Optically Detected Spin Locking of Zero Field Electronic Triplet States and Cross Relaxation in the Rotating Frame

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The spin locking method known from NMR is shown to be useful also in ESR for investigating spin lattice relaxation problems and "slow" motions, e. g. questions of energy transfer by triplet states in organic molecular crystals, and probing of nuclear quadrupolar splittings even smaller than the ESR line width at zero magnetic field.

Optically detected ESR spin locking experiments for isolated triplet states in zero field are demonstrated. It is shown how the complication of incoming and decaying triplet states and relaxation between all three triplet sublevels has to be handled during spin locking. An application, the study of the cross-relaxation between electronic triplet spin states and deuteron or proton spins is presented. These experiments are possible in spite of the first order quenching of the hyperfine coupling in zero magnetic field. Another application is briefly mentioned, in which the adiabatically demagnetized state in the rotating frame is used to probe the electronic triplet state transfer and nuclear spin lattice relaxation.

1. Introduction

In a magnetic field H_0 the magnetization of a spin-1/2-system, for example, relaxes towards its thermal equilibrium value with the longitudinal spin lattice relaxation time T_1, and this has been used extensively for probing properties of the condensed matter. Similar applications are found for the longitudinal relaxation time $T_{1\varrho}$ in the rotating frame [1, 2]. Here the magnetization has been tilted perpendicular to the external field H_0, for example by a so-called 90°-radio frequency pulse. The magnetization would then decay with the transverse spin lattice relaxation time T_2, unless a "strong" radio frequency H_1-field is switched on. H_1 must be perpendicular to H_0 and must precess both synchronous and collinearly with the magnetization. The decay time $T_{1\varrho}(H_1)$ of the magnetization along H_1 can be longer than T_2, with $T_2 \lesssim T_{1\varrho}(H_1) \lesssim T_1$; the spins are "locked".

Typical problems concerning $T_{1\varrho}$ are:

1. The probing of the spectral density of perturbation with long correlation times, such as diffusion or molecular reorientation.
2. Cross relaxation experiments, in which different kinds of nuclear spins participate.

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Spin locking has been not only applied to spin-1/2-systems in high field NMR, but also to zero field quadrupolar resonance [3]. There exists a quite general analogy between the case in which a strong r. f. field acts on two levels and the case of a resonance experiment with a spin-1/2-system in high magnetic field [4]. This analogy allows a geometrical interpretation of the equation of motion, and it holds in the case of a microwave field acting on electronic zero field triplet states [5, 6]. Recently it has been shown that a spin locking with these triplet states is feasible [7]: The longitudinal spin lattice relaxation time in the rotating frame proves to be more than a factor of 10^4 longer than the transverse relaxation time T_2. At low temperatures only the lifetimes of the triplet substates limit the spin locking time. Hence spin locking experiments analogous to those in NMR can be performed. The spin locking in zero field ESR has been used already in a diffusion type problem where triplet states jump out of shallow traps into the exciton band [8].

Here cross relaxation between the electronic triplet spin states to nuclear spin states occurs in a similar way to that in the experiment of Hartmann and Hahn [3]. This has two aspects: Information can be obtained about small quadrupolar splittings in the electronic ground- and triplet states and the

hyperfine coupling between the electronic triplet and nuclear spins; also it can be distinguished between cross relaxation effects to nuclear spins and other relaxation effects in the rotating frame.

The use of zero external magnetic field has a severe disadvantage because the hyperfine coupling of the integer electronic triplet spin is quenched in first order (see below). It seemed questionable on the basis of results from NMR experiments [9] that cross relaxation effects could be observed. However, a basic technical advantage exists in zero field: the ESR lines are much narrower (1 . . . 3 MHz) than in high field (~ 30 MHz), thus the H_1-field required for spin locking can be much lower. The probing of small quadrupolar interactions below 1 MHz thus becomes easier. The theory of spin locking at high and low H_1-fields with adiabatic demagnetization in the rotating frame is treated first, then cross relaxation of electronic triplet spin states to nuclear spins is considered.

2. The Spin Locking Wavefunctions and their Decay Rates

2.1. Spin Locking Wavefunctions for high H_1-fields

At the beginning we neglect population changes of the triplet state sublevels due to intersystem crossing and relaxation among the sublevels; then the spin locked states are best expressed in terms of the zero field triplet spin functions $\tau_x \, \tau_y$, τ_z. With the usual notation their spin Hamiltonian is:

$$\mathcal{H}_{SS} = D\,(\mathbf{S}_z{}^2 - 1/3\,\mathbf{S}^2) + E\,(\mathbf{S}_x{}^2 - \mathbf{S}_y{}^2)\ . \qquad (1)$$

The $\tau_y \longleftrightarrow \tau_z$ transition is chosen for the purpose of the experiments described in this work. An r. f. field with amplitude $2\,H_1$ and a frequency ω, with a polarization of its magnetic component parallel to the x-direction, gives rise to the following time dependent perturbation

$$\mathcal{H}_{rf} = -\,2\,\hbar\,\gamma\,H_1\,\mathbf{S}_x \cos \omega\,t\ .$$

The spin operator $\mathbf{S}_x$ indicates the polarization of the r. f. field in the physical frame. γH_1 is the matrix element of the allowed transition $\tau_y \longleftrightarrow \tau_z$ induced by the perturbation $\mathcal{H}_{rf}$. For an electronic triplet spin the factor γ equals the gyromagnetic ratio of the electron. The new time dependent wave functions are linear combinations of the original wavefunctions τ_y and τ_z with coefficients $a(t)$, $b(t)$

and their conjugated complex $a^+(t)$, $b^+(t)$:

$$\psi_1(t) = a(t)\,\tau_y + b(t)\,\tau_z\ ;$$
$$\psi_2(t) = -\,b^+(t)\,\tau_y + a^+(t)\,\tau_z\ ; \qquad (2)$$

according to usual perturbation theory with the condition of ψ_1 and ψ_2 being orthogonal to each other. To get the equation of motion for the total Hamiltonian $\mathcal{H}_{ss} + \mathcal{H}_{rf}$, it is convenient to use the so-called vector model [4]: For that, two vectors $\boldsymbol{r}$ and $\boldsymbol{\omega}$ are defined in an abstract space:

$$\boldsymbol{r} = \{r_1, r_2, r_3\}$$
$$= \{a\,b^+ + a^+\,b,\ i\,(a\,b^+ - a^+\,b),\ a\,a^+ - b\,b^+\}\ ,$$
$$\boldsymbol{\omega} = \{\omega_1, \omega_2, \omega_3\} = \{0,\ -\,2\,H_1\,\gamma \cos \omega\,t,\ \omega_0\}\ . \quad (3)$$

ω_0 represents the transition frequency $\tau_y \longleftrightarrow \tau_z$. Then the equation of motion can be written in the form of a "Bloch"-equation:

$$\mathrm{d}\boldsymbol{r}/\mathrm{d}t = \boldsymbol{\omega} \times \boldsymbol{r} \qquad (4)$$

which implicitly describes the time dependence of a and b. This perturbation theory result does to require that $\hbar\,\gamma\,H_1$ is small against the zero field energy splitting, because the following matrix elements vanish [4]:

$$\langle\,\tau_y\,|\,\mathcal{H}_{r.f.}\,|\,\tau_y\,\rangle = 0\,; \quad \langle\,\tau_z\,|\,\mathcal{H}_{r.f.}\,|\,\tau_z\,\rangle = 0\ . \quad (4\,\mathrm{a})$$

$(\gamma/2\,\pi)\,H_1$ must be large against the ESR linewidth $\Delta\omega/2\,\pi$ to get a uniform effect over the whole line.

For the treatment of spin locking on exact resonance the analogy to a spin-$1/2$-system is applied: There, a linearly polarized H_1-field is decomposed into two circularly polarized components perpendicular to H_0. During spin locking one of these components precesses parallel to the magnetization of the spin-$1/2$-system, the other component has no effect.

The corresponding circularly polarized component of $\boldsymbol{\omega}$ perpendicular to the static pseudofield $\{0, 0, \omega_0\}$ in the abstract space is:

$$\{-\,\hbar\,\gamma\,H_1\,S_x \sin \omega\,t,\ -\,\hbar\,\gamma\,H_1\,S_x \cos \omega\,t, 0\}\ . \quad (4\,\mathrm{b})$$

The onset for the pseudomagnetization then becomes:

$$\boldsymbol{r}(\psi_1) = -\,\boldsymbol{r}(\psi_2) = \{|\,r\,| \sin \omega\,t,\ |\,r\,| \cos \omega\,t, 0\}\ . \quad (4\,\mathrm{c})$$

With the definition out of Eq. (3) for the components of $\boldsymbol{r}$ one obtains $a(t)$ and $b(t)$, and the time dependent spin locking functions have to be orthogonal to each other:

$$\psi_1 = 1/\sqrt{2} \left[\exp\left\{ (i\,\omega/2) t \right\} \tau_y \right.$$
$$\left. + i \exp\left\{ (-i\,\omega/2t\right\} \tau_z \right] \exp\left\{ -i\,\varphi \right\},$$
$$\psi_2 = 1/\sqrt{2} \left[-i \exp\left\{ (i\,\omega/2) t \right\} \tau_y \right. \qquad (5)$$
$$\left. + \exp\left\{ (-i\,\omega/2) t \right\} \tau_z \right] \exp\left\{ i\,\varphi \right\}.$$

The normalisation $\langle \psi_1 | \psi_1 \rangle = \langle \psi_2 | \psi_2 \rangle = 1$ is used; the common phase angle φ may be chosen to zero.

In the *physical space*, ψ_1 and ψ_2 have equal but opposite expectation values for S_x; they oscillate with time. Thus an oscillating real magnetization along the r. f.-field in the physical space occurs.

2.2. Population, Decay, Relaxation

The equation of motion (4) has been used to explain the light level change in an ODMR-experiment during irradiation with short r. f. pulses [5, 6], where additional effects due to populated changes by intersystem crossing or relaxation can be neglected [6a]. This is not possible during long r. f. pulses, and additional changes of the r vector with time have to be considered. Generally the operators appropriate to the rates of intersystem crossing (population and decay) and relaxation are independent of time and linearly dependent on τ_y and τ_z. Consequently, any nonstationary spin state, which can be represented as a linear combination of τ_y and τ_z, changes its population with rates proportional to the projections on τ_y and τ_z [6b, 6c]. In Eq. (4) the change due to those rates has to be added to the change of r due to the H_1-field. It seems to be more convenient to use the original equations for $a(t)$ and $b(t)$ of the perturbation treatment. However, in the case of spinlocked states on exact resonance $\omega = \omega_0$, the correction of Eq. (4) is still advantageous. Here the projections of the spin locked states on τ_y und τ_z are equal. Any population via intersystem crossing populates the spin states ψ_1 and ψ_2 of Eq. (5) equally, the population difference between them remains unaffected and the r-component along H_1 does not change. In Ref. [8] this result was explained from a different point of view; the incoming population builds up an r-component along $\{0, 0, \omega_0\}$, the static pseudofield in the abstract space, then precesses perpendicular to H_1 and decays within times of the order of μsec belonging to the rotary echo experiment [7]. Again the r-component along H_1 does not change. Experimentally it is confirmed that the spin locking signal remains unaffected whether a steady state exciting light source is switched on or not.

A decay rate out of one triplet spin sublevel enters with half of its associated rate into the decay out of ψ_1 and ψ_2. This is demonstrated by calculating the radiative decay rate out of ψ_1 and ψ_2 into the singlet ground state S_0, which might be vibrationally excited. As an abbreviation we use the symbol S_0 to indicate the total electronic wavefunction with spin and orbital part; similarly the spin functions of the triplet sublevels shall also indicate the whole wavefunction:

$$k^{\mathrm{rad}}(\psi_1) = |\langle \psi_1 | \mu | S_0 \rangle|^2 ;$$
$$= 1/2 \,|\langle \tau_y | \mu | S_0 \rangle|^2 + 1/2 \,|\langle \tau_z | \mu | S_0 \rangle|^2$$
$$+ \sin \omega\, t \cdot |\langle \tau_y | \mu | S_0 \rangle \langle \tau_z | \mu | S_0 \rangle; \qquad (6)$$
$$= 1/2 \, k_y^{\mathrm{rad}} + 1/2 \, k_z^{\mathrm{rad}} + (\text{cross term}) ;$$
$$= k^{\mathrm{rad}}(\psi_2) .$$

The cross term either vanishes [10] or at least averages out over several microwave periods $1/(2\,\pi\,\omega)$. If there is only the radiative decay, the change in the population difference with time is:

$$\frac{\mathrm{d}}{\mathrm{d}t} \left[N(\psi_1) - N(\psi_2) \right]$$
$$= -k^{\mathrm{rad}}(\psi_1) [N(\psi_1) - N(\psi_2)] . \qquad (7)$$

There are other kinds of depopulation out of one triplet sublevel, which enter in the same manner into $k^{\mathrm{total}}(\psi_1)$; the nonradiative decay rates k_y^{nonrad} and k_z^{nonrad} into the ground state, the spin lattice relaxation rates w_{yx} and w_{zx} from τ_y and τ_z to the third level τ_x. The back-relaxation rates w_{xy} and w_{xz} are analogous to a population and thus cannot change $N(\psi_1) - N(\psi_2)$. Finally there are decay rates which enter fully into $k^{\mathrm{total}}(\psi_1)$ and not only by their half values: the "genuine" spin lattice relaxation rate along H_1 in the rotating frame, which in this work is called $1/T_{1\varrho}$ to emphasize its analogy to the $1/T_{1\varrho}$ out of NMR experiments. It includes w_{yz}, w_{zy} and also the cross relaxation to other spins. If there are no additional rates along H_1 compared with the spin lattice relaxation rates in the laboratory frame, then $1/T_{1\varrho}$ is just the arithmetic mean of the spin lattice relaxation rates from τ_y to τ_z and back from τ_z to τ_y:

$$1/T_{1\varrho} = 1/2 \, w_{yz} + 1/2 \, w_{zy} ; \qquad (8)$$
$$\sim w_{yz} .$$

Another relaxation rate k^{P} is caused by occasional change of the zero field splitting, for example by jumps of the triplet state into the exciton band [8]. Then the precession frequency of the pseudomagne-

tization occasionally is different from that of the H_1-field and there is no spin locking during the time of the changed zero field splitting.

The sum of all decay rates of the spin locking signal is:

$$k^{\text{total}} = k^{\text{total}}(\psi_1) = k^{\text{total}}(\psi_2) ;$$
$$= 1/2\,(k_y{}^{\text{rad}} + k_z{}^{\text{rad}}) + 1/2\,(k_y{}^{\text{nonrad}} + k_z{}^{\text{nonrad}})$$
$$+ 1/2\,w_{yz} + 1/2\,w_{zx} + 1/T_{1\varrho} + k^P . \qquad (8\,\text{a})$$

In a spin locking experiment on exact resonance $\omega = \omega_0$, with $(\gamma/2\,\pi)\,H_1$ large against the linewidth, the $\boldsymbol{r}$ vector changes according to

$$\mathrm{d}\boldsymbol{r}/\mathrm{d}t = \boldsymbol{\omega} \times \boldsymbol{r} - k^{\text{total}}\,\boldsymbol{r} . \qquad (8\,\text{b})$$

where population, decay and relaxation are included.

3. Measurement of the Decay in the Rotating Frame, ADRF

A scheme for performing a spin locking experiment in NMR on a spin-1/2-system at low H_1-fields $[\,(\gamma/2\,\pi)\,H_1$ smaller than the linewidth] was described in Reference [11]. There, a $\pi/2$ r.f. pulse is first applied to tilt the magnetization perpendicular to the external field into the x-y-plane. Following this, the spin locking r.f. field with a $\pi/2$ phase shift to the first r.f. pulse is switched on. This H_1-field is then adiabatically lowered from its high value [with $(\gamma/2\,\pi)\,H_1$ larger than the linewidth] to a desired value, where relaxation or crossrelaxation in the new H_1-field takes place. This reversible adiabatic adjustment brings about a slow change of the direction of the effective field in the rotating frame and keeps as much magnetization as possible along its direction. After some fixed time the original high value of $(\gamma/2\,\pi)\,H_1$ is adiabatically restored and the H_1-field is switched off abruptly. A free induction decay of the residual magnetization follows, the amplitude of which depends on the effects during spin locking.

In the optical detection method one uses a similar r.f. pulse sequence (Fig. 1 a) and deals with a pseudomagnetization in an abstract space.

Fig. 1. Scheme of spin locking with optical detection, where the r.f. field H_1 can be made so low, that $(\gamma/2\,\pi)\,H_1$ is much smaller than the ESR linewidth. As an example we chose the 2E-transition $\tau_y \longleftrightarrow \tau_z$ of the lowest triplet state of d_2-TCB in d_{14}-durene. a) Sequence of r.f. pulses. The x and y indicate the relative phase positions of the r.f. field. b) Change of phosphorescence light intensity corresponding to the microwave irradiation as seen on the signal averager. A large spin polarisation $(N_z : N_y = 3:1)$ has been built up during steady state illumination. The population rates are $p_z : p_y = 3:1$, the total decay rates are nearly equal: $k_y = (30 \pm 3)\ \text{sec}^{-1}$, $k_z = (27 \pm 3)\ \text{sec}^{-1}$, the radiative rates are quite different: $k_z{}^{\text{rad}} \sim 0$; $k_y{}^{\text{rad}}$ is of the order of k_y. (A) indicates the steady state light level, (B) the saturation and (C) the inversion light level. During range I the light level is constant because of $k_y \sim k_z$. During range II the light level may decrease depending on whether $(\gamma/2\,\pi)\,H_1 \ll 5\ \text{MHz}$ (dotted line) or $(\gamma/2\,\pi)\,H_1 = 5\ \text{MHz}$ (solid line). The increase in light level at the end of range II has to be clearly distinguished from the spin locking signal, so range III has to be long enough to provide a sufficiently well-defined baseline for this purpose. c) The decay of the spin locking signal ΔI for $(\gamma/2\,\pi)\,H_1 = 5\ \text{MHz}$ or $\Delta I'$ for $(\gamma/2\,\pi)\,H_1 < 5\ \text{MHz}$ may be plotted against t or t'. With $(\gamma/2\,\pi)\,H_1 = 5\ \text{MHz}$ the decay is exponential; it becomes non-exponential at ca. 200 kHz. d) Another way to plot the results in c) is to keep t' constant and to plot $\Delta I'$ in units of ΔI versus $(\gamma/2\,\pi)\,H_1$. This is useful for the cross relaxation experiments.
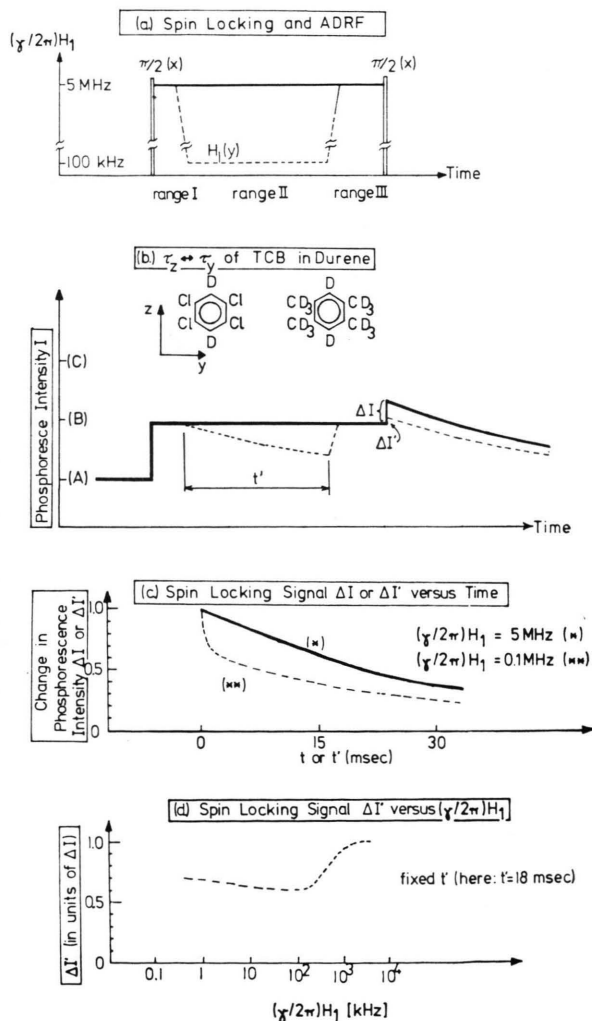
One correction to the pulse sequence described above is to add a $\pi/2$-pulse (phaseshifted with respect to the spin locking pulse by $\pi/2$). Then the residual pseudomagnetization is tilted back into the direction of the static pseudofield $\{0, 0, \omega_0\}$. There a corresponding sudden jump in phosphorescence intensity occurs (Figure 1 b). The last $\pi/2$-pulse thus transforms a pulse sequence for conventional detection of the free induction decay to one for optical detection [12]. Another important departure from the usual pulse sequence is to keep the spin locking field high for a time of about 1 msec at the beginning and the end of the spin locking pulse (ranges I and III in Figure 1 a). At high H_1-fields the whole line is in uniform spin locked condition and well defined light intensity baselines are obtained. They go to an equilibrium value with a time constant depending on decay and relaxation rates. Any light intensity change brought about by lowering or raising of the H_1-field (as described in Sect. 3.4) may be clearly distinguished from that caused by the spin locking signal.

3.1. Experimental Arrangement

The experimental arrangement was essentially the same as in Ref. [7] and most of the details have been described in Reference [8]. For the purpose of applying small spin locking fields some remarks to special points are made.

a) The time dependent phosphorescence light intensity was accumulated on a 1024-multichannel signal averager. Due to the short lifetime (~ 30 msec) of the sublevels used in the experiment typically 500 time scans could be sampled within about a minute.

b) The highest $(\gamma/2\pi)H_1$-value used in these experiments was 5 MHz. It was controlled by adjusting a π-pulse of 100 nsec duration. Lower $(\gamma/2\pi)H_1$ were obtained by using two Hewlett-Packard 33122 A pin diode attenuators in series. The driving current for the pin diodes was supplied by a ramp pulse generator. The attenuation was compared with fixed calibrated attenuators. The absolute accuracy of $(\gamma/2\pi)H_1$ was at 5 MHz about 10%, around 100 kHz about 20%, around 10 kHz about 30%. The relative accuracy between two $(\gamma/2\pi)H_1$-values differing by a factor of 10 was 10% [8a].

c) An amplitude change of the H_1-field usually means a change in the r. f. phase because of the 20 W-travelling wave tube amplifiers used. However, this shift is not critical because it is also adiabatic upon an adiabatic change of $(\gamma/2\pi)H_1$.

d) The microwave source, a Hewlett-Packard 8690 B sweep oscillator, was stable within ± 15 kHz. This is necessary to obtain clear results at small $(\gamma/2\pi)H_1$ down to about the 15 kHz.

The experiments were performed on the lowest $\pi\pi^*$-triplet state of 1,2,4,5-tetra-chlorobenzene (TCB) in a durene host. Besides its high sensitivity in ODMR, this system has the advantage that the dynamic rates of the triplet sublevels do not change upon deuteration [13]. The isotopic substitution is important to change the nuclear spin species in the cross relaxation experiments below. All measurements are done on the 2E-transition with the total decay rates of the states [13, 14]:

$$k_y^{\text{total}} = (30 \pm 3) \sec^{-1}, \quad k_z^{\text{total}} = (27 \pm 3) \sec^{-1}.$$

If there were no relaxation, this would give (28.5 ± 3) sec^{-1} for the decay rate of the spin locking signal.

3.2. Results Using High H_1-field

To apply the equations to the light level change in a spin locking experiment, the frequency of the H_1-field was set about equal to the center of gravity of the ESR line (which is generally asymmetric). This also has the advantage that the effective frequency, $\omega_{\text{eff}}/2\pi$, in the rotating frame (Fig. 2 a) can later be made small enough to match the transition frequency of nuclear spins. In addition, the matrix elements for cross relaxation are expected to be large when $\omega_{\text{eff}}/2\pi$ is parallel to H_1.

At high H_1-fields, no cross relaxation is expected. An experiment was set up to see whether the $(\gamma/2\pi)H_1$-value of 5 MHz used as a maximum value was really enough to keep the whole ESR-line with its width of $\Delta\omega/2\pi = 2 \ldots 3$ MHz in a uniformly spin locked condition. The result is plotted in Figure 3. For d_2-TCB in d_{14}-durene as a host (with the 2E-transition centered at 1822 MHz) a pure exponential decay over two lifetimes is obtained. The total decay rate was (36 ± 4) sec^{-1} which is close to the theoretical limitation of (28.5 ± 3) sec^{-1} given above. This is reasonable because the spin lattice relaxation rate should be smaller than 5 sec^{-1} at 2 °K, and no extraordinary additional contribution should occur in the rotating frame. For the case of h_2-TCB in h_{14}-durene (with the 2E-transition centered at 1744 MHz) a nonexponential decay with an initial decay rate of (63 ± 10) sec^{-1} was obtained. This is surprising because here the total decay rates of τ_y and τ_z are the same and the spin
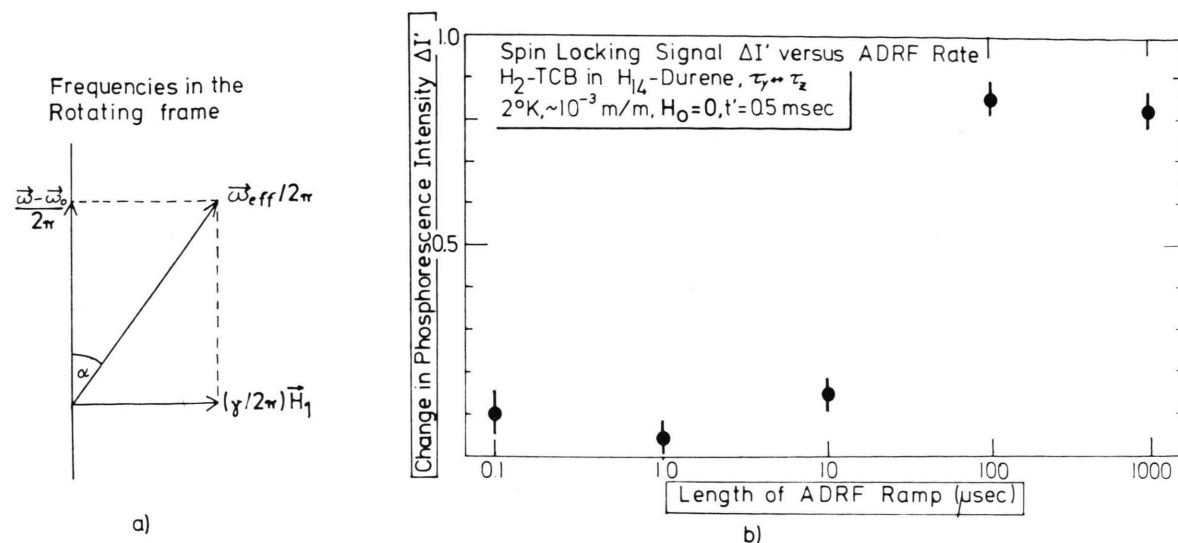
Fig. 2. a) Effective frequency $\omega_{\text{eff}}/2\,\pi$ in the rotating frame as a vector sum of $(\gamma/2\,\pi)\,H_1$ and the distance from resonance $(\omega-\omega_0)/2\,\pi$. The local fields due to interaction of the triplet spin with other spins are neglected. b) Variation of the spin locking signal $(\Delta I')$ with respect to the ADRF ramp time $(\gamma/2\,\pi)\,H_1$ was lowered from 5 MHz to below 10 kHz. Ramp times as low as 100 μsec may be used in practice.
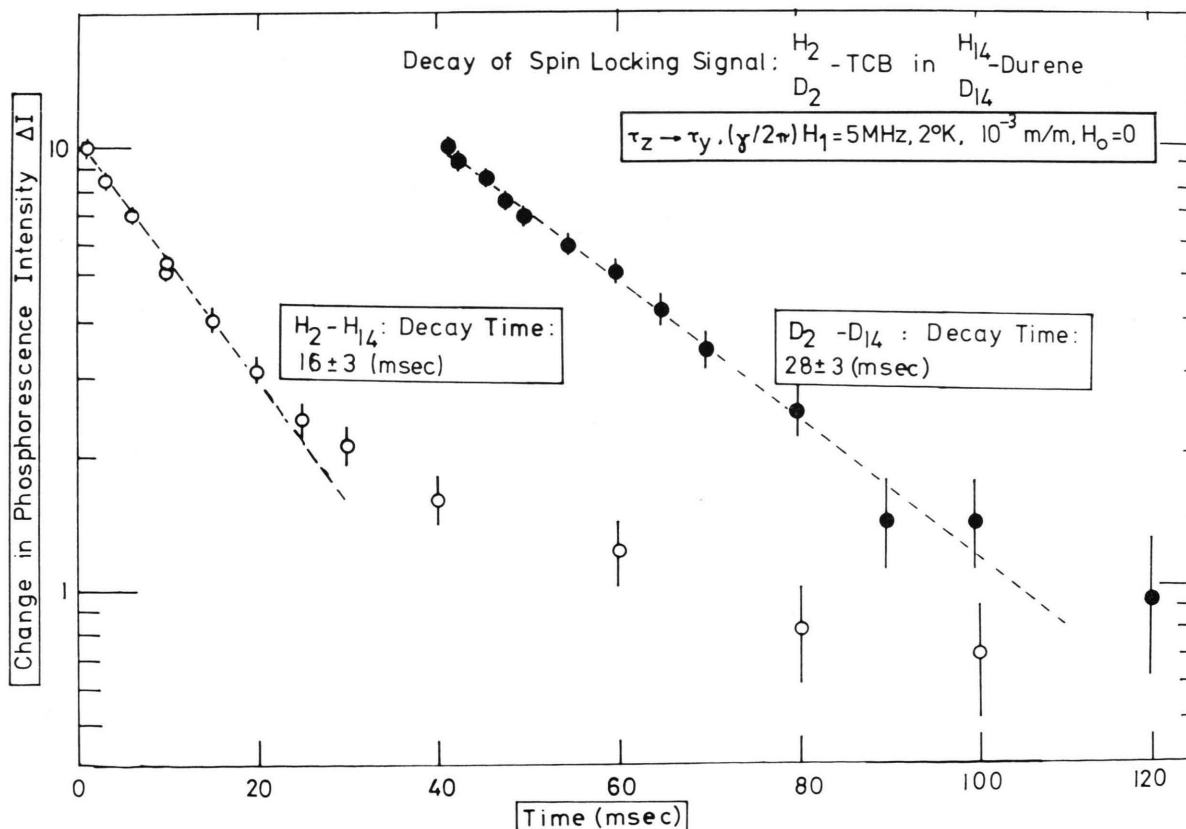

Fig. 3. Decay of the spin locking signal ΔI with time t at $(\gamma/2\,\pi)\,H_1=5$ MHz. The decay is clearly exponential in the d_2-d_{14} case but not so in the h_2-h_{14} case. This is interpreted as a cross relaxation to the protons already at high $(\gamma/2\,\pi)\,H_1$ (but compare also Ref. [6a]).

lattice relaxation rates in the laboratory frame should not be shorter either. In the light of the cross relaxation experiments described below it seems that the nonexponential decay is caused by cross relaxation between triplet spins and proton spins and that the process is different in different parts of the ESR-line [6c]. In another experiment the concentration of h_2-TCB in h_{14}-durene was reduced from the usual 10^{-3} mol/mol to 10^{-4} mol/mol and no change occurred within the error limits. Thus, effects due to interactions between guest molecules could be excluded. In conclusion $(\gamma/2\pi)H_1 = 5$ MHz is sufficient for measuring rates faster than 17 sec^{-1} in the $d_2 - d_{14}$ case and rates faster than 33 sec^{-1} in the $h_2 - h_{14}$ case, and slow cross relaxation must be taken into account in the $h_2 - h_{14}$ case.

3.3. Adiabatic Demagnetization in the Rotating Frame (ADRF)

To test the condition for adiabaticity the ramp time for reducing H_1 was varied. The corresponding spin locking signal heights are plotted in Figure 2 b. There $(\gamma/2\pi)H_1$ was changed linearly from 5 MHz to below 15 kHz and after a time as short as 0.5 msec returned to its original value to minimize cross relaxation. It seems evident from these results that a ramp time of 100 μsec is below enough to ensure adiabaticity for practical applications.

Theoretically the correct condition for adiabaticity is: The change of the direction of the effective frequency $\omega_{\text{eff}}/2\pi$ in the rotating frame has to be slow compared with its absolute value [15]. From the definitions of Fig. 2 a this gives

$$|\,d\alpha/dt\,| \ll \omega_{\text{eff}}. \qquad (9)$$

The condition is most severe for parts of the line with small $|\omega - \omega_0|/2\pi$. If one takes into account nonadiabaticity in a range as large as $|\omega - \omega_0|/2\pi < 100$ kHz and uses $<$ instead of $\ll$ in (9), a brief calculation yields about 100 μsec as the shortest allowed ramp time. Obviously nonadiabaticity in the center part does not mean a complete loss of the magnetization. An experimental justification of using that conveniently short ramp time instead of a longer one is given by the cross relaxation experiments described later. All of these proved to be quite insensitive to changes to longer ramp times.

3.4. Phosphorescence Light Level Change at low H_1-fields

The phosphorescence light level during a long spin locking pulse with high H_1-fields $\gamma H_1 > \Delta\omega$ changes in the same manner as during a normal saturation pulse with the same H_1-field. When H_1 is adiabatically changed or switched off, the light level goes to a new steady state equilibrium value with time constants like those following a change in H_1 or following the end of a saturation pulse. If the ESR-line is not in a uniformly spin locked condition, population and depopulation in the wings of the line (with ω_{eff} not perpendicular to $\{0, 0, \omega_0\}$) create different populations in τ_y and τ_z. This pseudomagnetization, however, does not contribute to a population difference in ψ_1 and ψ_2 as long as the H_1-field is switched on abruptly or adiabatically at the center of the line $\omega = \omega_0$. The beginning of the strong r.f. irradiation simply leads to equal population of τ_y and τ_z and a corresponding increase in light intensity occurs.

So far the light level changes are not consequent of the spin locked condition. The spin locking manifests itself only by the light change due to the last $\pi/2$-pulse.

When H_1 is switched on adiabatically with a frequency ω belonging to the wings of the ESR-line, the pseudomagnetization along $\{0, 0, \omega_0\}$ is adiabatically trained along H_1 and contributes to the spin locking signal. But this part increases with time t or t' and thus may be clearly distinguished from the signal of interest.

4. Cross Relaxation Experiments Between Triplet Spins and Nuclear Spins

Cross relaxation is expected to be more efficient if the participating spins are as close as possible to each other and it seemed sensible to give primary consideration to cross relaxation between triplet spins and nuclear spins rather than between the triplet spins themselves. For a systematic study of the total spin Hamiltonian the hydrogen isotopes were varied in both the TCB and the durene host. As already mentioned, this isotopic substitution does not affect population and depopulation of the triplet substates.

In Fig. 1 c the pulse sequences for spin locking with small $(\gamma/2\pi)H_1$ were applied to the 2E-transi-

tion of d_2-TCB in d_{14}-durene and the decay of the spin locking signal proved to be strongly nonexponential with time for small $(\gamma/2\pi)H_1$, e.g. 100 kHz (Figure 1 c). For the purpose of discussion the spin locking signal $\Delta I'$ is plotted against $(\gamma/2\pi)H_1$ with the fixed coupling time t' as a parameter (Figure 1 d). The complete set of results is given in Figure 4 b. Those for d_2-TCB in d_{14}-durene indicate maximum losses of $40\ldots50\%$ of the spin locking signal. They are largest below 500 kHz and the fastest loss rate is smaller than 1000 sec^{-1}. These fastest loss rates occur in the range with the largest losses.

For h_2-TCB in h_{14}-durene the results are remarkably different (Figure 4 a). The maximum losses are up to 70%, they are largest below 200 kHz and the fastest loss rates are larger than 3300 sec^{-1}. The

fastest loss rates are found below 100 kHz, also in the range with the largest losses.

For d_2-TCB in h_{14}-durene (Fig. 4 c) the maximum losses are around $50\ldots60\%$ at frequencies around 100 kHz. However, the fastest loss rates of more than 1000 sec^{-1} occur below 32 kHz, not in the range of highest losses. This range with largest losses has smaller loss rates ranging from 330 sec^{-1} to 100 sec^{-1}.

5. Discussion of the Cross Relaxation Experiments

The losses of the spin locking signal were found to be strongly dependent on $(\gamma/2\pi)H_1$ and on isotopic substitution. To explain these results by cross relaxation effects a model of an electronic triplet spin state located on only one molecule is used. The triplet state should not interact with other electronic triplet states but only with nuclear spins on the same or neighbouring molecules. In the absence of external magnetic fields (r. f. field off) the triplet spin S and the nuclear spins I are described by the Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{SS} + \mathcal{H}_{SI} + \mathcal{H}_{II} + \mathcal{H}_{QI}. \qquad (10)$$

$\mathcal{H}_{SS}$ is the usual electronic triplet zero field splitting operator.

$\mathcal{H}_{SI}$ represents the sum of the hyperfine coupling of the triplet spin to all nuclear spins. Here we have four nuclear spin species: ^{1}H, ^{2}H, ^{35}Cl, ^{37}Cl.

$\mathcal{H}_{II}$ represents the sum of the dipolar coupling of each pair of nuclear spins. Indirect coupling is neglected.

$\mathcal{H}_{QI}$ is the quadrupolar splitting of nuclei with $I \geq 1$; in the usual notation we have (with the asymmetry parameter η):

$$\mathcal{H}_{QI} = \{e^2 q Q / 4 I (2 I - 1)\} + \eta (I_x^2 - I_z^2)\}. \qquad (11)$$

Formally, $\mathcal{H}_{SS}$ is just a special case of $\mathcal{H}_{QI}$ with $I = 1$, where D, E would replace the quantities

$$3/4\, e^2 p\, Q, \quad 1/4\, e^2 q\, Q\, \eta. \qquad (12)$$

In zero magnetic field the quenching of spin-spin-interactions has to be considered. It is known from integer spins that the dipolar coupling between them and to other spin species is greatly reduced in first order [16]. The same is true for the hyperfine coupling
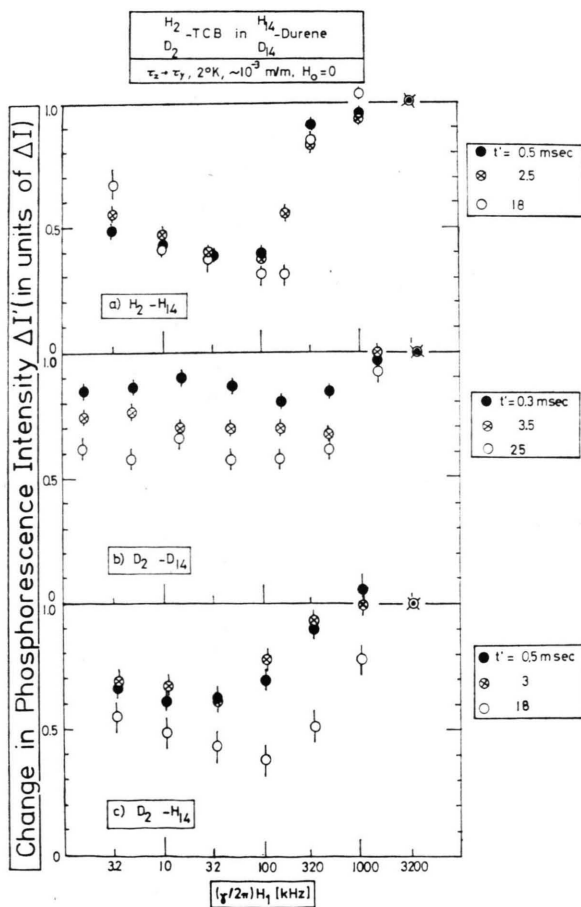

Fig. 4. Decay of the spin locking signal $\Delta I'$ in units of ΔI as a function of $(\gamma/2\pi)H_1$ with the contact time t' (the time during which H_1 is low) as a parameter. This way of plotting the results is also explained in Figure 1 d).

of the integer electronic triplet spin and nuclear spins.

When a magnetic field H_0 is applied the second moment of the transition changes [17]. For a spin $S = 1$ or $I = 1$ the quenching is lifted according to the factor:

$$(2 \gamma H_0/\varDelta E)^2 \{1 + (2 \gamma H_0/\varDelta E)^2\}^{-1} . \quad (13)$$

γ is the gyromagnetic ratio for the spin in question, $\varDelta E$ is equal to one of the zero field transition energies depending on whether or not the external field is parallel to one of the principal tensor axes of $\mathcal{H}_{SS}$ or $\mathcal{H}_{QI}$.

This first order quenching is also lifted when $\varDelta E = 0$, e. g. when $\eta = 0$, as can be estimated from the factor given above (for an electronic triplet state this means $2 E = 0$). In the case of $E \neq 0$ in zero field, the electronic triplet states have only the second order hyperfine splitting, which is typically of the order of $1/30$ that of the unquenched splitting in high field [18]. It has been shown that the same unquenching factor applies also in the rotating frame [9]. Thus the cross relaxation from the triplet state to the nuclei is expected to be small; even smaller when the nuclei have integer spins too.

At low temperatures and zero magnetic field there is nearly no cross relaxation of the electronic triplet spins to the nuclear spins. However, a transfer of spin polarization by such a route is optimally facilitated by matching the energy levels between the spin species, e. g. by using a spin locking state and creating a new energy difference $\hbar \gamma H_1$ within the electronic triplet manifold. Now it is convenient to use the interaction representation, that is to consider the situation from the rotating frame viewpoint. The transformation matrix is $U = \exp \{- i/\hbar \cdot \mathcal{H}_{SS} \cdot t\}$, and the transformed Hamiltonian is

$$\mathcal{H}^* = U^{-1}(\mathcal{H} + \mathcal{H}_{rf}) U - \mathcal{H}_{SS} ;$$
$$= - \hbar \gamma H_1 I_x + U^{-1} \mathcal{H}_{SI} U + \mathcal{H}_{II} + \mathcal{H}_{QI} . \quad (14)$$

The transition frequencies arising from the $\mathcal{H}_{II}$ and $\mathcal{H}_{QI}$ Hamiltonians for the four nuclear spin species occurring in the sample, are surveyed as follows:

a) For protons in molecular crystals the spectrum of $\mathcal{H}_{II}$ is known to be in the range from zero to around $10 \dots 20$ kHz as was found by measuring the NMR linewidth. For the other nuclear spins in the sample the maximum $\mathcal{H}_{II}$ frequencies belong to the dipolar coupling between these nuclei and the proton spins. These frequencies are lower by a fac-

tor approximately given by their relative gyromagnetic ratios. Their maximum (less than 5 kHz) corresponds to the coupling between proton and deuteron spins.

b) The $\mathcal{H}_{QI}$ for protons is zero. For deuterons it is known to be around 140 kHz in the ground singlet state of paradichlorobenzene [9] with η being very small. Similar values in both the singlet and triplet state of TCB are expected. For ^{35}Cl and ^{37}Cl spins the $\mathcal{H}_{QI}$ frequencies are both around 35 MHz in the excited triplet state of TCB [13], and also about the same in the ground state.

These values must be compared with the $(\gamma/2\pi) H_1$-frequency range from 15 kHz up to 5 MHz which was available in the experiment. Now the following questions arise: what kind of separation of the spin quantum numbers can be made, what kind of energy reservoirs dominate besides $- \hbar \gamma H_1 S_x$ and which of the terms in Eq. (14) can be treated as a perturbation? To answer these questions a detailed theoretical study of $U^{-1} \mathcal{H}_{SI} U$ would be required which, because of the number of nuclear spins involved, is beyond the scope of this work. Here, it is simply noted that $\mathcal{H}_{SI}$ in the nontransformed frame causes the ESR linewidth around $2 \dots 3$ MHz. (Its shape is strongly asymmetric.) One part of the broadening is due to second order hyperfine interaction with more than one proton spin [18], another part is due to hyperfine interaction with chlorine spins [19]. The first part would vanish in the presence of only one spin $I = 1/2$, the second part is already nonzero in the presence of one chlorine spin (^{35}Cl, ^{37}Cl). The broadening due to deuteron spins should be much smaller. Possible effects of the chlorine spins are considered first: Their $\mathcal{H}_{QI}$-frequencies are too large, their $\mathcal{H}_{II}$-frequencies are too small to participate as an energy reservoir in the cross relaxation experiment. The role of $U^{-1} \mathcal{H}_{SI} U$ is less obvious. The cross relaxation results from the d_2-TCB-triplet in d_{14}-durene sample (Fig. 4b) show that any cross relaxation rate due to $U^{-1} \mathcal{H}_{SI} U$ must be smaller than $1000 \sec^{-1}$. In the $h_2 - h_{14}$ case, however, $U^{-1} \mathcal{H}_{SI} U$ for I: chlorine spins is the same; but here the results suggest that $U^{-1} \mathcal{H}_{SI} U$ can act at most as an energy reservoir with frequencies below 300 kHz. An exceptional change of the spin locking losses at that frequency did not occur in the $d_2 - d_{14}$ case. Thus, any cross relaxation due to such an energy reservoir can occur only at frequencies below 300 kHz with rates below $1000 \sec^{-1}$.

The effect of the Hamiltonian operators belonging to proton and deuteron spins is as follows: In the $h_2 - h_{14}$ case $(U^{-1} \mathcal{H}_{SI} U + \mathcal{H}_{II})$ for I: proton spins gives remarkably fast cross relaxation rates up to 100 kHz. The transition frequencies to $\mathcal{H}_{II}$ itself obviously are too small, so only the sum of these two operators can be considered and a separation is not possible. If in the $d_2 - d_{14}$ case $(U^{-1} \mathcal{H}_{SI} U + \mathcal{H}_{II})$ were important, maximum relaxation rates should occur at lower frequencies according to the lower gyromagnetic ratio of the deuteron; the high frequencies found in that case prove that $\mathcal{H}_{QI}$ (deuteron) has to be the energy reservoir. Indeed the $\mathcal{H}_{QI}$ frequencies lie in the range of $(\gamma/2\pi) H_1$-values where the fastest cross relaxation takes place. This fastest rate is remarkably small compared with that occurring in the $h_2 - h_{14}$ case, and is just as expected for the double quenching of the interaction between the integer triplet spins and the integer deuteron spins.

In the $d_2 - h_{14}$ case the region below 32 kHz with its fast rate should be attributed only to $(U^{-1} \mathcal{H}_{SI} U + \mathcal{H}_{II})$ for I: proton spins. However, due to the larger distance between triplets and protons the cross relaxation rates are smaller than in the $h_2 - h_{14}$ case, and also the transition frequencies are approaching the frequencies belonging to $\mathcal{H}_{II}$. The small rates at higher frequencies obviously involve $\mathcal{H}_{QI}$, but the cross relaxation range extends to much higher frequencies than in the $d_2 - d_{14}$ case. This forbides to separate $\mathcal{H}_{QI}$ from the rest of $\mathcal{H}$.

Besides the fast loss rates in the $d_2 - h_{14}$ case there are loss rates around the quadrupolar frequency of the deuteron which are much smaller than in the $d_2 - d_{14}$ case. The strong dependency on isotopic substitution emphasises the importance of the nuclear spins on both the triplet state molecule and neighbour molecules.

6. Inhomogeneity of the ESR Line

In the following it is shown how the experiments demonstrate that the ESR line is inhomogeneous and some conclusions are drawn from that.

The decay rate of the spin locking signal for $(\gamma/2\pi) H_1$-values as small as 3.2 kHz can be taken as the decay rate for $H_1 = 0$, i. e. the decay of the ADRF state. If effects during the time of the first msec with $H_1 = 0$ are neglected, the decay rate of the state is of the order of the decay rate of the zero

field triplet substates. The decay of the ADRF state itself has been investigated in a different manner [20] for the triplet state of d_2-TCB in d_{14}-durene. This rate also proves to be very close to the decay rates of the triplet sublevels participating in the transition.

On the other hand the ESR line broadening in these zero field triplet states is caused mainly by hyperfine interaction with nuclear spins. Any change of the nuclear spin configuration would then enhance the decay of the ADRF state. This allows the following conclusions:

a) The nuclei on the molecule carrying the triplet state have a small spin lattice relaxation rate (smaller than $1/2$ of the triplet sublevel decay rate).

b) Any motion of the triplet state away from its molecule of origin is supposed to proceed in jumps with times of less than 10^{-9} sec, which is short compared with the inverse ESR linewidth $2\pi/\Delta\omega$. Hence, when the triplet state changes the molecule it cannot carry with it the same nuclear spin configuration but may have to accept one, and such a time dependence of the hyperfine interaction contributes to the decay rate of the ADRF state. The results presented here exclude any large transfer rate of this type.

Such a shortening of the decay time should be observable in the migration of triplet states out of shallow traps via the exciton band into another shallow trap. In contrast to this, a relaxation along a strong H_1-field already occurs when the triplet state is removed into the exciton band with different zero field triplet splitting [8] and the time in that band exceeds a lower limit ($\sim 10^{-9}$ sec for a splitting of ~ 60 MHz). However, the removal into the exciton band does not necessarily include triplet state transfer to another location.

The results in Fig. 4 not only indicate small decay rates of the ADRF state but also comparable decay rates for spin locking with small $(\gamma/2\pi) H_1$, provided the effects during the first msec are again neglected. In the triplet state of d_2-TCB in h_{14}-durene the decay of the spin locking signal at $(\gamma/2\pi) H_1$-values of 32 kHz during the first msec was interpreted as a coupling of the triplet spin with proton spins on surrounding molecules. So many protons are surrounding one triplet spin, that if the triplet spins of the whole ESR line were coupled to the

proton spins present, a total loss of the spin locking signal would have occurred. As a consequence mutual energy conserving spin flips between triplet states must have a frequency of less than 1 kHz. The result is expected in zero field for the triplet spin concentrations used (about 1 in 10^4 of the TCB molecules are carrying a triplet state). The experiment is equivalent to a "hole burning" in the ESR line, where a part of the ESR line is saturated with an H_1-field at a fixed frequency and a second weak H_1-field probes the ESR line shape [20]. There, however, a quantitative interpretation seems to be more difficult.

Conclusion

The large gyromagnetic ratio of the electronic triplet spin overcomes the quenching of the hyperfine coupling and allows cross coupling to nuclear spins even at zero field. Experiments with noninteger nuclear spins seem especially appropriate, but integer nuclear spins still show an effect in spite of the double quenching of the hyperfine interaction.

The possibility to probe interactions of nuclear spins which are smaller than the ESR linewidth is remarkable; even if only an estimate of the proton-proton dipolar coupling or the deuteron quadrupolar splitting is obtained so far, this method might serve, in some cases, as a complementary method to ENDOR studies.

The experimental observations confirm that within the lifetime of the triplet sublevels the following effects have to be very small: a) the spin lattice relaxation for nuclei on molecules carrying the triplet state, b) triplet state transfer between TCB-molecules in a concentration of 10^{-3} mol/mol in the host lattice, c) establishment of a common spin temperature at zero field within the electronic triplet spins.

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