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DNP and CIDEP Study of Cross-Relaxation Processes in Short-Lived Radicals in Solution

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Dynamic nuclear polarization (DNP) and chemically induced electron polarization (CIDEP) of transient radicals in solution are measured at L- and X-band frequencies to investigate their electron−nuclear cross-relaxation. It is demonstrated experimentally and theoretically, that a strong multiplet-type electron spin polarization leads to a multiplet-type DNP spectrum with the same relative line intensities as they are observed in the CIDEP spectrum. DNP spectra are found in cases such as this to be separable from the always superimposed SNP (stimulated nuclear polarization) spectra via measurements at different microwave powers. Examination of radicals $(CH_3)_2XC\bullet$ with X = CH_3, OH, D, and $C(O)CH_3$ shows the existence of efficient electron−nuclear flip-flop ($\Delta m = 0$) cross-relaxation for *t*-butyl and 2-hydroxy-2-propyl radicals, whereas for 2-acetyl-2-propyl radicals DNP is absent. The results indicate that phase inversions, observed in time-resolved CIDEP spectra of *t*-butyl and 2-hydroxy-2-propyl radicals, are attributable to an efficient flip-flop electron−nuclear cross-relaxation. The relaxation must result from an internal molecular motion modulating the isotropic hyperfine interaction in these species with a correlation time of $\tau \gg 1$ ps.

1. Introduction

The electron spin system of transient radicals in solution, as a rule, is polarized by the radical pair mechanism (RPM). The polarization is generated in spin correlated radical pairs (RPs) and causes in time-resolved ESR (TRESR) spectra the low-field ESR lines to appear in emission (E) and the high-field ones in enhanced absorption (A), or vice versa, depending on the multiplicity of the RPs and the sign of the exchange interaction.[1] CIDEP is developed in geminate RPs as well as in free diffusive encounters (F-pairs).

In a number of TRESR spectroscopic investigations of radicals created by laser flash photolysis, the spectra have exhibited an E/A polarization pattern at early times after the laser flash, as expected for radicals created from triplet precursors, but an A/E pattern typically 15−40 μs later.[1−12] This behavior has been reported for quite a number of radicals. Although it has turned out later that in many cases the phase inversions have been instrumental in origin, the phenomenon has been found to be genuine for $(CH_3)_2(OH)C\bullet$,[10−12] $(CH_3)_2HC\bullet$,[2,7] and $(CH_3)_3C\bullet$[2,9,11,12] radicals. After a long discussion, the phase change of the CIDEP, observed for these radicals, has been attributed to an efficient electron−nuclear flip-flop ($\Delta m = 0$) cross-relaxation.[10−12]

In the case of efficient cross-relaxation, the polarization transfer between the electron and nuclear spin systems should also generate a considerable nuclear polarization.[13−15] Indeed, some time-resolved CIDNP studies have reported the observation of cross-relaxation induced nuclear spin polarizations in systems involving the 2-hydroxy-2-propyl radical.[13−17] However, a later accurate CIDNP investigation of systems containing *t*-butyl and 2-hydroxy-2-propyl radicals has shown that, for these radicals, there is no detectable cross-relaxation at all in the ^{1}H CIDNP measured in the high magnetic field of an 200 MHz NMR spectrometer.[18] The effects, ascribed to cross-relaxation in the previous investigations of the 2-hydroxy-2-propyl radical, were attributed to side reactions and a fast solvent-dependent nuclear relaxation.[18]

Cross-relaxation due to flip-flop transitions ($\Delta m = 0$) is a well-known phenomenon.[19] Although this effect is rather common in solid-state ENDOR, only a few investigations have been published dealing with radicals in solution. If dominant, this relaxation is caused by stochastic modulation of the isotropic hyperfine interaction *a(t)* and occurs with a rate[19]

$$W(\Delta m = 0) = 2\pi^2 \overline{a^2(t) - \bar{a}^2} \frac{\tau}{1 + \omega^2\tau^2} \qquad (1)$$

For the above radicals which show the phase change of CIDEP, the largest matrix element $\overline{a^2(t) - \bar{a}^2}$ is associated with the CH_3 group rotation. Therefore, the stochastic modulation of this rotation was considered as the main source for the effective cross-relaxation in these species.[10,12] Also, the correlation time, calculated from an experimentally obtained T_{cr} for *t*-butyl radicals, gave a reasonable value of $\tau = 0.2$ ps,[12] close to the inverse collision frequency in liquids. However, if that is the true mechanism, then the cross-relaxation should be visible in

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both EPR and NMR spectroscopy, despite the considerably higher value of ω in the NMR experiment. As there is no cross-relaxation in these radicals at the NMR magnetic field, it follows that: (i) either cross-relaxation results from another internal molecular motion having a longer τ, so that at NMR frequencies the condition $\omega^2\tau^2 \gg 1$ holds, or (ii) the observed CIDEP phase inversion is not caused by cross-relaxation at all and, hence, needs another explanation.

The most direct technique for the investigation of cross-relaxation processes is dynamic nuclear polarization (DNP), i.e., irradiating the EPR transitions of the radicals and detecting the induced changes of nuclear populations by NMR of the diamagnetic reaction products.[20−25] The DNP technique should allow to study the polarization transfer process from electron to nuclear spins by cross-relaxation at the magnetic field strength of the ESR experiment. DNP of short-lived neutral radicals has been studied in a variety of investigations.[20−25] For example, it has been shown[21] that the DNP of the ring protons of *p*-benzoquinone is emissive and is formed due to cross-relaxation with $\Delta m = 2$, whereas for the methyl derivatives of *p*-benzoquinone (*p*-toluquinone and 2,6-dimethyl-*p*-benzoquinone) the DNP is absorptive and generated via scalar cross-relaxation ($\Delta m = 0$), probably induced by modulation of the hfi due to methyl group rotation.[22,23] Thus, it is proven that DNP is a very suitable technique to investigate cross-relaxation mechanisms in transient radicals.

However, there is an intrinsic problem with the DNP experiments on transient radicals in solution. The resonant microwave (mw) irradiation, applied during radical generation and reaction, induces ESR transitions not only in free radicals but also S−T transitions in radical pairs, which give rise to an additional signal, the stimulated nuclear polarization (SNP) signal. In general, the NMR spectra of the reaction products always show both DNP and SNP signals, which have to be separated. In all DNP experiments up to now this did not seem to be a problem because in all reactions, investigated previously in high magnetic field under continuous light illumination, the DNP has been generated by saturation of transitions between Boltzmann populated electron spin levels. Then, all lines in the DNP spectrum have the same sign (positive for scalar cross-relaxation ($\Delta m = 0$) and negative for relaxation due to dipole−dipole interaction ($\Delta m = 2$)), with the relative line intensities in the DNP spectrum being the same as in the ESR spectrum. On the other hand, the SNP spectrum in this case has a multiplet-type structure with the signs of the hyperfine lines determined by the signs of the nuclear spin projections. Using this difference in the structures of the spectra, the SNP and DNP contributions could be separated along simple rules.[21]

However, it is obvious that the shape of the DNP spectrum described above is true only if the populations of the electron Zeeman levels of the radicals are in thermal equilibrium. If the radicals carry a substantial electron spin polarization, then the signs of the resonance lines in the DNP spectrum will be determined by the signs of the electron polarization. For the case of net electron polarization this has already been shown to be true in a low field DNP investigation of radical ion reactions in the presence of electron hopping.[26,27] In laser flash photolysis experiments the radical concentration is usually rather large, the radical lifetime accordingly short and, hence, the electron spin system can carry a rather pronounced RPM induced multiplet polarization. Then, the transferred DNP will be substantially higher than that transferable from a Boltzmann polarization, it will have a multiplet-type structure, and the distinction between the DNP and SNP contribution to the total NMR signal can become a problem. This has not been considered before, and some of the previous DNP/SNP analyses, therefore, may have to be revised because DNP contributions to the NMR signal might have been mistaken as SNP. This point, as well as the possibility of SNP and DNP separation via their different dependence on the mw field amplitude B_1, will also be addressed in this investigation.

2. Theory

A qualitative picture of DNP formation from a net absorptive and multiplet polarized electron spin system is shown in Figure 1a. If the emissive low-field ESR transition is saturated, then $\Delta m = 0$ cross-relaxation leads to an additional loss of α_n and a gain of β_n nuclear spins, whereas the opposite occurs upon saturation of the absorptive high-field ESR line. Thus, a multiplet-type electron spin polarization obviously leads to a multiplet-type DNP spectrum.

To demonstrate the rise of multiplet DNP and to investigate its peculiarities we have calculated DNP spectra and the dependence of their intensity on the electron relaxation and the cross-relaxation time. Radicals having M nuclei with spin I_i and hfi constants a_i have been assumed in the calculation, as well as a radical decay by a kinetics of first order.

The Liouville equation for the density matrix ρ of the radicals is

$$\frac{\partial \rho}{\partial t} = -i[\hat{H}, \rho] - \hat{\hat{R}}\rho - k_{\mathrm{sc}}\rho \tag{2}$$

where $\hat{H}$ is the spin Hamiltonian in a frame rotating with frequency ω, i.e.,

$$\hat{H} = (\omega^{\mathrm{e}} - \omega)\hat{S}_z + \omega_1^{\mathrm{e}}\hat{S}_x - \omega_1^{n}\sum_{i=1}^{M}\hat{I}_{ix} - \omega\sum_{i=1}^{M}\hat{I}_{iz} + \sum_{i=1}^{M}a_i\hat{I}_i\hat{S} \tag{3}$$

$$\omega^{\mathrm{e}} = g_{\mathrm{e}}\beta_{\mathrm{e}}B_0/\hbar$$

$$\omega_1^{\mathrm{e}} = g_{\mathrm{e}}\beta_{\mathrm{e}}B_1/\hbar$$

$$\omega_1^{n} = g_{\mathrm{n}}\beta_{\mathrm{n}}B_1/\pi$$

The Zeeman interaction for the nuclei is neglected. The last term in eq 2 describes the exponential radical decay with rate constant k_{sc}. The superoperator $\hat{\hat{R}}$ represents the electron and the electron−nuclear cross-relaxations of the spin system. The relaxation processes were taken into account via relaxation times T_1 and T_2 for electron as well as $T_{\mathrm{cr}}{}^{\mathrm{dd}}$ ($\Delta m = 2$, for example $\alpha_{\mathrm{e}}\alpha_{\mathrm{n}}\alpha_{\mathrm{n}} \Leftrightarrow \beta_{\mathrm{e}}\beta_{\mathrm{n}}\alpha_{\mathrm{n}}$) and $T_{\mathrm{cr}}{}^{\mathrm{hfi}}$ ($\Delta m = 0$, for example $\alpha_{\mathrm{e}}\alpha_{\mathrm{n}}\beta_{\mathrm{n}} \Leftrightarrow \beta_{\mathrm{e}}\alpha_{\mathrm{n}}\alpha_{\mathrm{n}}$) for cross-relaxation, respectively. For simplification we neglected the dependence of all relaxation times on the nuclear quantum states. This is, of course, not fully correct but it suffices for our model calculation.

The nuclear polarization in the diamagnetic reaction products is given by the population difference of the α_{n} and β_{n} spin states. Thus, for calculation of the nuclear polarization $P_{\mathrm{n}i}$ of the ith transition in the NMR spectrum it is necessary to take the trace over all other nuclei and to compute the population difference of the spin states $\alpha_{\mathrm{n}i}$ and $\beta_{\mathrm{n}i}$ of the nuclei n_i

$$P_{\mathrm{n}} = k_{\mathrm{sc}}\{(Sp_{n_{\mathrm{e}}}(Sp_{\mathrm{e}}\bar{\hat{\rho}}))_{\alpha\alpha} - (Sp_{n_{\mathrm{e}}}(Sp_{\mathrm{e}}\bar{\hat{\rho}}))_{\beta\beta}\} \tag{4}$$

$Sp_{\mathrm{e}}(\bar{\hat{\rho}}(t))$ is the trace of the electron−nuclear spin density matrix $\bar{\hat{\rho}}(t)$, taken over the electron spin states, and $k_{\mathrm{sc}}Sp_{\mathrm{e}}(\bar{\hat{\rho}}(t))$ describes the change of the nuclear density matrix per time unit. $\bar{\hat{\rho}}$ can be obtained from the Laplace transformed of eq 2

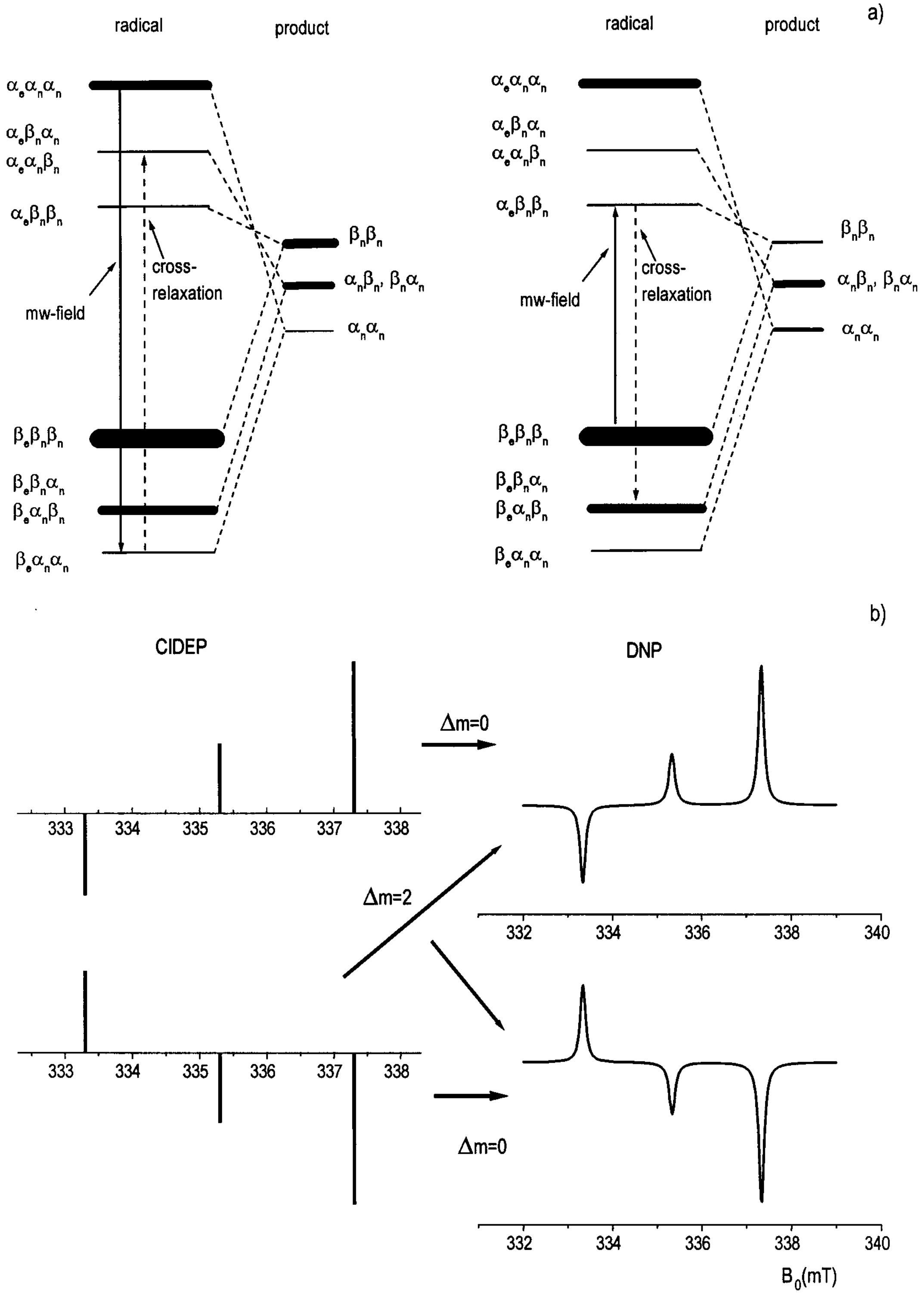

Figure 1. (a) Schematic illustration of the mechanism of multiplet DNP formation by $\Delta m = 0$ cross-relaxation for a radical with two nuclei $I_1 = I_2 = 1/2$ with positive hfi constants $a_1 = a_2$. The solid arrows show mw-induced resonance transitions and the broken ones cross-relaxation transitions. (b) DNP spectra of the spin system in (a) calculated with $a_1 = a_2 = 2.0$ mT, $T_1 = T_2 = 1$ μs, and $k_{sc} = 10^5$ s^{-1} for $\Delta m = 0$ ($1/T_{cr}^{dd} = 0$, $T_{cr}^{hfi} = 10$ μs) and $\Delta m = 2$ ($1/T_{cr}^{hfi} = 0$, $T_{cr}^{dd} = 10$ μs) cross-relaxations in the case of net and multiplet electron polarization.

over time at $s = 0$

$$\hat{\rho} = \int_0^\infty \rho(t)\mathrm{d}t = \bar{\rho}(s = 0) \qquad (5)$$

$$\bar{\rho}(s = 0) = (-i\hat{\hat{L}} + k_{sc}\hat{\hat{E}} - \hat{\hat{R}})^{-1}\,\rho(0)$$

where $\hat{\hat{L}}$ is the Liouvillian corresponding to the spin Hamiltonian, and $\hat{\hat{E}}$ the unity matrix.

Figure 1b shows two DNP spectra calculated for cross-relaxations with $\Delta m = 0$ and $\Delta m = 2$, respectively. Radicals with two equivalent protons have been assumed, as well as an electron polarization consisting of a net absorptive and a multiplet-type contribution. As one can see, the ratios between the line intensities in the DNP spectra equal those of the CIDEP spectra and are of the same sign for $\Delta m = 0$ and of opposite sign for $\Delta m = 2$ relaxation. In the case of a radical decay via

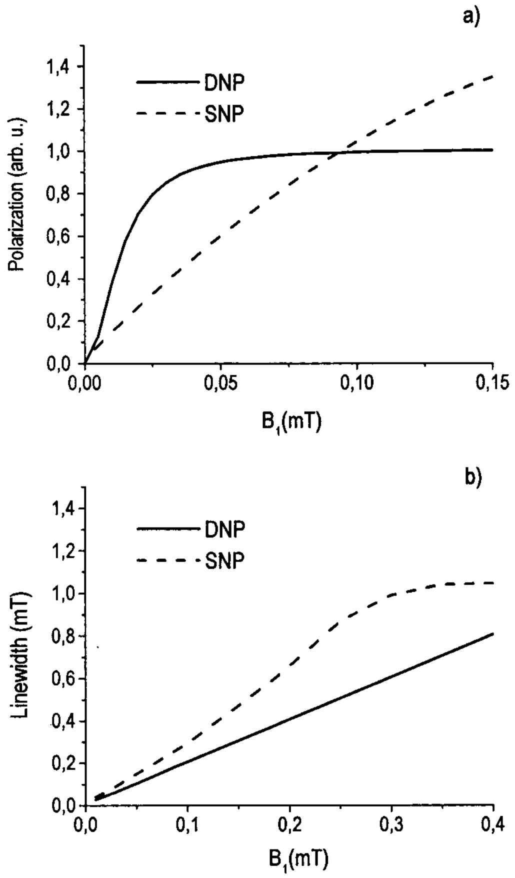

Figure 2. (a) Dependences of SNP and DNP intensities on B_1, calculated for model radical pairs and radicals, respectively, containing one nucleus $I = 1/2$ with coupling $a_{hfi} = 2.0$ mT. Parameters of the SNP computation: 1 ns RP lifetime, rate of scavenging $k_{sc} = 10^5$ s^{-1}, rate of recombination from singlet state 10^{10} s^{-1}. Parameters of the DNP computation: $T_1 = T_2 = 1$ μs, $T_{cr} = 10$ μs, $k_{sc} = 10^5$ s^{-1}. (b) Calculated dependences of SNP and DNP line widths on B_1. The same parameters as in (a) were used for computation.

a kinetics of second order and a significant F-pair contribution to the CIDEP, the relative line intensities in the DNP spectrum would equal those of the CIDEP spectrum when integrated over time.

As has already been mentioned, a resonant mw irradiation affects the nuclear polarization of the diamagnetic products via two mechanisms, (i) inducing ESR transitions in the free radicals (DNP) and (ii) inducing singlet−triplet conversion in RPs (SNP). The SNP spectral shape at low B_1 field amplitudes is very similar to the shape of the multiplet type DNP spectrum. Nevertheless, a separation of both contributions is still possible because their line widths and their intensities depend on the B_1 amplitude in different ways.[26] The DNP line width is close to $2B_1$ for $B_1 > 1/T_1+1/T_{cr}$, whereas the SNP line width is determined by the lifetime of the RPs and exceeds $2B_1$ substantially (see Figure 2b). Dependences on B_1 of the SNP and DNP intensities are shown in Figure 2a. They have been calculated for a model radical pair and model radical, respectively, containing only one nucleus $I = 1/2$. The DNP signal becomes saturated at $B_1 > 1/T^*$, where $1/T^* = 1/T_1 + 1/t_l$ (T_1 being the electron relaxation time and t_l the radical lifetime), whereas the SNP intensity increases with B_1 up to values comparable with the hfi constant in the RP. The dependence of SNP spectra on the B_1 field has been studied before.[26] For the calculation here, we have used the analytical formula, which has been given by Michailov et al.[26b] It is emphasized that the calculations have been performed for model cases in order only to demonstrate that saturation takes place at different B_1 values for SNP and DNP. The SNP and DNP intensities, of course, depend on a variety of parameters such as the lifetimes of the RPs and radicals, their electron and electron−nuclear cross-relaxation times, etc. Thus, for different chemical systems the ratios between SNP and DNP intensities will in general be different.

3. Experimental Section

DNP Experiments. Previously described setups have been used for DNP measurements at L-band[27] and X-band frequencies.[28] The sample solutions were irradiated by excimer laser pulses (Lambda Physics COMPex, $\lambda = 308$ nm, 20 ns pulse duration) while slowly flowing through a quartz cell inside the mw cavity, positioned in a variable magnetic field. Afterward they were transferred in fast flow through a capillary into the probe head of an NMR spectrometer, to keep relaxation of the nuclear polarization at a minimum. For the L-band measurements a homemade mw cavity with resonance frequency $f =$ 1530 MHz and a Bruker MSL-300 NMR spectrometer were used. Standard ESR cavities (Bruker ESP380-1052 DLQ-H for nonpolar and JEOL JES−RE1X for polar solvents) and a JEOL JNM-GSX270 NMR spectrometer were employed for the studies at X-band frequency ($f = 9329$ MHz). In time-resolved experiments the dependence of the polarization on a variable time delay between laser and mw pulse was investigated. The duration of the mw pulse was 10 μs with a pulse edge of 20 ns. The DNP spectra were obtained by measuring the difference of an NMR line amplitude with and without resonant mw irradiation, and plotting this difference versus the external magnetic field. The difference we denote as DNP intensity I_{DNP} and the NMR line amplitude without mw irradiation as CIDNP intensity I_{CIDNP}.

Time-Resolved ESR (TRESR) Experiments. Details of our experimental setups for L-band[29] ($f = 1901$ MHz) and X-band[11,12] ($f = 9400$ MHz) TRESR measurements have also already been given elsewhere. Sample solutions were irradiated at $\lambda = 308$ nm by pulsed excimer lasers (Lambda Physics). In the L-band experiments a cylindrical quartz cell (2 mm inner diameter) and a homemade loop-gap resonator were used. The microwave circuit of the JEOL L-band ESR system (ER812704) was improved for high sensitivity detection of the TRESR signal with reduced noise from the microwave devices. The TRESR spectra were accumulated in a digital storage oscilloscope (LeCroy 9430).

Compounds and Sample Solutions. Within this work the electron−nuclear cross-relaxation in three radicals has been investigated, namely in *t*-butyl, 2-hydroxy-2-propyl, and 2-acetyl-2-propyl radicals. They are listed in Table 1 together with the parent compounds from which they have been generated by photolysis and the solvents that have been used. The photochemistry of these compounds is well-known (see references given in Table 1). After excitation in the n-π^* absorption region at 308 nm, followed by intersystem crossing, the symmetrical ketones I and II undergo α cleavage from the triplet state to yield a geminate acyl−alkyl radical pair, which may either recombine to the starting compound, terminate by disproportionation, or separate into freely diffusing particles. The acyl radicals decarbonylate to CO and the corresponding alkyl species with rate constants $k_{-co} = 4 \times 10^5$ s^{-1} for I[30] and $k_{-co} = 2.4 \times 10^7$ s^{-1} for II[16] at room temperature. The freely diffusing radicals also terminate to combination or disproportionation products upon collision. Results of a few preliminary experiments

TABLE 1: List of Parent Compounds, Solvents, Generated Radicals, and References Regarding the Photochemistry

	compound	solvent	radical	ref	I_{DNP}/I_{CIDNP}[a]
I	$((CH_3)_3C)_2CO$	C_6D_6, CH_3CN	$(CH_3)_3C\bullet$	30	0.4
II	$((CH_3)_2COH)_2CO$	$CHCl_3$, C_6D_6	$(CH_3)_2(OH)C\bullet$	31	0.5
III	$(CH_3)_2ClCC(O)CH_3$	C_6D_{12}	$(CH_3)_2(CH_3C(O))C\bullet$	32, 33	0

[a] I_{DNP}/I_{CIDNP} is the ratio of the DNP intensity (induced with a mw field amplitude of $B_1 = 0.26$ mT) to the CIDNP intensity, measured at L-band frequency on the $m_I = -3/2$ and $m_I = -1$ DNP resonances of the radicals I and II, respectively.

examining the cross-relaxation in isopropyl radicals are also reported here. These species have been generated by photolysis of diisopropyl ketone and α,α′-dideutero-diisopropyl ketone, which follow the same reaction scheme as the ketones I and II.

The photolysis of compound III seems to consist of a primary Cl elimination[32,33] followed by fast hydrogen abstraction from the solvent (cyclohexane) by the Cl atom. On the time scale of our experiments the reaction includes the formation of a geminate radical pair consisting of a cyclohexyl and 2-acetyl-2-propyl radical. The combination and disproportionation products of these two species are observed in the NMR spectra.

Di-*t*-butyl ketone and diisopropyl ketone were purchased from Aldrich. α,α′-Dideutero-diisopropyl ketone was prepared from diisopropyl ketone by boiling in 50 times excess of D_2O in the presence of dried K_2CO_3. 2,4-Dihydroxy-2,4-dimethylpentane-3-one (II) and 2-chloro-2-methylbutane-3-one (III) were synthesized as described in ref 34. Benzene-d_6 (for DNP, Izotop (Russia) or Aldrich), benzene-h_6 (for ESR, Kanto Chemical), and cyclohexane-d_{12} (Izotop, Russia) were distilled before use. Acetonitrile-d_6 (Aldrich) and acetonitrile-h_6 (Kanto Chemical) were dried with phosphoric anhydride (Wako) and distilled. Sample solutions were ca. 0.007 M of I and II and 0.02 M of III. All solutions were deoxygenated by bubbling with nitrogen, argon, or helium gas before measurement.

4. Results and Discussion

***t*-Butyl Radical.** As has been pointed out above, the experimentally observed mw-induced nuclear polarization spectra contain both SNP and DNP contributions, which have to be separated in order to obtain the DNP fraction, which solely is a measure for the cross-relaxation in the radicals. An example for the separation via the dependence of the nuclear polarization (NP) on the mw field amplitude B_1 is given in Figure 3. Part (b) shows for three values of B_1 the mw-induced NP, observed at 54.6 mT (L-band) after photolysis of di-*t*-butyl ketone. The spectrum has been measured on the NMR line of the CH_3 groups of the disproportionation product $(CH_3)_2C{=}CH_2$ and is given as the difference of the CH_3 line intensity with and without mw irradiation, divided by the latter one. At small microwave field amplitudes $B_1 < 0.2$ mT, the spectral shape is E/A and is determined by the DNP contribution. With increasing B_1 the SNP contribution (A/E) becomes increasingly important and starts to dominate the spectrum. At $B_1 = 1$ mT, the SNP is already substantially larger than the DNP, and the spectrum consists of the broad A/E SNP contribution superimposed by the E/A DNP spectrum. For comparison, Figure 3a gives pure SNP spectra in dependence on B_1. They have been calculated for *t*-butyl-pivaloyl RPs, which solely determine the flanks of the total SNP spectrum. Especially there, the differences between the SNP and the experimentally observed NP spectra, in structure and line positions, are clearly visible up to mw field amplitudes of $B_1 \approx 1$ mT. Thus, in principle the DNP contribution can always be separated unequivocally by just fitting the total NP spectra as superpositions of SNP and DNP spectra with relative weights varying with B_1. But in many cases even this is not necessary because the spectrum can be measured at B_1 fields, which are low enough to be dominated by only the DNP signal. This has been the case in all of our measurements.

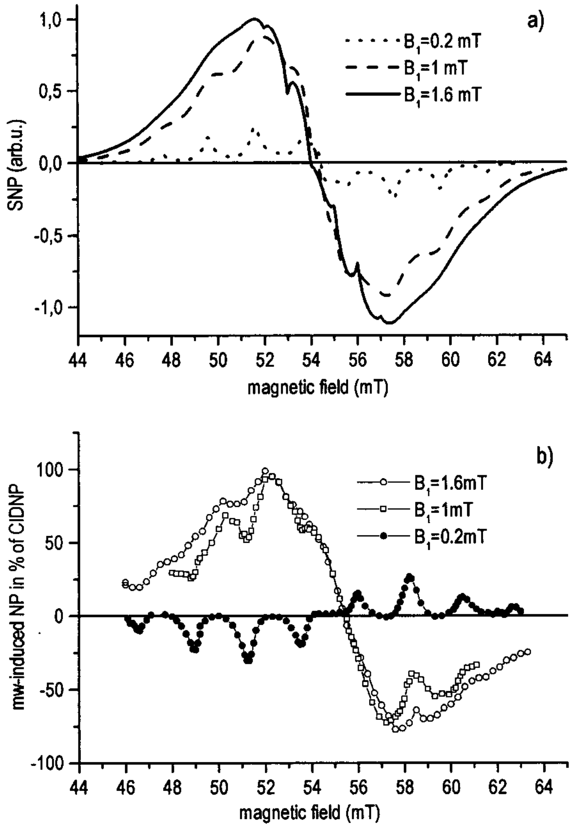

Figure 3. (a) Calculated SNP spectra of the RP $(CH_3)_3CC(O)\bullet$ $\bullet C(CH_3)_3$ at different B_1. (b) Experimentally observed NP spectrum detected after photolysis of I on the CH_3 proton resonance of $(CH_3)_2CH{=}CH_2$ for different B_1.

Figure 4a,b gives the inner eight ESR resonances of *t*-butyl radicals, as they are observed by X- and L-band TRESR briefly after laser flash irradiation of di-*t*-butyl ketone (I) solutions. They exhibit an E/A multiplet-type polarization caused by the RPM and an additional net polarization, the origin of which is not quite clear. Interestingly, this net polarization changes sign when going from X- to L-band frequency, which might indicate some S−T mixing at low magnetic fields. The DNP spectra obtained at X- and L-band frequencies after flash photolysis of di-*t*-butyl ketone are shown in Figure 4c,d. The ratios of the resonance line intensities are found to be exactly the same in the CIDEP and corresponding DNP spectra. This fact unambiguously proves that the electron polarization is effectively transferred to the nuclear polarization via a $\Delta m = 0$ cross-relaxation process.

2-Hydroxy-2-propyl Radical. Also the ESR lines of 2-hydroxy-2-propyl radicals show a superposed E/A RPM and net polarization when observed by X- and L-band TRESR spectroscopy directly after flash photolysis of II (see Figure 5a,b). For this compound the net absorption of the radicals is known to result from the triplet mechanism.[18] The reduction of the net absorption in the L-band spectrum again points to a marked

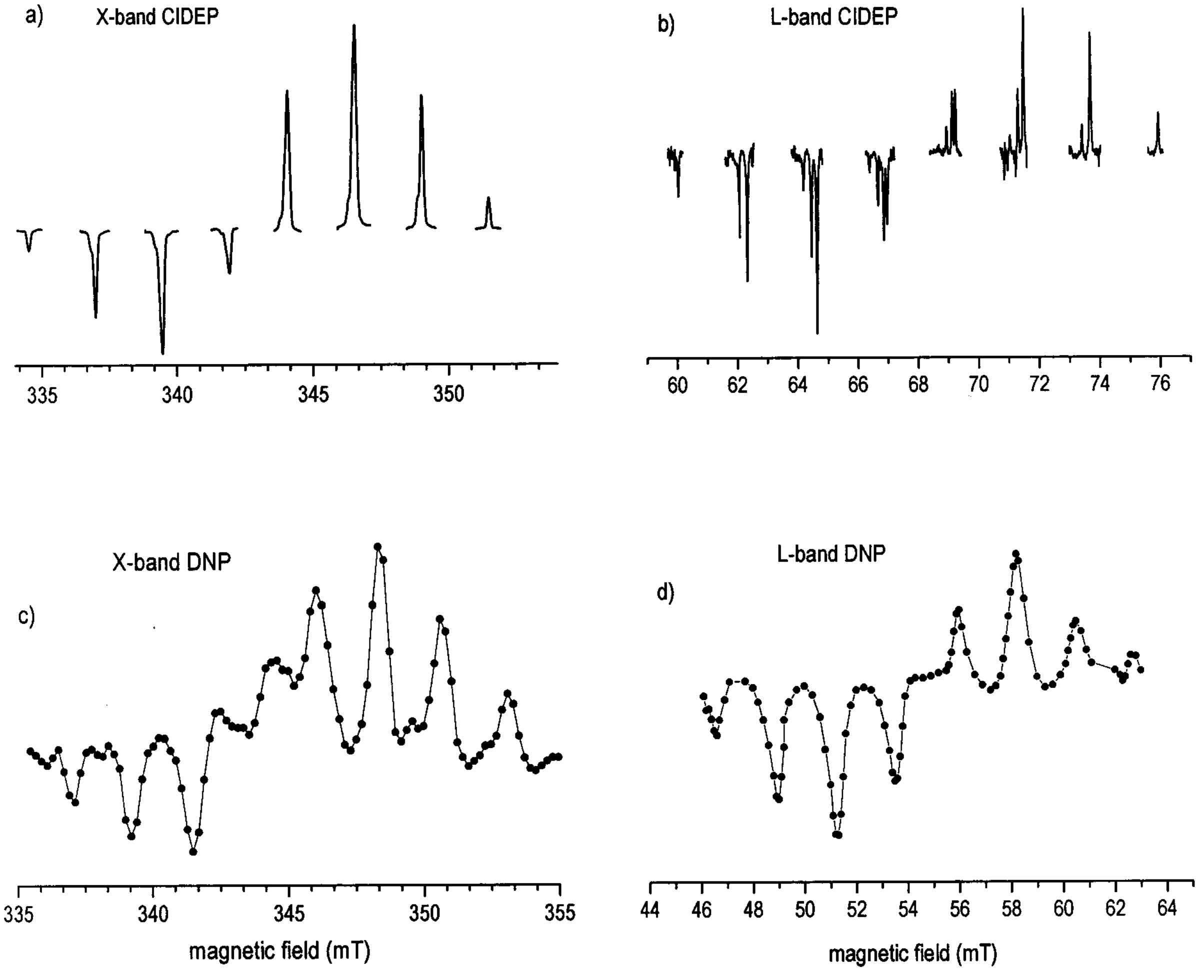

Figure 4. TRESR and DNP spectra detected after photolysis of I in benzene. (a) X-band TRESR spectrum integrated from 0.5 to 1.5 μs; (b) L-band TRESR spectrum integrated from 1.5 to 2 μs; (c) X-band and (d) L-band DNP spectra detected on the proton resonance of $(CH_3)_3CC(CH_3)_3$ for $B_1 = 0.2$ mT.

contribution of the S−T level crossing mechanism, which, in fact, should become more pronounced if the magnetic field is decreased. The mw-induced nuclear polarization spectra detected after photolysis of II consist of SNP and DNP contributions, and the changes in the spectral shape with increasing B_1 are similar to those having been discussed already for the *t*-butyl radical. Figure 5c,d gives the DNP spectra, detected after photolysis of II on the NMR lines of acetone at low B_1. Nearly identical spectra have been obtained also on the CH_3 resonance of the disproportionation product $CH_2{=}C(OH)(CH_3)$. At both frequencies the relative intensities of the hyperfine lines in the DNP spectra closely follow those observed in the corresponding TRESR spectra. Thus, also in 2-hydroxy-2-propyl radicals there is an effective $\Delta m = 0$ cross-relaxation transferring the CIDEP into nuclear polarization.

As the DNP in the transient free radicals is induced by the effect of the resonant mw field on the nonequilibrium electron polarization, the dependence of the DNP on time should reflect the time dependence of the electron polarization. We have checked this for both *t*-butyl and 2-hydroxy-2-propyl radicals by measuring the dependence of the DNP signals on a variable time delay between the laser and a microwave pulse (10 μs length). In fact, the decrease of the DNP signals with increasing delay time was found to occur on a time scale ($\approx 1-2$ μs) similar to that for the CIDEP decay observed in the TRESR experiments. Unfortunately, the time-resolved DNP signal did not allow a determination of the cross-relaxation time, because the decay of the CIDEP is determined by a variety of much faster processes such as T_1 relaxation, Heisenberg spin exchange, and radical termination. The cross-relaxation has to be assumed to proceed at least 1 order of magnitude slower, to explain the sign change of the CIDEP described in previous work.[12] The amount of polarization, which in *t*-butyl and 2-hydroxy-2-propyl radicals is transferred via cross-relaxation to the nuclear spin system, is characterized in Table 1 by the numbers given there for the intensity ratio I_{DNP}/I_{CIDNP}.

Isopropyl Radical. We have also made a few DNP measurements during photolysis of diisopropyl ketone, because previous TRESR studies of this system have revealed also a sign inversion of the CIDEP of isopropyl radicals.[6] However, only a surprisingly small mw-induced nuclear polarization of the reaction products was observed. Probably, this is mainly caused by the opposite signs of the hfi constants of the α- and β-protons. They lead to a SNP spectrum with opposite signs for the protons of the CH_3 groups and the CH proton, in contrast to the compounds I and II, where all protons deliver polarization contributions of equal sign into the same NMR line of the diamagnetic products. In addition, during transfer of the diamagnetic products to the NMR spectrometer probe there will be in zero magnetic field a partial polarization transfer between the CH_3 and CH groups, which will lead to a decrease of the observable polarization.[35] In fact, some preliminary experiments with the deuterated ketone $(CH_3)_2CDCOCD(CH_3)_2$ revealed a noticeable influence of the polarization transfer. For the deuterated compound the intensity of the mw-induced nuclear polarization was considerably larger, and the spectra detected

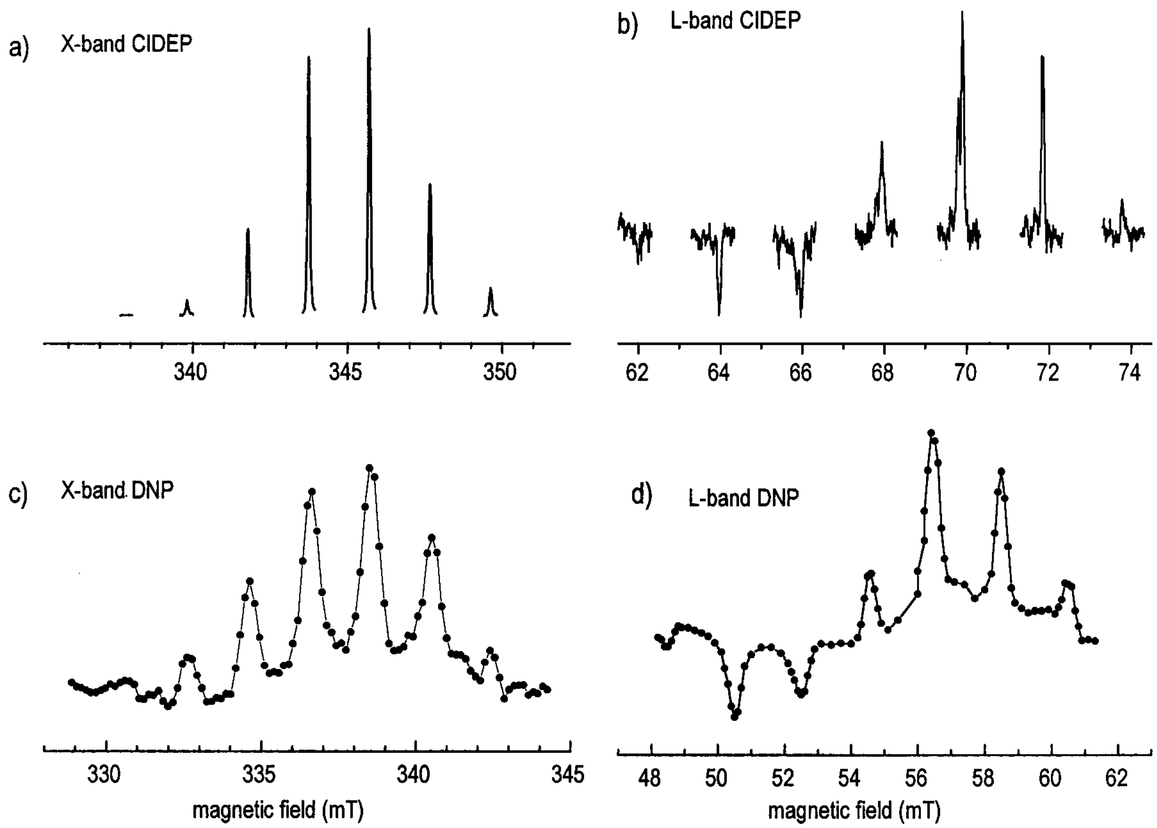

Figure 5. TRESR and DNP spectra detected after photolysis of II in benzene. (a) X-band TRESR spectrum integrated 0.5 to 1.5 μs; (b) L-band TRESR spectrum integrated from 1.2 to 2 μs.; (c) X-band and (d) L-band DNP spectra detected on the NMR line of acetone for $B_1 = 0.2$ mT.

on the CH_3 group NMR lines of propane CH_3CDHCH_3 and propene CH_3CDCH_2 showed both a multiplet E/A DNP at low B_1 and an A/E SNP at high B_1. However, these systems need additional investigation before any definite conclusions can be drawn concerning the extent of flip-flop cross-relaxation taking place in isopropyl radicals.

2-Acetyl-2-propyl Radical. TRESR spectra taken after photolysis of compound III in cyclohexane show the presence of both cyclohexyl and 2-acetyl-2-propyl radicals. At early and later times after the laser flash they exhibit an E/A multiplet-type electron spin polarization superimposed by some net absorption. The 2-acetyl-2-propyl radical does not show any phase inversion of the initial E/A multiplet electron polarization.[11] Thus, one would expect the $\Delta m = 0$ cross-relaxation in this radical to be at least less pronounced than in the species discussed above. Indeed, analysis of the mw-induced nuclear polarizations on nine lines in the NMR spectrum of the reaction products did not give any indication for DNP at X-band and L-band frequency. The nuclear polarizations induced in all in-cage and escape products could be accounted for solely on the basis of the SNP effect. Some examples are given in Figure 6a,b. Figure 6b shows two normalized mw-induced NP spectra observed on proton resonances of the predominant cage products $CH_2{=}(CH_3)CC(O)CH_3$ and $(CH_3)_2C(C_6D_{11}){-}C(O)CH_3$. They are satisfactorily described by the SNP spectrum calculated for in-cage products of RPs consisting of a 2-acetyl-2-propyl and a cyclohexyl radical. Also, the mw-induced nuclear polarization spectra observed on the NMR lines of the escape products $(CH_3)_2CHC(O)CH_3$ and the recombination product $(CH_3C(O)C(CH_3)_2)_2$ are in a good agreement (Figure 6a) with the SNP spectrum calculated by taking into account SNP contributions of both the geminate RPs composed of a cyclohexyl and a 2-acetyl-2-propyl radical as well as the F-pairs of two 2-acetyl-2-propyl radicals. Thus, the contribution of DNP, i.e., cross-

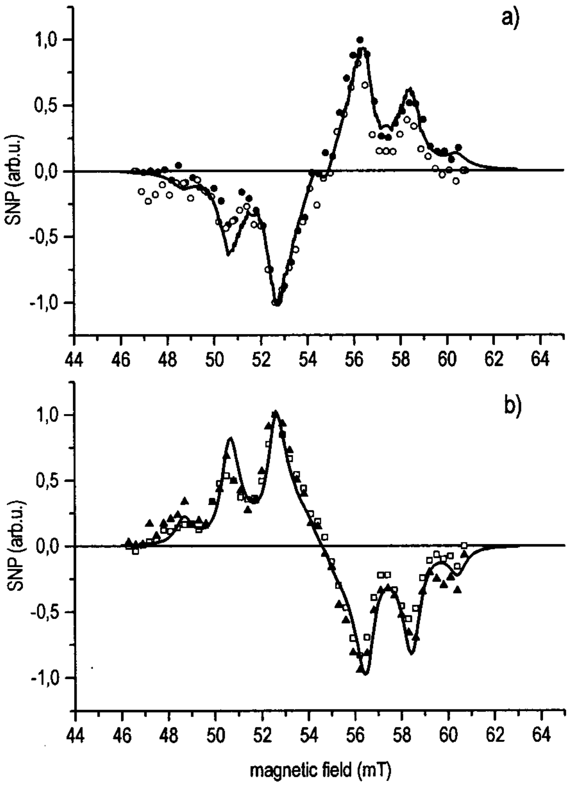

Figure 6. SNP spectra detected after photolysis of 2-chloro-2-methyl-3-butanone (III) in C_6D_{12} (a) measured on the escape products $CH_3C(O)C(C\mathit{H}_3)_2C(C\mathit{H}_3)_2C(O)CH_3$ (○) and $(C\mathit{H}_3)_2CHC(O)CH_3$ (●) (the solid curve is the calculated SNP spectrum considering the contributions from both the geminate and the F-pairs) and (b) measured on the in-cage products $C\mathit{H}_2{=}C(CH_3)C(O)CH_3$ (□) and $(C\mathit{H}_3)_2C(C_6D_{11})C(O)CH_3$ (▲) (the solid curve is the SNP spectrum calculated for the geminate RP).

relaxation, to the experimentally observed NP spectra is negligibly small.

Discussion. The DNP measurements at magnetic fields of 40−330 mT have revealed pronounced scalar electron−nuclear cross-relaxation in *t*-butyl and 2-hydroxy-2-propyl radicals, whereas this type of relaxation is absent in 2-acetyl-2-propyl radicals. The time-resolved CIDEP spectra of the first two species show a sign change of the electron polarization about 15 to 40 μs after their flash-photolytic generation. This sign change is not observed for the latter species. Thus, it can be concluded that the sign change of the CIDEP of *t*-butyl and 2-hydroxy-2-propyl radicals is indeed caused by a strong $\Delta m = 0$ cross-relaxation, as has been proposed previously.[10−12] As this cross-relaxation is not observed in the CIDNP spectra of the radical reaction products, measured at 4.7 T, it follows that at 4.7 T the condition $\omega^2\tau^2 \gg 1$ holds. This leads to a correlation time of $\tau \gg \omega^{-1} \approx 1$ ps for the stochastic modulation of the scalar hyperfine interaction causing the relaxation, i.e., τ is at least 1 order of magnitude longer than a typical inverse collision frequency in solution. The exact nature of the corresponding internal molecular motion in the radicals remains unclear. But it is worth mentioning that *t*-butyl and 2-hydroxy-2-propyl radicals are known to be slightly bent at the radical center,[36] whereas the 2-acetyl-2-propyl species should be forced to planarity by its resonance stabilization. Possibly the nonplanarity leads to some coupling of the methyl group rotation to the inversion vibration, thus limiting the spectral density of the rotational hfi modulation to lower frequencies. In fact, an extensive μSR and μLCR investigation of *t*-butyl radicals over a wide temperature range has found strong indications for such a coupling between the methyl group rotation and the inversion vibrational mode.[36]

Conclusion

Dynamic nuclear polarization measurements on systems of reactive radicals exhibiting chemically induced electron polarization have to take into account the electron spin polarization. It determines the DNP intensities, and also the DNP kinetics can become completely dominated by rise and decay of the CIDEP. In the case of a multiplet-type CIDEP pattern both DNP and SNP contribute an antiphase spectral pattern to the total nuclear polarization. A separation of both contributions is possible via measurements at different microwave powers.

A marked electron−nuclear flip-flop cross-relaxation takes place in *t*-butyl and 2-hydroxy-2-propyl radicals in low viscous solution at magnetic field strengths of 55 and 350 mT. Phase changes of the electron spin polarization, observed for these radicals in time-resolved ESR measurements at X-band frequency, can, therefore, be attributed to this relaxation. As the cross-relaxation does not cause any detectable CIDNP at an NMR field strength of 4.7 T it can be concluded that it results from an internal molecular motion, which modulates the isotropic hfi stochastically with a correlation time of $\tau \gg 1$ ps.

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