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OPTICALLY DETECTED ELECTRON SPIN LOCKING

AND ROTARY ECHO TRAINS IN MOLECULAR EXCITED STATES

by

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Abstract

Electron spin locking, rotary echoes and rotary echo trains have been detected for molecules in their excited triplet states by monitoring the microwave-induced modulation of the phosphorescence. It has been found that $T_{1\rho}$ in these excited states is on the order of the lifetime of the state and that extremely long $T_{2\rho}$ times (600 μsec.) can be achieved by partially decoupling the electrons in the excited state from the surrounding nuclei.

The techniques are capable of measuring as few as 10^4 excited state spins in the sample. The preliminary results of these studies suggests that the techniques should be applicable to such problems as the optical detection of non-radiative nuclear and electron spins, acoustic phenomena in molecular solids, energy transfer, spin-exchange and a wide variety of additional processes that are coupled even weakly to the electron spins of the excited triplet state ensemble.

spins be long compared to the time required to connect the electron spins to another spin reservoir or long compared to the correlation time of other phenomena that can affect T_2. Unfortunately in the laboratory frame, T_2 in excited triplet states is only on the order of microseconds. We wish to show two approaches that can circumvent this difficulty. Both approaches have the effect of making T_2 long by the application of an rf field and capitalize on the inherent sensitivity associated with optically detected magnetic resonance. Initially, we will demonstrate the first optically detected spin locking[8] in molecular excited states. This has the effect in the rotating frame of making $T_2 = T_{1\rho}$, which for triplet states at low temperatures, we will show, is on the order of the lifetime of the excited state. Secondly, we will demonstrate the first optically detected electron spin rotary echoes[9] and echo trains in molecular excited states in which T_2 has been made long by substantially removing nuclear spin contributions to T_2 via hyperfine interactions and nuclear spin diffusion. This is accomplished by the application of a microwave field of sufficient strength to insure that the resonant frequency in the rotating frame, $\gamma \mathcal{H}_1$, is large compared to electron-nuclear coupling and by minimizing diffusional contributions to T_2 by observing echo trains where the time between echoes (2τ) is made short. Both of these techniques have the capability of detecting as few as 10^4 spins in the sample depending upon the details of the radiative processes being monitored.   Finally, we will indicate how these precursory experiments can serve as a basis for a general technique

of optically detecting other features associated with solids that can be coupled to the spins by measuring either the change of electron spin polarization in the rotating frame or the effect on the electron T_2 in the rotating frame.

Optically detected magnetic resonance in phosphorescent triplet states in zero field can be viewed[10] as a zeeman spin system in its rotating frame where "magnetization" along z in the interaction representation is related to spin alignment in the laboratory frame weighted by the relative radiative rate constants for phosphorescence from the two individual spin sublevels being coupled by a time dependent rf field. Usually in optical detection only the z component of the "magnetization" in the rotating frame, M_z, is observable via a rf induced modulation of the phosphorescence intensity.[10] To surpass this limitation and observe phasing or dephasing phenomena optically, such as electron spin echoes[11] which occur in the x,y-plane, an additional $\pi/2$ pulse is applied at various times at the end of a normal pulse experiment in order to restore population to the z-axis and observe the resulting change in phosphorescence intensity.[12] It is expected therefore that if the unpaired electrons in excited phosphorescent triplet state can be spin locked, that the spin locking and loss of spin alignment in the rotating frame can be optically detected in the following way. A $\pi/2$ microwave pulse applied along x at the frequency of one of the zero field transitions tilts the "magnetization" into the x,y-plane. Immediately after, the H_1 field is phased shifted 90° locking the spins along y and preventing the free induction decay. With the "magnetization"

parallel to the H_1 field the decay of the spin alignment to an equilibrium value occurs with the characteristic time $T_{1\rho}$ whose value depends in detail upon the interaction of the electron spins with other spins in addition to their interaction with the phonons. The decaying spin alignment locked in the rotating frame can be measured by switching off the spin locking field and immediately applying another $\pi/2$ pulse with the same rf phase as the initial pulse. This places the magnetization along $-z$ and results in a new value of the spin sublevel populations and hence a different value for the phosphorescence intensity. If no decay of spin alignment has occurred during spin locking, the new value of phosphorescence would correspond to a light level where the spin sublevel populations have been inverted. If all the spin alignment has been lost during spin locking the final $\pi/2$ pulse causes no additional change in the phosphorescence intensity as the spin sublevel population appears saturated as they do while in the x,y-plane. To prove that the excited state electron spin ensemble has been spin locked, the free induction decay has been monitored after a spin locking time τ long compared to T_2. This is illustrated in Figure 1 for the $^3\pi\pi^*$ state of d_2-tetrachlorobenzene[13] where the spin locking field has been removed at $\tau = 15$ μsec. Following this the free induction decay was monitored point by point by measuring the fraction of population restored to $-z$ by a $\pi/2$ pulse applied at various intervals τ'.

The relationship of the radiative decay channels to the level of phosphorescence intensity[14] and the state of spin alignment in the

rotating frame can be easily seen. After the application of the initial

$\pi/2$ pulse connecting the τ_x and τ_y spin sublevels, the light level goes

from its initial steady state value to a light level corresponding to

the saturation of the spin sublevel populations. If the exciting source

is removed at the onset of the sequence the presence of a strong

resonant $\mathcal{H}_1$ field will cause the phosphorescence intensity, $I_{SL}(t)$, during spin

locking to   decay with a time constant characteristic of the radiative

and radiationless decay channels of both spin sublevels.

$$I_{SL}(t) \sim [(N_x + N_y/2] \exp(-(k_x + k_y)/2t) \tag{1}$$

N_x and N_y are the initial spin sublevel populations while k_x and k_y are

the total depletive rates for the τ_x and τ_y spin sublevels respectively.

For the present case, the $^3\pi\pi^*$ of d_2-tetrachlorobenzene, it has been

shown[13,15] that emission to the electronic origin occurs principally

from τ_y and that $k_y \gg k_x$; thus,

$$I_{SL}(t) \sim [(N_x + N_y)/2] \exp(-(k_y/2)t) \tag{2}$$

During spin locking the magnetization along x can decay to zero with a

characteristic time $T_{1\rho}$ which is related to the radiative and radiationless

decay channels in addition to the spin lattice relaxation rate in the

rotating frame. Defining the latter as an $\mathcal{H}_1$ dependent quantity, $k_{1\rho}(\mathcal{H}_1)$,

we note that:

$$1/T_{1\rho} \equiv (k_x + k_y)/2 + k_{1\rho}(H_1) \simeq (k_y/2) + k_{1\rho}(H_1) \qquad (3)$$

for d_2-tetrachlorobenzene. The decay of the spin alignment during spin locking is simply given by the loss of M_x in the interaction representation, i.e.,

$$M_x(t) \sim [(N_x + N_y)/2] \exp(-t/T_{1\rho}) \qquad (4)$$

Hence $T_{1\rho}$ can be measured by restoring M_x to M_z at the end of spin locking by the application of additional $\pi/2$ pulse. This causes a change, ΔI (Cf Figure 2), in the phosphorescence intensity which corresponds to the amount of population carried to the $-z$ axis in the rotating frame. It is expected therefore that a plot of ΔI versus the spin locking time τ yields $T_{1\rho}$. After this final $\pi/2$ pulse the phosphorescence intensity will decay with a time constant characteristic of the individual levels which for tetrachlorobenzene is restricted to τ_y. This is illustrated in Figure 2 for the $^3\pi\pi^*$ state of d_2-tetrachlorobenzene in a d_{14}-durene host in which phosphorescence to the electronic origin was monitored. All other experimental details are similar to those reported earlier.[16] An important feature of the data is that $T_{1\rho}$ (42 ms) is long being only slightly less than the average (63 ms) of the τ_x and τ_y spin sublevel lifetimes.[13] This is because the phonon contributions to relaxation in the rotating frame at these temperatures (2°K) are small relative to the decay rates, i.e.,

$$k_{1\rho}(H_1) < (k_x + k_y)/2 \qquad (5)$$

Additionally, we found that the spin locking field, γH_1, could be varied over a considerable range without appreciably decreasing $T_{1\rho}$. Thus, the essential prerequisites, a long $T_{1\rho}$ and a variable γH_1, for transferring the spin alignment in the excited triplet state to or from other spin reservoirs (electrons or nuclei) in the rotating frame are satisfied. Consequently, optically detected double resonance experiments analogous to the experiments originally developed by Hartmann and Hahn[17] for the detection of rare spins in solids are possible.

It should now be possible, for example, to optically detect NMR and nonradiative excited states in solids or for that matter virtually any process that contributes to a loss of spin polarization or spin alignment in the rotating frame. In addition to the detection of other spins via optically detected double resonance, direct polarization or alignment of other spins (electrons or nuclei) in the rotating frame to a spin temperature approaching that of the triplet state ensemble, becomes feasible. The triplet spin temperature can be extremely low, approaching, in some cases, an equivalent proton spin temperature of ~0.001°K.[18] This is because of the high selectivity of intersystem crossing into the individual spin sublevel of the triplet state.

A second approach to multiple resonance experiments, designed to investigate phenomena associated with or coupled to phosphorescent triplet states, is to observe via optical detection the contributions various processes have in dephasing the triplet spin

ensemble. In order to observe phenomena correlated to the electron spins

for times longer than a few microseconds, it is necessary first to remove

the contribution to the electron T_2 from nuclear spin flips in the bulk

solid adjacent to the excited triplet states since these limit T_2 to a time

corresponding to nuclear spin diffusion. For fluctuating local fields due

to protons the electrons dephase in a time on the order of a few microseconds.

Secondly, it is desirable to have a method which is capable of experimentally

investigating a spectrum of correlation times. Both of these requirements

are satisfied by the optical detection of rotary echo trains[9] where echo

decay is measured as a function of the time between echoes (2τ) in the

presence of an H_1 field. The field is made sufficiently large to ensure that the

frequency of the electron spins at resonance, γH_1, is much larger than the

coupling of the electron spins to the surrounding spins. The net result

is to substantially decouple the nuclei of the bulk media and provide the

electron spins a "correlation time," 2τ, which is continuously variable

and yet capable of sensing other contributions to T_2 from phenomena such

as energy transfer, electron spin exchange, and spin-phonon interactions.

Each of these can have, in principle, different correlation times and hence

different contributions to the echo decay at any given 2τ.

Figure 3 shows a typical pulse train for τ = 1 microsecond and the

resulting optically detected rotary echo train in the phosphorescence from

the $^3\pi\pi^*$ state of the tetrachlorobenzene Y-trap[19] at 1.75°K. Phosphorescence

to the electronic origin of the Y-trap was used to monitor the rotary

echoes associated with the zero field $D-|E|$ transition at 3608.6 ± 1 MHz.

Other experimental details are similar to those reported earlier.[16] A

microwave H_1 field of 1.8 gauss is continuously applied throughout the

train; however, it is phase shifted by 180° at times τ, 3τ, 5τ... leading

to the resultant formation of echoes at times 2τ, 4τ, 6τ... During the

first τ period the magnetization dephases as it precesses about H_1 giving

rise to optically detected rotary precession.[20] Following the application

of the 180° phase shift at τ, the precession reverses, and the sample and

H_1 field inhomogeneities rephase culminating in the formation of the echo

at a time 2τ. An advantage of rotary echoes particularly suited to optical

detection is the fact that the echoes form along z in the rotating frame,

and thus their amplitudes are directly related to the zero field spin

sublevel populations of the triplet state in the laboratory frame and hence

to the phosphorescence intensity.[10] In the echo train, the amplitudes

decay exponentially in the rotating frame, ρ, with a decay constant $T_{2\rho}$

which can be a sensitive function of τ. In our measurements in

the above excited state, $T_{2\rho}$ was found to be ~600 μseconds for a $\tau = 1$

μsecond. T_2 found for this compound from a plot of the optically detected

Hahn echoes vs. 2τ in the laboratory frame was only 8 μsec, a value attributable

to nuclear spin diffusion . In addition, $T_{2\rho}$ was found to vary signi-

ficantly with τ, presumably because of spin exchange and energy migration

between traps in these crystals.[21]

The results of these preliminary experiments suggest that other

phenomena associated with the dephasing of the triplet spins can be studied. For example, it might be possible to optically detect the static and dynamic properties of spin-phonon interactions in these crystals by monitoring the change induced in $T_{2\rho}$ by the application of an acoustic pulse. In a similar way, the dynamics of triplet energy migration and spin exchange could be investigated directly by the application of a pulsed magnetic field gradient and the observation of its effect on $T_{2\rho}$. These and other applications of the above techniques are presently under investigation.
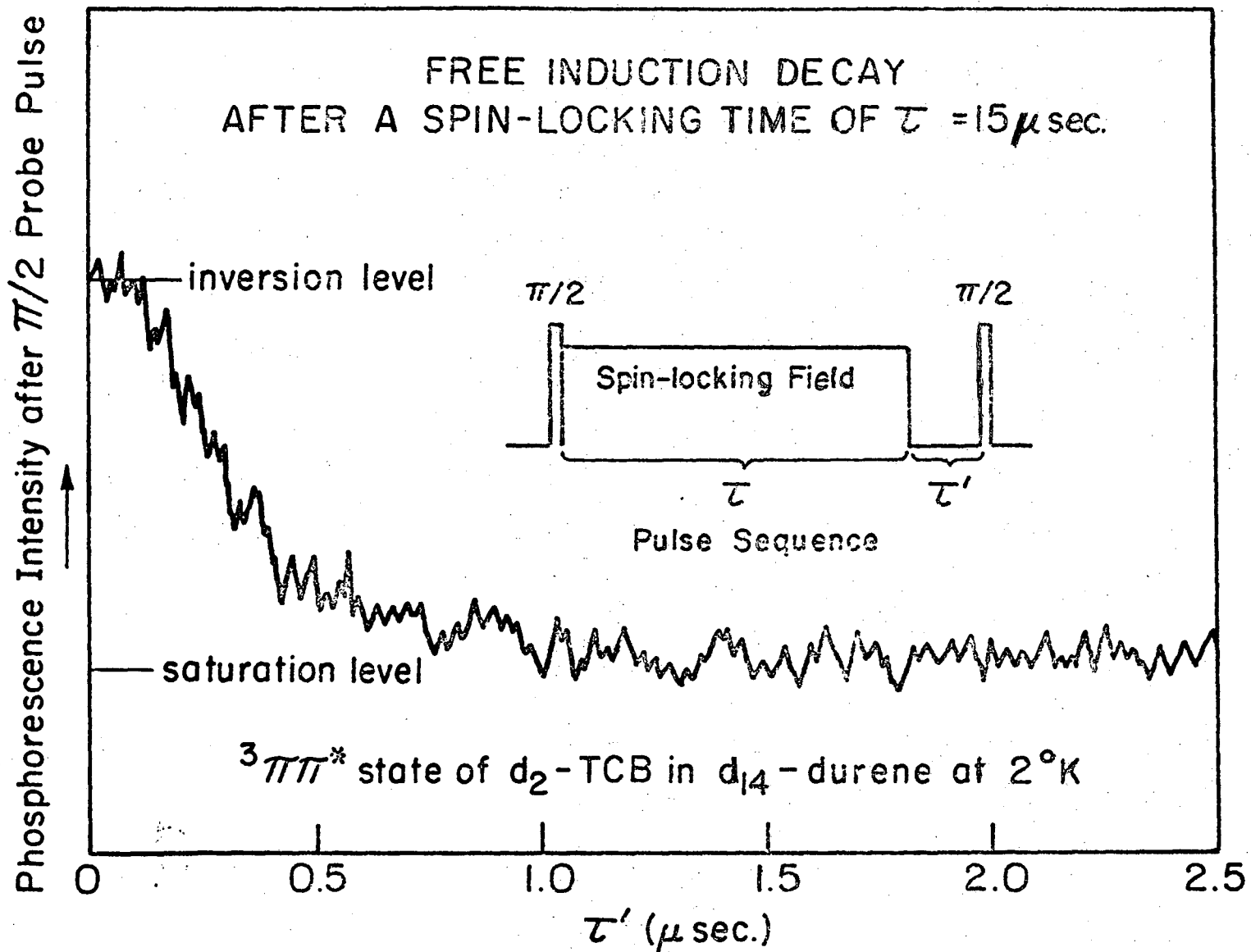
References

*Alfred P. Sloan Foundation Fellow

1. J. Brossel and F. Bitter, Phys. Rev. **86**, 308 (1952).

2. A. Kastler, J. Phys. Radium **11**, 255 (1950); Physica **17**, 191 (1951).

3. J. N. Dodd, G. W. Series, and M. J. Taylor, Proc. Roy. Soc. (London) **A263**, 353 (1961).

4. S. Geschwind, G. E. Devlin, R. L. Cohen, and S. R. Chinn, Phys. Rev. **137**, 1087 (1965).

5. M. Sharnoff, J. Chem. Phys. **46**, 3263 (1967); A. L. Kwiram, Chem. Phys. Lett. **1**, 272 (1967); J. Schmidt and J. H. van der Waals, Chem. Phys. Lett. **2**, 640 (1969); D. S. Tinti, M. A. El-Sayed, A. H. Maki and C. B. Harris, Chem. Phys. Lett. **3**, 343 (1969).

6. K. F. Renk and J. Deisenhofer, Phys. Rev. Letters **26**, 764 (1971).

7. D. S. McClure, J. Chem. Phys. **20**, 682 (1952); M. S. de Groot, I. A. M. Hesselman, and J. H. van der Waals, Mol. Phys. **12**, 259 (1967).

8. A. G. Redfield, Phys. Rev. **98**, 1787 (1955); I. Solomon, Compt. rend. **248**, 92 (1959).

9. I. Solomon, Phys. Rev. Letters **2**, 301 (1959).

10. C. B. Harris, J. Chem. Phys. **54**, 972 (1971).

11. E. L. Hahn, Phys. Rev. **80**, 580 (1950).

12. W. G. Breiland, C. B. Harris, and A. Pines, Phys. Rev. Letters **30**, 158 (1973).

13. W. G. Breiland and C. B. Harris, Chem. Phys. Letters, in press.

14. C. B. Harris and R. J. Hoover, J. Chem. Phys. 56, 2199 (1972).

15. A. H. Francis and C. B. Harris, J. Chem. Phys. 57, 1050 (1972).

16. M. J. Buckley and C. B. Harris, J. Chem. Phys. 56, 137 (1972).

17. S. R. Hartmann and E. L. Hahn, Phys. Rev. 128, 2042 (1962).

18. 0.001°K is the equivalent spin temperature for protons in the presence of a 25 kilogauss field assuming a triplet spin alignment at 1 GHz of 100:1.

19. A. H. Francis and C. B. Harris, Chem. Phys. Lett. 9, 188 (1971).

20. J. Schmidt, W. G. van Dorp, and J. H. van der Waals, Chem. Phys. Letters 8, 345 (1971); C. B. Harris and R. J. Hoover, unpublished results.

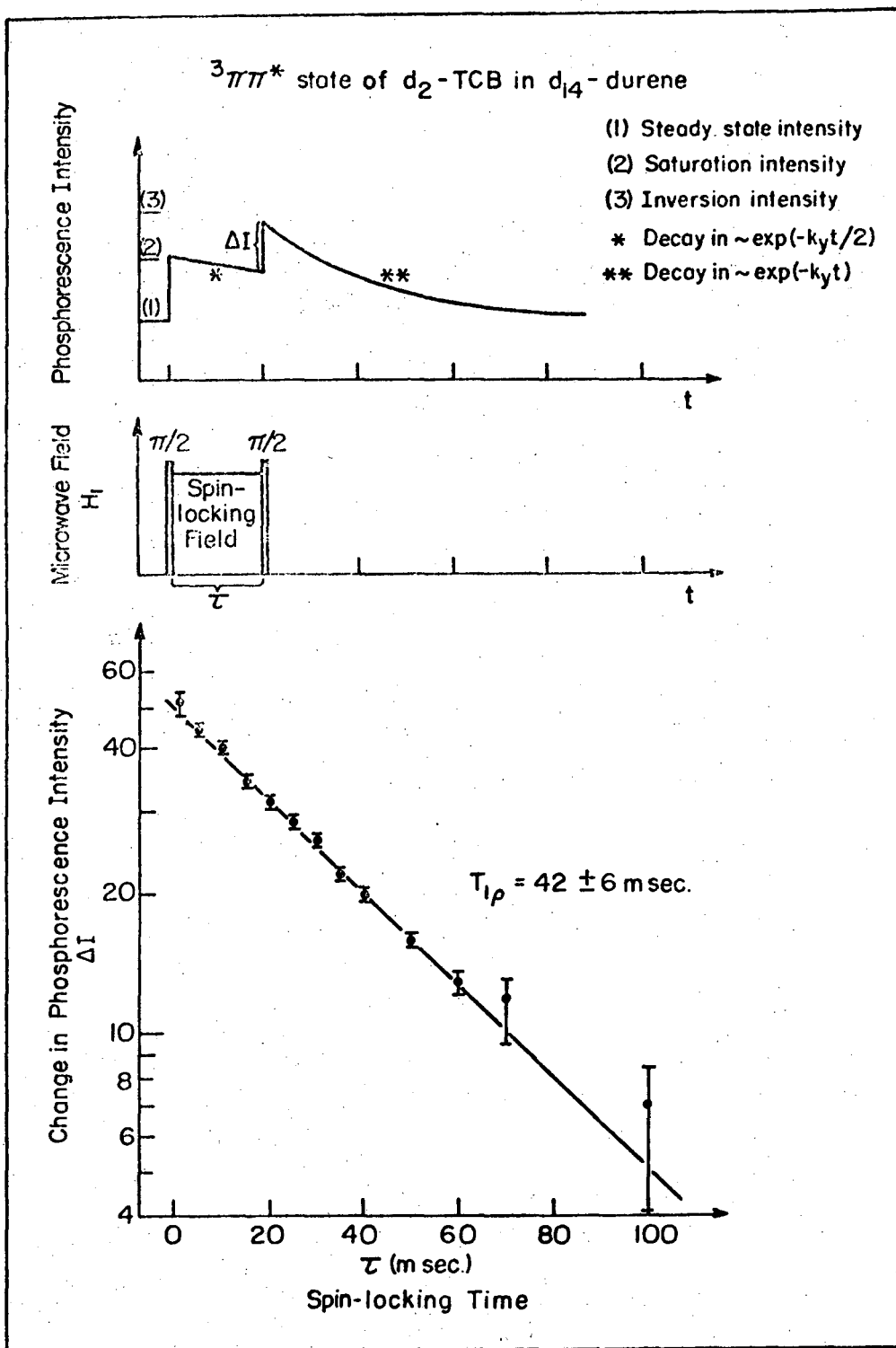21. A. H. Francis and C. B. Harris, J. Chem. Phys. 55, 3595 (1971).

Figure Captions

Figure 1   Optically detected free induction decay after a spin locking

time $\tau = 15$ μsec. Phosphorescence to the electronic origin

from the $^3\pi\pi^*$ state of d_2-tetrachlorobenzene doped 1% (m/m)

in d_{14}-durene was monitored at 2°K. The $\pi/2$ pulses and the

spin-locking field were applied at the D-$|E|$ zero field transi-

tion frequency (3644.6 MHz).

Figure 2   Optically detected spin lattice relaxation in the rotating

frame in the $^3\pi\pi^*$ state of d_2-tetrachlorobenzene. Similar

results were obtained for the excited state in h_2-tetrachloro-

benzene (Y-trap).

Figure 3   Optically detected electron spin rotary echo train for the

D-$|E|$ zero field transition of the $^3\pi\pi^*$ state of h_2-tetrachloro-

benzene (Y-trap) with $\tau = 1$ μsec. The microwave pulse sequence

is shown at the bottom with the relative phase of each pulse

shown in degrees. The nonlinearity of the echo train sweep

was caused by the manner in which the echoes were recorded.

The dotted lines indicate positions of phase shift.

FREE INDUCTION DECAY
AFTER A SPIN-LOCKING TIME OF τ =15μ sec.

Phosphorescence Intensity after $\pi/2$ Probe Pulse

inversion level

$\pi/2$

$\pi/2$

Spin-locking Field

τ

τ'

Pulse Sequence

saturation level

$^3\pi\pi^*$ state of d_2-TCB in d_{14}-durene at 2°K

τ' (μ sec.)

XBL 731-5685

Fig. 1.

$^3\pi\pi^*$ state of d_2-TCB in d_{14}-durene

(1) Steady state intensity
(2) Saturation intensity
(3) Inversion intensity
* Decay in $\sim \exp(-k_y t/2)$
** Decay in $\sim \exp(-k_y t)$

$T_{1\rho} = 42 \pm 6$ m sec.

XBL 731-5684

Fig. 2.

OPTICALLY DETECTED ROTARY SPIN ECHO TRAIN
IN THE $^3\pi\pi^*$ STATE OF h_2-TCB (y-trop)

PHOSPHORESCENCE INTENSITY

STEADY STATE INTENSITY

SATURATION INTENSITY

INVERSION INTENSITY

MICROWAVE POWER

0°   180°   0°   180°   0°

0   1.0   3.0   5.0   7.0

TIME (μsec.)

XBL731-5696

-16-

Fig. 3.