1^2 \qquad (17)$$

$$T_1 > (\gamma H_1)^{-1} \qquad (18)$$

Thus, an upper and lower time on the time required for inversion are

established. For a rf field $H_1 = 1$ gauss. The time through

resonance must be longer than about 10^{-7} sec and T_1 must be longer

than 10^{-8} sec. Both of these conditions are easily obtainable at

liquid He temperature.

Adiabatic inversion via rapid fast passage can be used to measure

directly the process of intersystem crossing. Consider, for instance,

the situation where intersystem crossing because of selective spin

orbit coupling occurs predominantly to one magnetic sublevel, say ϕ_y

and the (0, 0) and (0, vibration) phosphorescence have their origin

from ϕ_x and ϕ_y respectively. This is basically the prevailing

conditions found in 2,3 dichloroquinoxaline doped in durene[31] or

tetrachlorobenzene at 1.6 K and is represented in Figure (1) where

the (0, vibration) is (0, -260 cm^{-1}). If at time, $t = t_1$, the exciting light is

turned off and the populations between ϕ_x and ϕ_y are inverted via rapid fast passage in the forward direction (i.e., dH_{eff}/dt = positive) the phosphorescent intensity in the (0, 0) band will go from N_x/τ_p^x to N_y/τ_p^x while the (0, ν) emission will go from N_y/τ_p^y to N_x/τ_p^y. At a later time t_2, where $(t_2 - t_1) \ll \tau_p^x$ and τ_p^y, the direction of the microwave sweep is reversed (i.e., dH_{eff}/dt = negative) the populations will be inverted again and consequently, the (0, 0) and (0, v) emission will return to their values at t_0. If incomplete inversion occurs at $t = t_1$ and $t = t_2$ the emission at t_2 will not return to the $t = 0$ value but rather to the values:

$$\left[I_{(0,\,0)} \right]_{t_2} = \left[N_x \left\{ (1 - f)^2 + f^2 \right\} + N_y \left\{ 2f(1 - f) \right\} \right] / \tau_p^x \qquad (19)$$

$$\left[I_{(0,\,\nu)} \right]_{t_2} = \left[N_y \left\{ (1 - f)^2 + f^2 \right\} + N_x \left\{ 2f(1 - f) \right\} \right] / \tau_p^y \qquad (20)$$

where f is the fraction of inversion. It should be noted that saturation of the levels $(f = 1/2)$ results in no change in emission at $t = t_2$ since the levels are equalized at $t = t_1$.

If the same sequence of events is repeated in the presence of exciting light and inversion is complete at t_1 and t_2, the phosphorescent intensity at t_2 is expected to be different from the steady state value at t_0 because of intersystem crossing into ϕ_y.

First, the initial inversion at t_1 produces a population distribution different than that at steady state (t_0) ; thus, the system will respond to achieve a new steady state condition. Specifically, an additional population will build up in ϕ_y via intersystem crossing, (isc), at a rate proportional to the intersystem crossing rate constant $\left[\tau_{isc}^y \right]^{-1}$. Consequently, in the time duration $(t_2 - t_1)$ a population, $N_y^{isc} (t_2 - t_1)$, dependent upon τ_{isc}^y and $(t_2 - t_1)$ builds

up in ϕ_y. When the system is subjected to inversion at t_2 the

phosphorescent intensity in the $(0, 0)$ and $(0, \nu)$ bands will then be

$$\left[\dot{I} (0, 0) \, (t_2 - t_1) \right]_{t_2} = \left[N_x + N_y^{isc} \, (t_2 - t_1) \right] / \tau_p^x \qquad (21)$$

$$\left[I(0, \nu) \, (t_2 - t_1) \right]_{t_2} = N_y / \tau_p^y$$

From such experiments[31] one can ascertain the selectivity of

intersystem crossing and the relative rates or intersystem crossing

ratios $\tau_{isc}^i / \tau_{isc}^j$ where i and j are the different spin sublevels

ϕ_i and ϕ_j.

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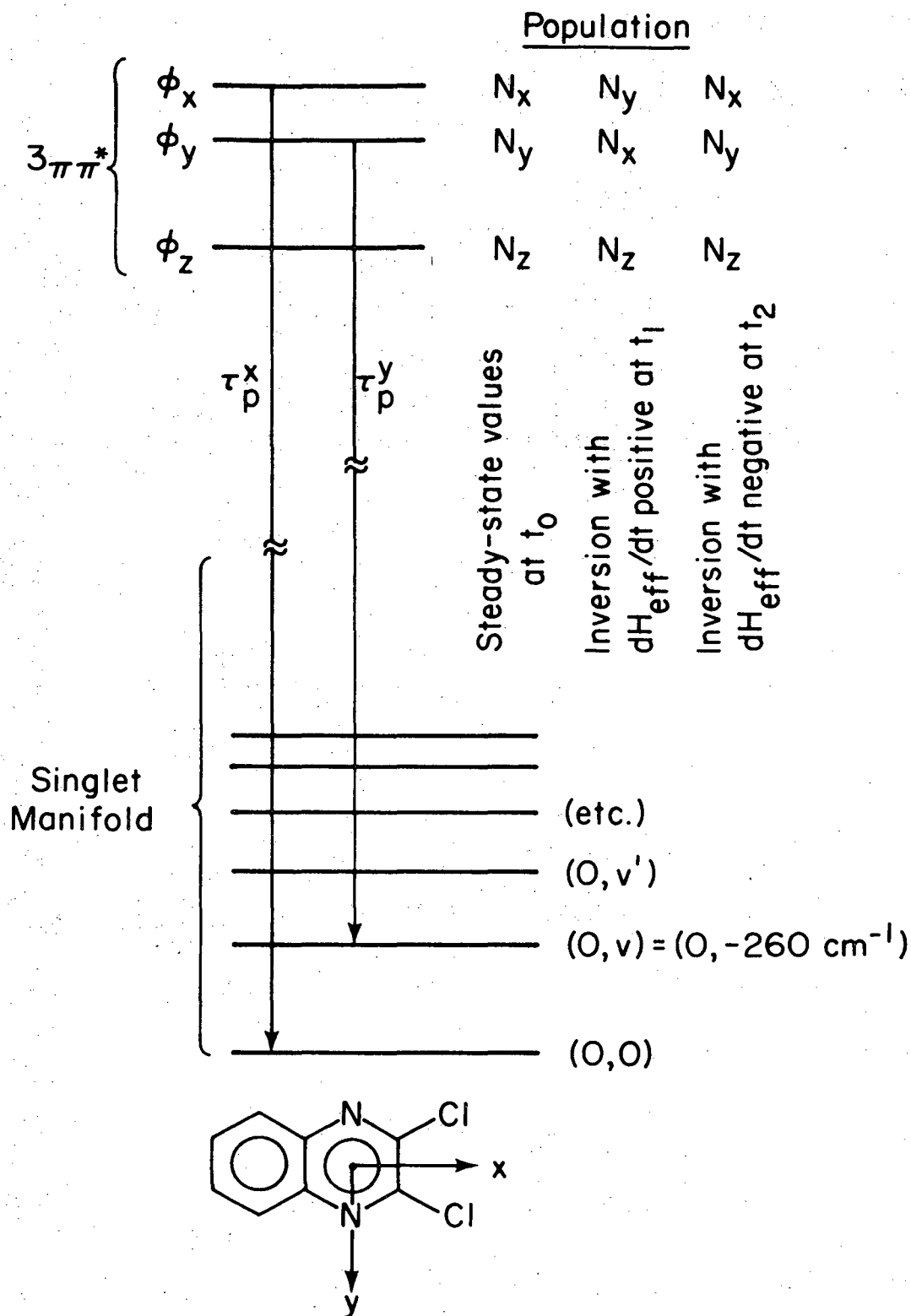
Fig. 1. Adiabatic inversion scheme via rapid fast passage to measure
intersystem crossing in 2, 3 dichloroquinoxaline.