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Transfer of CIDNP Among Coupled Spins at Low Magnetic Field

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Abstract. Coherent polarization transfer among groups of dynamically polarized spins is explored and applied to field cycling experiments where spin evolution proceeds at low magnetic field while observation is performed at high field. The case of two nonequivalent spins-1/2 with scalar spin coupling is considered theoretically in detail for the cases of sudden and adiabatic field change. The criterion for efficient polarization transfer is derived theoretically and consistently confirmed experimentally for three photochemical reactions, involving spin systems of increasing complexity that exhibit chemically induced dynamic nuclear polarization: (1) the two polarized protons of the purine base of adenosine monophosphate; (2) four coupled indole protons of tryptophan; and (3) long-range polarization transfer among the aliphatic protons of cycloundecanone. The importance of polarization transfer in other cases with non-equilibrium population of the nuclear spin levels and the possibility of its utilization in field cycling NMR studies are discussed.

1 Introduction

The nuclear magnetic resonance (NMR) spectra of reaction products resulting from a radical reaction often exhibit chemically induced dynamic nuclear polarization (CIDNP) [1], which manifests itself in anomalous intensities and phases of the NMR signals. It arises from the spin evolution in transient radical pairs and is often used to characterize short-lived radical intermediates of chemical reactions. Since CIDNP is stored in the stable reaction products during the time needed for nuclear spin–lattice relaxation, typically several seconds for protons, it can be considered a fingerprint of the elusive radical species, which are often beyond the reach of electron paramagnetic resonance (EPR) spectroscopy, despite the remarkable achievements in high-field EPR spectroscopy [2] during the last decades.

In particular, the dependence of CIDNP on the external magnetic field can be utilized to determine the magnetic properties – hyperfine interaction (HFI) constants and g-factors – of the short-lived radicals. The strategy for determination of these quantities is as follows [1, 3–6]. CIDNP at low field (observed at magnetic fields lower than or comparable to the effective HFI constants) is affected only by the HFI and thus allows one to determine the HFI constants of the radicals. Once obtained, the HFI constants can be used to derive from the CIDNP at high field (observed at magnetic fields much stronger than the effective HFI constants) the difference in g-factors of the radicals which constitute the transient radical pair. This strategy has been successfully employed by us [4, 7, 8] to characterize the radicals of the amino acids histidine, tyrosine and methionine, taking into account the so-called "zero-field multiplet effect" [3, 4, 7, 9].

In other cases this method of extracting the HFI constants and g-factors meets more serious difficulties when at low magnetic field the nuclear spin states of the reaction products are strongly coupled by scalar spin–spin coupling. As has been pointed out by de Kanter and Kaptein [10], such a coupling may lead to the transfer of CIDNP to nuclei which do not have any HFI in the transient radicals and therefore cannot be polarized at high magnetic fields. Such an effect of polarization transfer is not unique for CIDNP but is observed also with other methods of dynamic polarization such as para-hydrogen induced polarization (PHIP) [11], when the hydrogenation reaction that is responsible for the formation of polarization is performed at low magnetic field [12–14]. Furthermore, in all experiments employing a variable magnetic field strength it is important to consider also the effects of sample transfer (field variation) from the polarization field to the detection field. Field variation may lead to the redistribution of population among the nuclear spin states, especially when there are coupled spin levels which pass through an avoided crossing.

The main goal of the present work is to study experimentally and theoretically how the scalar spin–spin interaction that in liquid samples acts as the predominant coupling of the nuclear spins at low magnetic field affects the CIDNP spectra recorded at high magnetic field. The experimental studies were carried out by using the fast field-cycling device [15, 16] that allows for precise positioning of the sample at any desired field in the range of 0–7 T where the CIDNP is formed with subsequent detection of the NMR spectra at 7 T. All the above-mentioned effects will be demonstrated for three different spin systems of increasing complexity that exhibit significant photo-CIDNP: (1) the H-2 and H-8 protons of adenosine monophosphate (AMP); (2) the aromatic protons of N-acetyl tryptophan (Trp); and (3) the protons of a large cyclic ketone. Here we will not go deeply into details of the CIDNP formation and determination of the HFI constants and g-factors of the radicals involved but only employ CIDNP to illustrate the effects under consideration. Analysis of the magnetic properties of the radicals involved is beyond the scope of the present work and will be published elsewhere.

Afterwards, we will discuss under what conditions the phenomena under study manifest themselves in other systems that involve strongly coupled polarized spins. As was already mentioned, the effects we consider here are by no means limited to CIDNP and can be observed in other cases where strong nonequilibrium populations of nuclear spin levels are present in field-cycling experiments.

2 Theory

In some of our CIDNP experiments performed at low magnetic field we observed polarization of spins that are not polarized at high fields (see below). In high magnetic fields all nuclear spins are polarized directly in accordance with their HFI at the radical stage, a fact that has been used to determine HFI constants. Especially, the absence of high-field CIDNP is an indication of small HFI of the nucleus in the transient radical. In contrast, the low-field CIDNP patterns in some of our observations do not reflect the spin density distribution in the radicals and some of the nuclei do not acquire their polarization directly due to proper HFI but rather are polarized indirectly. Neither can their polarization be explained by cross-relaxation causing CIDNP redistribution, because the cross-relaxation times T_{CR} are typically too long as compared with the timing of our experiments. Thus, an alternative explanation for the low-field CIDNP patterns has to be found.

Following de Kanter and Kaptein [10], we suggest that CIDNP is redistributed due to scalar spin–spin coupling. When spins are coupled sufficiently strongly, the eigenstates of the entire spin system are not characterized by the states of the individual spins but represent their collective states. Therefore, the spin order is not represented by polarization of certain nuclei but by a more complex distribution of population among all coupled spins. As a result, even though only some of the nuclei have considerable HFI in the radicals and thus can be considered the origin of polarization, spins strongly coupled to them in low magnetic fields may also exhibit strong CIDNP when observed at high field. In usual terminology "low-field CIDNP" is addressed to polarization formed at a field smaller than or comparable to the HFI, whereas the term "high-field CIDNP" stands for CIDNP formed at fields much stronger than the HFI. However, as far as the CIDNP redistribution is concerned the terminology should be changed because of the spin dynamics in the stable reaction products. For instance, the behavior of two nuclear spins-1/2, S_1 and S_2, at magnetic field B is described by the following Hamiltonian (in units of h):

$$\hat{\mathscr{H}} = -\nu_1 \hat{S}_{1z} - \nu_2 \hat{S}_{2z} + J(\hat{S}_1 \cdot \hat{S}_2), \tag{1}$$

where $\nu_i = \nu(1 - \sigma_i) = \gamma_N B(1 - \sigma_i)/2\pi$ is the Larmor precession frequency of the ith spin (determined by its chemical shift σ_i), γ_N is the nuclear gyromagnetic ratio and J is the scalar spin–spin coupling of the two spins. Depending on the frequency offset of the two spins at a field B

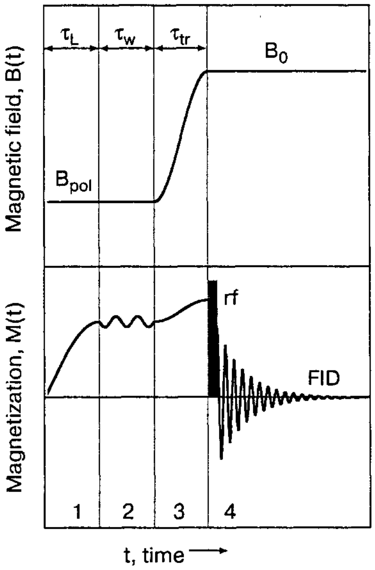

Fig. 1. Timing scheme of the field-cycling CIDNP experiment: variation of the external magnetic field $B(t)$ and evolution of nuclear magnetization $M(t)$. The sample is irradiated during time t_L at polarization field B_{pol} (step 1), kept at B_{pol} during time t_w (step 2), and transferred during time t_{tr} to the high field B_0 (step 3) where the NMR spectrum is acquired (step 4).

$$\delta\nu = \gamma_N B(\sigma_1 - \sigma_2)/2\pi = \gamma_N B\Delta\sigma/2\pi,$$

the condition of either strong (when J is larger than or comparable to the difference in Zeeman interaction, $\delta\nu$), or weak coupling of spins ($J \ll \delta\nu$) is met. Henceforth, polarization of the strongly and weakly coupled spins will be termed low-field CIDNP and high-field CIDNP, respectively, corresponding to strong and weak entanglement of the individual spin states in the reaction products.

In our analysis we will address the scheme of the CIDNP experiment with field cycling that consists of four consecutive steps sketched in Fig. 1: (1) CIDNP generation by inducing photoreactions at the desired field B_{pol} during time τ_L; (2) CIDNP evolution at field B_{pol} after irradiation during the waiting time τ_w; (3) transfer of the polarized reaction products to the observation field B_0 of the NMR spectrometer (i.e., switching the external magnetic field from B_{pol} to B_0) during time τ_{tr}; (4) measurement of the polarization by FT-NMR at $B = B_0$.

2.1 CIDNP Transfer Due to Strong Coupling of Spins

When the effects of CIDNP redistribution due to the strong coupling among spins at the polarization field were first considered by de Kanter and Kaptein [10] to explain the low-field CIDNP spectra, they assumed that the period τ_L during which CIDNP is formed by light irradiation is rather long in comparison with the reciprocal scalar coupling J between the interacting spins in the diamagnetic molecules, $\tau_L \gg 1/2\pi J$. Therefore, they neglected the role of any spin coherence (represented by off-diagonal elements of the respective spin density matrix) in the redistribution of polarization among the spins. However, when using intensive laser irradiation, it is possible to shorten τ_L to the limit that $\tau_L \leq 1/2\pi J$ and spin coherences can no longer be neglected. Experimental evidence for that was observed recently [17]. Thus, one objective of the present paper is to extend the description of polarization redistribution to short irradiation times with taking into account nuclear spin coherence. We will discuss this subject in more detail considering different timing schemes of the experiment with the aim to determine the criterion for the occurrence of CIDNP transfer (indirect polarization) and the actual transfer time.

In the simplest way, the effects of indirect polarization of the spins can be discussed for a system of two spins as the problem can be tackled analytically. In the following we will express all observables via the spin density matrix ρ of the reaction products, which is given in the eigenbasis of Hamiltonian (1). Its elements at a given field B_{pol} are conditioned by the spin evolution in the precursor radical pair and can be expressed via the density matrix, σ, of the radical pair projected onto its electron singlet state. This quantity can be conveniently written in the two-spin Zeeman basis [7]

$$|1\rangle = |\alpha\alpha\rangle, \quad |2\rangle = |\alpha\beta\rangle, \quad |3\rangle = |\beta\alpha\rangle, \quad |4\rangle = |\beta\beta\rangle. \tag{2}$$

Here we will not go into any details of calculating σ, which is beyond the scope of the present work.

The spin eigenstates $|i\rangle$ of the diamagnetic reaction product having two spins-1/2

$$\begin{aligned} &|1\rangle = |\alpha\alpha\rangle, \quad |2\rangle = \cos\theta|\alpha\beta\rangle - \sin\theta|\beta\alpha\rangle, \\ &|3\rangle = \sin\theta|\alpha\beta\rangle + \cos\theta|\beta\alpha\rangle, \quad |4\rangle = |\beta\beta\rangle, \end{aligned} \tag{3}$$

at B_{pol} have the following populations p_i resulting from CIDNP [7]:

$$\begin{aligned} &p_1 = n_{\alpha\alpha}, \quad p_2 = \cos^2\theta n_{\alpha\beta} + \sin^2\theta n_{\beta\alpha} + \sin 2\theta \operatorname{Re}\{\sigma_{\alpha\beta,\beta\alpha}\}, \\ &p_3 = \sin^2\theta n_{\alpha\beta} + \cos^2\theta n_{\beta\alpha} - \sin 2\theta \operatorname{Re}\{\sigma_{\alpha\beta,\beta\alpha}\}, \quad p_4 = n_{\beta\beta}. \end{aligned}$$

These state populations are in fact the diagonal elements of the spin density matrix ρ of the diamagnetic reaction product. Here, the mixing angle θ of the states $|2\rangle$ and $|3\rangle$ depends on the coupling strength J and the quantity $\delta\nu$ from Eq. (1) and at the polarization field is given by

$$\tan 2\theta = \frac{J}{\delta\nu}.$$

The populations n_{ij} of the spin states given in the two-spin Zeeman basis Eqs. (2) are the diagonal elements $\sigma_{ij,ij}$ of the spin density matrix σ. Their values are dictated by the spin evolution in the radical pair, as well as those of the nondiagonal elements $\sigma_{ij,kl}$ $(i,j \neq k,l)$ are.

Depending on the field strength and the HFI in the radicals, the quantities $\sigma_{ij,kl}$ take different values. Since here we are only interested in the indirect polarization of the nucleus having no HFI (for distinctness, hereafter the second nucleus), we simplify the expression for p_i taking

$$n_{\alpha\alpha} = n_{\alpha\beta} = n_1, \quad n_{\beta\alpha} = n_{\beta\beta} = n_2, \quad \sigma_{\alpha\beta,\beta\alpha} = 0$$

because the state population is independent of the spin orientation of the second nucleus in the radical; also the phase element $\sigma_{\alpha\beta,\beta\alpha}$ is zero.

The CIDNP patterns are substantially affected by the sample transfer to the field B_0 because $\delta\nu$ increases and the mixing angle θ decreases accordingly. For the sake of simplicity we consider only a weakly coupled system (AX system) at the detection field and $J > 0$, a situation facilitating the proper qualitative conclusions. In this situation the eigenstates $|i_{hf}\rangle$ at high field B_0 coincide with those of the Zeeman basis (2). Here, we will discuss the two different limiting cases of purely adiabatic and purely nonadiabatic (sudden) transfer. In the first case (slow field variation) the eigenstates of the spin system keep their populations during the field variation, with the result that at detection field the state populations P_i are

$$P_1 = P_{\alpha\alpha} = p_1 = n_1, \quad P_2 = P_{\alpha\beta} = p_2 = \cos^2\theta n_1 + \sin^2\theta n_2,$$
$$P_3 = P_{\beta\alpha} = p_3 = \sin^2\theta n_1 + \cos^2\theta n_2, \quad P_4 = P_{\beta\beta} = p_4 = n_2,$$

and the expectation values of the net magnetizations of the two nuclei [1]

$$\langle I_{1z}\rangle = \frac{P_{\alpha\alpha} + P_{\alpha\beta} - P_{\beta\alpha} - P_{\beta\beta}}{2}, \quad \langle I_{2z}\rangle = \frac{P_{\alpha\alpha} - P_{\alpha\beta} + P_{\beta\alpha} - P_{\beta\beta}}{2} \tag{4}$$

become

$$\langle I_{1z}\rangle = (1+\cos 2\theta)\frac{n_1 - n_2}{2}, \quad \langle I_{2z}\rangle = (1-\cos 2\theta)\frac{n_1 - n_2}{2}.$$

As is readily seen, both nuclei become polarized and the ratio of their CIDNP signals

$$\frac{\langle I_{2z}\rangle}{\langle I_{1z}\rangle} = \frac{(1-\cos 2\theta)}{(1+\cos 2\theta)}$$

vanishes only when the mixing angle θ of the states $|2\rangle$ and $|3\rangle$ at the polarization field is zero, i.e., when the spins are coupled only weakly at B_{pol}.

In the limit of sudden transfer (abrupt field jump) the high-field state populations are correlated with those at the polarization field in the following way:

$$P_i = \sum_j \left|\langle i_{hf}|j\rangle\right|^2 p_j, \tag{5}$$

which represents, in essence, the projection of the density matrix at the polarization field onto the high-field spin states $|i_{hf}\rangle$. This equation leads to the following expressions for the two-spin system:

$$P_{\alpha\alpha} = p_1 = n_1, \quad P_{\alpha\beta} = \left(1 - \frac{\sin^2 2\theta}{2}\right)n_1 + \frac{\sin^2 2\theta}{2}n_2,$$

$$P_{\beta\alpha} = \left(1 - \frac{\sin^2 2\theta}{2}\right)n_2 + \frac{\sin^2 2\theta}{2}n_1, \quad P_{\beta\beta} = p_4 = n_2,$$

and the net polarizations are as follows:

$$\langle I_{1z}\rangle = \frac{n_1 - n_2}{2}(1 + \cos^2 2\theta), \qquad \langle I_{2z}\rangle = \frac{n_1 - n_2}{2}(1 - \cos^2 2\theta)$$

giving us the polarization ratio

$$\frac{\langle I_{2z}\rangle}{\langle I_{1z}\rangle} = \frac{(1-\cos^2 2\theta)}{(1+\cos^2 2\theta)},$$

which approaches zero only for a system of spins that are weakly coupled at B_{pol}.

Figure 2 illustrates the CIDNP transfer in the approximation of adiabatic and sudden field variation. For the parameters chosen for the calculation (Fig. 2) the polarization is redistributed efficiently for fields up to at least tens of millitesla in both approximations. For the sudden field variation a polarization transfer is predicted that is always more efficient than for the corresponding adiabatic case.

Thus, at the two limits, because of strong coupling at the polarization field, the second nucleus (having no HFI in the radicals) takes a large part of CIDNP from the first nucleus. At intermediate speed of field variation a polarization transfer between the asymptotic curves is expected. It is important to emphasize

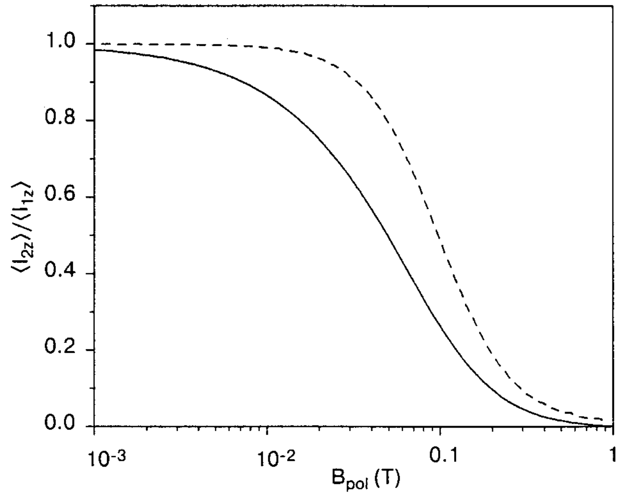

Fig. 2. Field dependence of the CIDNP transfer efficiency in the models of adiabatic (solid line) and sudden (dashed line) field variation for a two-spin system with only the first spin being polarized directly, whereas the second spin acquires CIDNP due to strong spin–spin coupling at the polarization field. Parameters of calculation: $J = 3$ Hz, $\Delta\sigma = 0.5$ ppm.

that the condition of strong coupling of the nuclei is almost always fulfilled at low magnetic field. Indeed, even when assuming $\Delta\sigma = 3$ ppm (which is fairly big for two protons), and J as small as 0.1 Hz (not resolvable by NMR because of field inhomogeneities), we obtain strong coupling of the two spins at fields B_{pol} below 1 mT. Thus, even in such cases indirect polarization of the nuclei, which are not polarized at the high field, is expected. However, this prediction is in contradiction with the experimental observations, because at low field, polarization is not found distributed over the whole molecule except for some special cases [13, 14, 18, 19] discussed below in the light of our present study. Thus, the strong coupling condition at B_{pol} alone does not provide an adequate CIDNP transfer criterion. Moreover, in the situation considered above CIDNP is counterintuitively redistributed in the molecule "instantaneously", that is, immediately after the diamagnetic molecule is formed. Since any interaction, even if it is switched on instantaneously, needs a finite time to affect the observables, this concept cannot apply to fast field-cycling experiments. Hence, a more accurate consideration is needed, which is presented below.

2.2 Polarization Transfer Criterion

The inconsistency has a simple reason. In the foregoing analysis, to obtain the state populations at the detection field, we tacitly assumed that the spin density matrix at the polarization field does not have any elements except for diagonal ones. However, this is not always true because, in general, at B_{pol} the spin eigenstates in the radicals do not coincide exactly with those in the reaction products [17, 20–22]. This inevitably leads to the formation of off-diadonal elements of ρ, e.g., the element

$$\rho_{23} = \frac{\sin 2\theta}{2}(n_{\alpha\beta} - n_{\beta\alpha}) + \cos 2\theta \operatorname{Re}\{\sigma_{\alpha\beta,\beta\alpha}\} + i \operatorname{Im}\{\sigma_{\alpha\beta,\beta\alpha}\} = \frac{\sin 2\theta}{2}(n_1 - n_2),$$

which represents the coherence between the states $|2\rangle$ and $|3\rangle$ that are defined in Eq. (3). Once formed, ρ_{23} starts oscillating at a frequency equal to the difference in energy of the states $|2\rangle$ and $|3\rangle$:

$$\frac{\Delta E_{23}}{h} = \nu_{23} = \sqrt{J^2 + (\Delta\sigma \cdot \nu)^2}, \tag{6}$$

i.e.,

$$\rho_{23}(t) = \rho_{23}(0)\exp(2\pi i \nu_{23} t). \tag{7}$$

If the irradiation time τ_L is large enough ($\nu_{23}\tau_L \gg 1$), the coherences will be completely washed out. However, if this condition is not met, the phases will still persist before the sample transfer.

Now, let us consider for the adiabatic and sudden cases the consequences of coherence formation and the effects of field variation on the redistribution of polarization.

Adiabatic transfer. In this case the coupled states $|2\rangle$ and $|3\rangle$ have enough time to adjust themselves to the variable magnetic field so that the populations of the eigenstates remain unchanged, whereas the coherences oscillate with the frequency $\nu_{23}(t)$ that gradually changes with time as the external magnetic field varies:

$$\rho_{23}(t) = \rho_{23}(0)\exp(2\pi i \nu_{23}(t) \cdot t).$$

No mixing between phases and populations occurs in this case, hence the coherences formed at field B_{pol} do not affect the net polarizations at detection field B_0.

Sudden transfer. At high field, Eq. (5) has to be extended to include off-diagonal terms:

$$P_i = \sum_{j,k} \langle i_{hf} | j \rangle \langle k | i_{hf} \rangle \rho_{jk}.$$

As a result, we get the following populations of states $|2\rangle$ and $|3\rangle$ at B_0:

$$P_2 = P_{\alpha\beta} = \cos^2\theta p_2 + \sin^2\theta p_3 + \sin 2\theta \operatorname{Re}\{\rho_{23}\},$$

$$P_3 = P_{\beta\alpha} = \sin^2\theta p_2 + \cos^2\theta p_3 - \sin 2\theta \operatorname{Re}\{\rho_{23}\}. \tag{8}$$

If we then assume that during irradiation and/or waiting time at B_{pol} the coherence between the coupled levels $|2\rangle$ and $|3\rangle$ does not undergo any changes, we immediately obtain that

$$P_{\alpha\beta} = n_{\alpha\beta}, \quad P_{\beta\alpha} = n_{\beta\alpha}$$

and

$$\langle I_{1z}\rangle = n_1 - n_2, \quad \langle I_{2z}\rangle = 0$$

Hence, no indirect polarization of the second nucleus occurs. If, however, coherence formed due to the spin evolution in the radicals undergoes some changes at the polarization field (e.g., due to finite irradiation or waiting times), the second nucleus acquires CIDNP.

Altogether, this allows us to conclude that CIDNP transfer to the second nucleus proceeds efficiently in the following cases: (i) adiabatic sample transfer; (ii) nonadiabatic sample transfer accompanied by evolution of coherences during the waiting time τ_{w} or their decay during the finite irradiation time τ_{L}; (iii) intermediate situation when the transfer is not completely adiabatic and the spin coherence has enough time to evolve at $B = B_{\mathrm{pol}}$. Certainly, strong coupling of the two nuclei at the polarization field is always a prerequisite for the CIDNP transfer. The various situations discussed are met depending on the timing scheme of the experiment. Indeed, to meet condition (i) it is necessary that $J\tau_{\mathrm{tr}} \geq 1$ (rough estimate for the time of adiabatic transfer [1]), for conditions (ii) and (iii) it is necessary that $J\tau_{\mathrm{L}} \geq 1$ and/or $J\tau_{\mathrm{w}} \geq 1$. Therefore, to transfer CIDNP, it is necessary that the τ_{L}, τ_{w}, and τ_{tr} times are not much smaller than the inverse of J, i.e., the timing of the experiments introduces limits for the redistribution of polarization between the coupled nuclei. Hence, the modified criterion for indirect polarization is as follows:

$$J \geq \delta\nu \text{ at } B_{\mathrm{pol}} \text{ and } J\tau_{\mathrm{L}},\ J\tau_{\mathrm{w}},\ J\tau_{\mathrm{tr}} \geq 1. \tag{9}$$

Accordingly, the redistribution time can be roughly estimated as J^{-1}. Even though in this more extended model, polarization is no longer transferred "instantaneously", the CIDNP redistribution time of J^{-1} is still considerably shorter than the longitudinal relaxation times T_1, whereas the latter are usually shorter than the cross-relaxation times T_{CR}. Therefore, the mechanism discussed above provides faster polarization transfer than cross-relaxation does.

In Fig. 3 we show how the indirect polarization of the second nucleus builds up as a function of the irradiation and waiting times. First we assume that the irradiation time is short ($\nu_{23}\tau_{\mathrm{L}} \ll 1$) and calculate the ratio of the individual net magnetizations $\langle I_{1z}\rangle$, $\langle I_{2z}\rangle$ and the total net CIDNP, $\langle I_z\rangle = n_1 - n_2$. From Eqs. (4), (7) and (8) we obtain the following dependence of the individual net magnetizations on the waiting time:

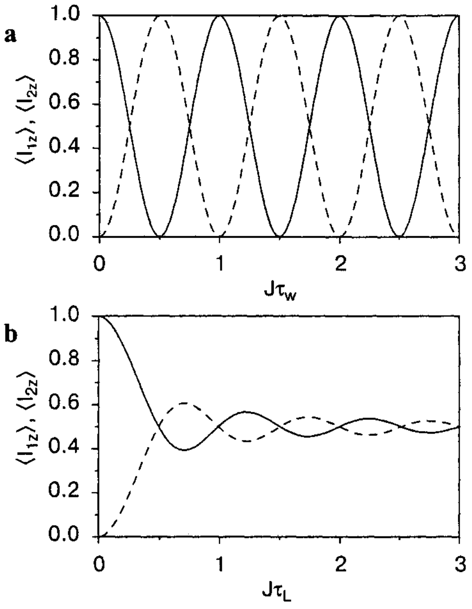

Fig. 3. Dependence of CIDNP transfer efficiency on the irradiation (**a**) and waiting (**b**) times. Here the first spin is polarized directly (its CIDNP is shown by the solid line), while the second spin acquires polarization indirectly (its CIDNP kinetics is shown by the dashed line); parameters of calculation: $J = 3$ Hz, $\Delta\sigma = 0.5$ ppm, $B_{\rm pol} = 10$ mT. CIDNP of the spins shown here is normalized by dividing it by the total polarization $\langle I_z\rangle$.

$$\frac{\langle I_{1z}\rangle}{\langle I_z\rangle} = 1 - \sin^2 2\theta \cdot \frac{1-\cos(2\pi\nu_{23}\tau_w)}{2},$$

$$\frac{\langle I_{2z}\rangle}{\langle I_z\rangle} = \sin^2 2\theta \cdot \frac{1-\cos(2\pi\nu_{23}\tau_w)}{2}.$$

As it is seen, both polarizations oscillate between their limiting values, $(1 - \sin^2 2\theta)$ and 1 for $\langle I_{1z}\rangle$ and 0 and $\sin^2 2\theta$ for $\langle I_{2z}\rangle$ (Fig. 3a). As it is seen after a quarter of a period ($2\pi J\tau_w = \pi/2$) polarization is already distributed efficiently among the spins. Here, for simplicity we neglect dephasing of the coherence, which leads to damping of the beats in Fig. 3a. Second, we take $\tau_w = 0$ and vary the irradiation time passing from very short ($\nu_{23}\tau_L \ll 1$) to very long ($\nu_{23}\tau_L \gg 1$) times τ_L. Obtaining analytical results requires the knowledge of the coherence at the end of the irradiation period, which is

$$\mathrm{Re}\{\rho_{23}\} = \sin 2\theta \cdot \left(\frac{1}{\tau_L} \int_0^{\tau_L} \cos[2\pi\nu_{23}(t-\tau_L)]\mathrm{d}t \right) \cdot \frac{n_1 - n_2}{2}$$

$$= \sin 2\theta \cdot \frac{\sin(2\pi \nu_{23}\tau_L)}{2\pi \nu_{23}\tau_L} \cdot \frac{n_1 - n_2}{2}.$$

This formula takes into account the evolution of the coherences formed during irradiation. As it is seen, continuous irradiation from 0 to τ_L results in washing out this coherence, which vanishes at large $\nu_{23}\tau_L$. Equations (4), (7) and (8) lead to the following CIDNP values:

$$\frac{\langle I_{1z}\rangle}{\langle I_z\rangle} = 1 - \frac{\sin^2 2\theta}{2}\left[1 - \frac{\sin(2\pi \nu_{23}\tau_L)}{2\pi \nu_{23}\tau_L}\right],$$

$$\frac{\langle I_{2z}\rangle}{\langle I_z\rangle} = \frac{\sin^2 2\theta}{2}\left[1 - \frac{\sin(2\pi \nu_{23}\tau_L)}{2\pi \nu_{23}\tau_L}\right].$$

Again, CIDNP $\langle I_{2z}\rangle$ fully builds up only if the time of the experiment (τ_L in this case) is long enough (Fig. 3b) as compared to the reciprocal coupling strength J^{-1}.

3 Experiment

A detailed description of the experimental setup is given elsewhere [15, 16]. The mechanical field cycling setup allows us to detect high-resolution NMR spectra under permanent slow sample rotation (0–150 Hz) at $B_0 = 7$ T. Light irradiation for polarization at any desired magnetic field strength B_{pol} between the earth magnetic field and 7 T is made possible by precisely positioning the probe head with the sample in the stray field of the spectrometer cryomagnet. At a field below 0.1 T, B_{pol} is set by control of the electric current through a pair of additional Helmholtz coils placed under the cryomagnet.

During τ_L (step 1 in Fig. 1) the sample is irradiated by a XeCl excimer laser at 308 nm with a repetition rate from 1 to 50 Hz and an energy of up to 150 mJ/pulse through a flexible liquid light guide. Typical times τ_{tr} of the sample transfer to the detection field (step 3) are between 290 ms and 1 s in our experiments. The detection of the spectra (step 4) is done by Fourier transform of the free induction decay recorded after an rf excitation pulse of variable flip angle. CIDNP spectra are the differences of spectra taken with and without light irradiation under otherwise identical conditions.

All samples were purged with pure nitrogen gas and sealed in a standard 5 mm Pyrex NMR tube. In order to avoid vortex formation and sample shaking during the transfer, a Teflon plug was inserted into the tube on top of the liquid. Trp, AMP, anthraquinone-2-sulphonate sodium salt (AQS), cycloundecanone $C_{11}H_{20}O$ (C-11), and the solvents D_2O and $CDCl_3$ were used as received from Sigma-Aldrich. 2,2′-Dipyridyl-d_8 (DP) was kindly provided by Herbert Zimmermann (MPI, Heidelberg). The structures of Trp, AMP, DP and AQS in D_2O at the

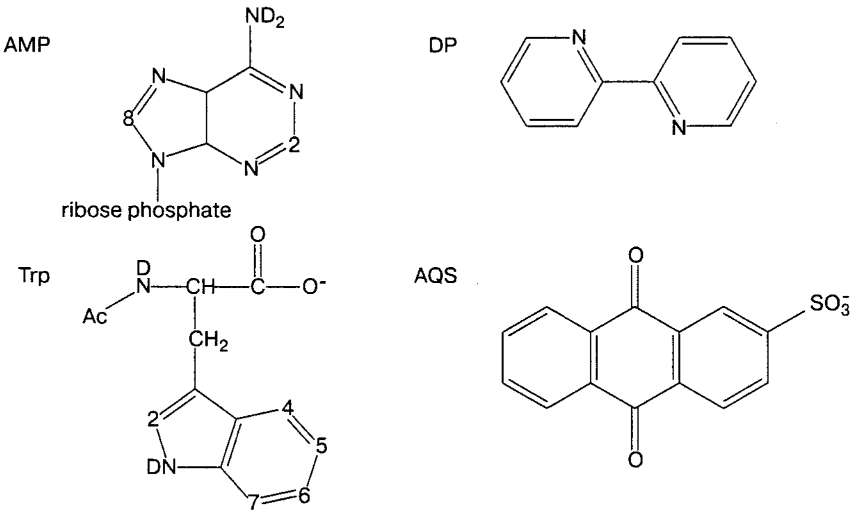

Fig. 4. Structures of the AMP, DP, Trp and AQS molecules.

pH values chosen are shown in Fig. 4. In the experiments we used the following samples: 5 mM of AMP and 0.7 mM of DP in D_2O at pH 5.0 (sample 1); 8 mM of Trp and 0.6 mM of AQS in D_2O at pH 11 (sample 2); and 27 mM of C-11 in $CDCl_3$ (sample 3). The pH value was adjusted by adding DCl and NaOD.

3.1 Photo-CIDNP Transfer in AMP

To illustrate the effects of CIDNP transfer and the transfer kinetics in the simple case that can be directly compared to the theory developed above, we chose the AMP molecule, where only two protons are present, at the H-2 and H-8 positions of the purine base, that acquire considerable polarization during the reversible electron transfer reaction between photoexcited DP in the triplet state and AMP:

$$\mathrm{DP} + \mathrm{AMP} \xrightarrow{h\nu,\mathrm{ISC}} {}^{3}\mathrm{DP} + \mathrm{AMP} \rightarrow {}^{3}\left\{\mathrm{DP}^{\bullet-}...\mathrm{AMP}^{\bullet+}\right\}$$

$$\xleftrightarrow{\mathrm{ISC}} {}^{1}\left\{\mathrm{DP}^{\bullet-}...\mathrm{AMP}^{\bullet+}\right\} \rightarrow \mathrm{DP} + \mathrm{AMP}^{*}$$

In the course of each reaction cycle, polarized AMP molecules (polarization is denoted by the asterisk) are formed due to the nuclear-spin-selective intersystem crossing (ISC) in the radical pair stage.

As follows from the intensities of CIDNP at high magnetic field (spectrum 2 in Fig. 5) in the radical stage the HFI constant of the H-8 proton is much larger than that of the H-2 proton. Hence, these two spins constitute a two-spin

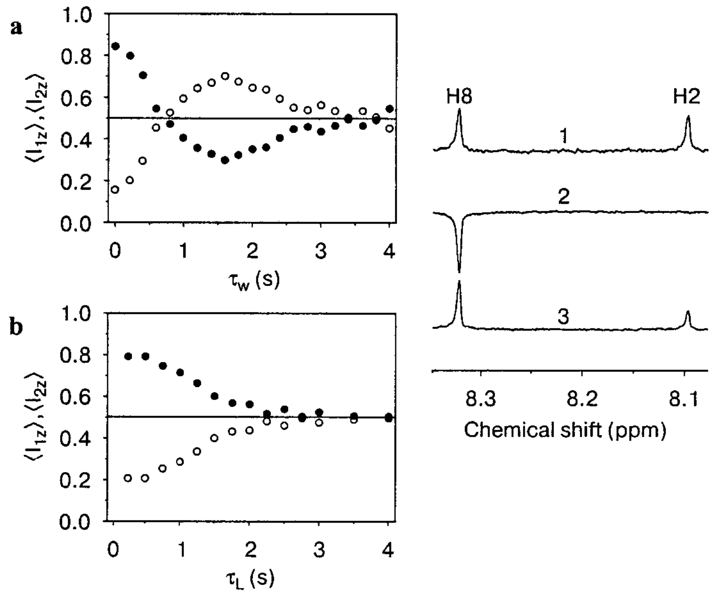

Fig. 5. Kinetics of CIDNP transfer between the H-2 and H-8 protons of AMP as a function of waiting time t_w at the polarization field recorded with t_L taken 0.2 s (**a**) and irradiation time t_L recorded with $t_w = 0$ (**b**). Full circles refer to the source spin of polarization (H-8 proton) and open circles to the target spin (H-2 proton). CIDNP is formed in the photoreaction of AMP with DP-d8 (sample 1). Also shown are the ^{1}H NMR spectra of AMP at 7 T (spectrum 1), the CIDNP spectra of AMP at $B_{pol} = 7$ T (spectrum 2) and at $B_{pol} = 1$ mT (spectrum 3) recorded with $t_L = 0.2$ s, $t_w = 0$, $t_{tr} = 0.3$ s, and an excitation flip angle of 90°. CIDNP amplitudes of the spins shown here are normalized by dividing them by the total polarization $\langle I_z \rangle$.

model system with only one proton having strong directly formed polarization and thus appropriate for studying the CIDNP transfer effects. The fact that at low magnetic fields their CIDNP intensities are close to each other with a ratio being almost constant (not shown here) indicates that CIDNP transfer tends to equalize the polarization of both spins as a result of scalar coupling. In one-dimensional high-resolution NMR experiments (line width of 0.2 Hz for the single line of water, HDO) the lines of the H-2 and H-8 signals were 0.4 and 0.7 Hz broad, respectively, and their shapes noticeably differed from a Lorentzian. We attribute this line width to nonresolved smaller couplings with protons of the ribose moiety and deuterium atoms of the amide group. Only at the top of the H-2 and H-8 lines some structure (two residual maxima with a distance of around 0.15 Hz) is seen; simulation allows us to estimate the coupling to be about 0.3 Hz. In addition, homonuclear ^{1}H COSY experiments at 9.4 T exhibit cross peaks showing the presence of scalar coupling between H-2 and H-8 and residual couplings of H-8 to the H-1′ proton of ribose. In order to make sure that the condition of strong coupling is met, the experiments were done at a magnetic field of 1 mT, where $\delta\nu$ is less than 0.01 Hz. To find further evidence for the polarization transfer mechanism we performed additional measurements at the same field and varied the parameters in the timing scheme of our experiments.

In the first set of experiments, keeping the irradiation time short (assuring that the coherences are not averaged out because of finite τ_L) we varied the waiting time at field B_{pol} (Fig. 5a). At small values of τ_w the CIDNP of H-8 is much stronger than that of H-2; however, at longer τ_w the polarization of H-2 grows and after one second it is even higher than that of H-8. Both polarizations, $\langle I_{1z}\rangle/\langle I_z\rangle$, and $\langle I_{2z}\rangle/\langle I_z\rangle$, are oscillating around the level of one half of the total polarization $\langle I_z\rangle$. Even though these beats have faded after 2.5 s due to relaxation, we can still resolve one oscillation period allowing us to obtain the beating frequency ν_{23}, which is about 0.3 Hz. From this result we estimate the coupling between H-2 and H-8 protons to be 0.3 Hz because at 1 mT $\nu_{23} \gg \delta\nu$, with the result that we obtain from Eq. (6) $\nu_{23} \approx J$.

In the second set of measurements we took $\tau_w = 0$ and recorded CIDNP as a function of the irradiation time τ_L (Fig. 5b). In order to keep the total number of photons constant that are absorbed by the sample we varied the laser repetition rate so that the number of laser flashes was the same for all τ_L values. As in the previous case, when the time of the experiment is short (small τ_L) the CIDNP of H-8 is much higher than that of H-2. With longer τ_L the polarization of the H-8 proton decreases and the polarization of the H-2 proton increases, and after $\tau_L = 2$ s their CIDNP signals have the same intensities (complete CIDNP redistribution). This is in accordance with the value of J obtained in the previous experiment.

Both experimental dependences in Fig. 5 agree with the theoretical predictions (Fig. 3). As is clearly seen, at short times of the experiment the H-2 proton is only slightly polarized, but gains polarization from the H-8 proton when the waiting and the irradiation times are long enough. The observation of beats in the experiment with variable τ_w allows us to conclude that the CIDNP transfer proceeds coherently due to strong coupling of the spins at low magnetic fields. It is important to note that for such a small J the field variation from 1 mT to 7 T proceeds nonadiabatically. In our experiments we failed to reach the regime of adiabatic field variation because the longitudinal relaxation times (about 2 s at low magnetic field) of the spins set a limit. At the same time, in our experiments polarization transfer from the H-8 to the H-2 proton is much more efficient than that to the H-1′ proton of ribose where no CIDNP is observed, presumably because in the former case the scalar coupling is larger (0.3 against 0.1 Hz), whereas the difference in chemical shift is much smaller (0.2 against 2.3 ppm).

Since polarized systems of two spins are rarely met in practice, we find it important to demonstrate that analogous polarization transfer effects manifest themselves in more general situations. CIDNP transfer between four coupled spins taking place in the reaction of the amino acid Trp is considered in the following section. Since the theoretical description of the four-spin system is more complex and cannot be performed analytically, we will restrict ourselves only to a qualitative consideration of the low-field CIDNP of Trp.

3.2 Photo-CIDNP Transfer in Trp

The reversible light-induced electron transfer between the photoexcited triplet dye AQS and Trp (Fig. 4) leading to the formation of polarized Trp* is as follows:

$$\mathrm{AQS} + \mathrm{Trp} \xrightarrow{h\nu,\mathrm{ISC}} {}^3\mathrm{AQS} + \mathrm{Trp} \rightarrow {}^3\left\{\mathrm{AQS}^{\bullet-}...\mathrm{Trp}^{\bullet+}\right\}$$
$$\xleftrightarrow{\mathrm{ISC}} {}^1\left\{\mathrm{AQS}^{\bullet-}...\mathrm{Trp}^{\bullet+}\right\} \rightarrow \mathrm{AQS} + \mathrm{Trp}^*$$

Photo-CIDNP spectra recorded for the system Trp + AQS at different magnetic field are shown in Fig. 6. At the high magnetic field of the NMR spectrometer, $B_{\mathrm{pol}} = 7$ T, five protons of Trp are polarized: two in nonequivalent β-positions and the H-2, H-4, H-6 protons in the indole moiety of the Trp molecule. At high magnetic field, where all the scalar couplings between the protons are weak, only the protons having significant spin density in the radical state are polarized. This is because each nucleus is polarized only directly and the magnitude of its polarization is conditioned only by its HFI constant. Therefore, from the high-field CIDNP spectrum (spectrum 2 in Fig. 6) we can conclude that only the β-CH_2, H-2, H-4 and H-6 protons have considerable HFI in the Trp radical, whereas the protons in the α-CH, H-5 and H-7 positions have not. This conclusion is further supported by the time-resolved CIDNP spectrum [23] detected immediately after the laser pulse, which reflects polarization cre-

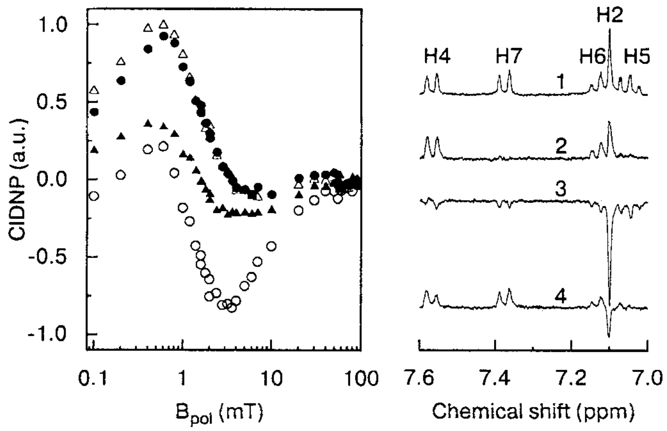

Fig. 6. CIDNP field dependences of the aromatic protons of Trp in the H-4, H-5, H-6 and H-7 positions as observed in the photoreaction of Trp with AQS (sample 2). CIDNP of the directly polarized nuclei is shown by filled circles (H-4 protons) and filled triangles (H-6 protons), and CIDNP of the indirectly polarized nuclei is shown by open circles (H-5 protons) and open triangles (H-7 protons). Also shown here are the ^{1}H NMR spectrum of Trp at 7 T (spectrum 1), and the CIDNP spectra of Trp at $B_{\mathrm{pol}} = 7$ T (spectrum 2), $B_{\mathrm{pol}} = 4$ mT (spectrum 3) and $B_{\mathrm{pol}} = 0.6$ mT (spectrum 4). Experimental conditions: $t_L = 1$ s, $t_{tr} = 0.4$ s, all spectra were recorded with a 45° rf-pulse flip angle.

ated only in the primary geminate recombination of the radical pairs and is not affected by secondary bulk reactions. Here we will discuss only the CIDNP of the protons in the six-membered ring (H-4, H-5, H-6 and H-7 protons), which have appreciable couplings of 7–8 Hz with their neighbors. As long as the field is low enough that the scalar coupling is of the same order as the difference in Zeeman interactions, the eigenstates of the nuclear spin system are not the states of individual spins but the collective states of the entire spin system, which is factorized further into two subsystems, one comprising four spins of the H-2, the α-CH and β-CH_2 protons and the other one comprising the protons of the six-membered ring. Here, we will not discuss the details of CIDNP redistribution in the first spin subsystem, since for the α-CH and the β-CH_2 protons it is described in a separate publication [17], but focus only on the CIDNP of the H-4, H-5, H-6 and H-7 protons.

At low magnetic field the situation is qualitatively different as compared with that at high field: all protons of the six-membered ring acquire significant CIDNP (spectra 3 and 4 in Fig. 6), moreover, their CIDNP field dependences are very similar and have their extremum at the same magnetic field (Fig. 6). Since only two (H-4 and H-6) of the four protons have significant HFI in the radical state and are thus polarized directly, we can conclude that the H-5 and H-7 protons are polarized by transfer of CIDNP from the other spins. A mechanism often proposed to be responsible for polarization transfer is cross-relaxation [10, 24]; however, in the case under study this mechanism cannot be effective since its time constant is too big in comparison with the chosen timing of our experiment. This can be concluded from a simple estimate: in any case the cross-relaxation time T_{CR} is longer than the spin–lattice relaxation time T_1 which is at least 2 s for the aromatic protons and is thus considerably longer than the time of the whole field-cycling experiment. As a consequence, the effect of the cross-relaxation processes cannot play an important role within the timing scheme of the experiment chosen and thus does not account for efficient polarization transfer, neither to the H-5 nor to the H-7 proton.

The theoretical considerations as discussed above allow us to explain qualitatively the CIDNP transfer effects in Trp. At fields B_{pol} below 0.3 T the four protons in the H-4, H-5, H-6 and H-7 positions form a strongly coupled system because the coupling constants of the H-4, H-5, H-6 and H-7 protons with their nearest neighbors is about 8 Hz and the $\Delta\sigma$ are smaller than 0.6 ppm. Thus, its eigenstates at these fields are not characterized by the individual (Zeeman) states of single protons but represent their mixture. Since the timing scheme of our experiments meets the conditions (9) for polarization transfer due to fairly large spin–spin couplings, we observe large CIDNP of the H-5 and H-7 protons having no HFI in the radical stage.

Thus, in Trp the H-5 and H-7 protons acquire polarization from their polarized neighbors due to strong coupling of the spin system at low magnetic field and the concepts discussed for the two-spin systems also hold for more complex spin systems. After having seen that in Trp CIDNP is transferred due to direct scalar coupling between the target (H-5 and H-7) and the source (H-4 and

H-6) spins of polarization, we went one step further and investigated whether the polarization transfer is also effective in multispin systems where the target and the source spins of polarization are coupled not directly but through a network of strong scalar couplings between the intermediate spins. This is important for channelling polarization to certain target spins that cannot be polarized directly. In order to study such a long-range polarization transfer we used the cyclic ketone cycloundecanone $C_{11}H_{20}O$ with its long methylene chain containing twenty protons. The protons in α-CH_2 and β-CH_2 positions acquire direct CIDNP [25] in the Norrish type I photolysis reaction, whereas the other protons with their small HFI can get their polarization only indirectly.

3.3 Long-range Polarization Transfer in Cycloundecanone

Typical CIDNP spectra of the ketone $C_{11}H_{20}O$ (C-11) taken at different fields are shown in Fig. 7. Here polarization is formed in the highly reversible photoreaction of *α*-cleavage (Fig. 8) [25].

As a result, after each reaction cycle polarized molecules of the starting compound C-11 are formed. In C-11, at high magnetic fields the α-CH_2 protons and the β-CH_2 protons of the alkyl moiety of the biradical have the strongest HFI of –2.2 mT and 2.8 mT, respectively [26], consequently, they acquire the strongest CIDNP. The α-CH_2 protons and the β-CH_2 protons have emissive and absorptive phase of their polarization, respectively, in accordance with Kaptein's rule [1]. For the other protons (in γ-, δ-, and ε-positions of the cyclic ketone) being far from either radical center the HFI is very small (less than 0.1 mT) [26] and therefore their polarization is negligible at $B_{pol} = 7$ T (see spectrum 2 in Fig. 7). At $B_{pol} = 30$ mT (spectrum 3) and 2 mT (spectrum 4), however, the

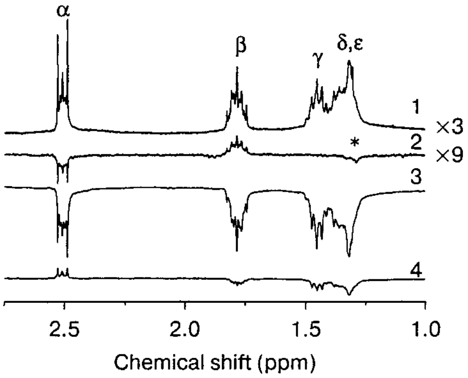

Fig. 7. ^1H NMR spectrum of cycloundecanone (C-11) at 7 T (spectrum 1) and the photo-CIDNP spectra of C-11 (sample 3) at $B_{pol} = 7$ T (spectrum 2), 30 mT (spectrum 3) and 2 mT (spectrum 4). The signal marked by asterisk belongs to a side product of the reaction. Experimental conditions: $t_L = 1$ s, $t_{tr} = 0.3$ s, all spectra were recorded with a 90° rf-pulse flip angle.

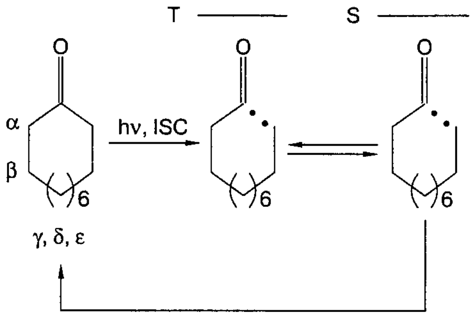

Fig. 8. Norrish type I photolysis of cycloundecanone (C-11).

observed CIDNP pattern is qualitatively different showing polarization distributed evenly among all the protons and its intensity is no longer consistent with the HFI of the corresponding nuclei. Since we know from the high-field spectra that only the α-CH_2 and β-CH_2 protons are polarized directly, we attribute the polarization of the protons in the in γ-, δ-, and ε-positions to indirectly formed CIDNP due to transfer from the α-CH_2 and β-CH_2 protons.

In the case under study (in contrast to the Trp case) the transfer is long-range, e.g., the protons in the β- and ε-positions are separated by five chemical bonds and the scalar spin–spin coupling between them is very weak so that it does not fulfil the criterion Eq. (9) with respect to the timing of polarization transfer and cannot account for the CIDNP patterns observed at low fields. Again, the cross-relaxation processes between these protons are very inefficient [27]. Nevertheless, the mechanism of polarization transfer due to the strong coupling of spins is still operative for the following reason. Each group of protons (those in α-, β-, γ-, δ-, ε-position) is strongly coupled to its nearest neighbors (e.g., the α-CH_2 protons to the β-CH_2 protons, the β-CH_2 protons to the γ-CH_2 protons and so on) at low fields. As a result, all the spins are strongly coupled indirectly via the network of the intervening protons. For instance, since the α-CH_2 protons are strongly coupled to the β-CH_2 protons, their individual spin states are entangled and the β-CH_2 protons do not interact with the γ-CH_2 protons individually, but together with the α-CH_2 protons. More generally, the eigenstates of the entire spin system are not the states of the individual protons in the α-, β-, γ-, δ-, or ε-position, but are the entangled combination of all of them. As a consequence, polarizing the states of the α-CH_2 and β-CH_2 protons in the course of the chemical reaction one produces nonequilibrium population of the states of the entire spin system and all the protons exhibit significant CIDNP at the detection field. With the spin–spin coupling constants and the chemical shifts taken from the spectra we estimate that the condition of strong coupling between the neighboring protons holds for fields lower than 0.25 T (the couplings between the neighboring protons in the aliphatic chain are typically about 7 Hz and the maximal $\Delta\sigma$ value is about 0.7 ppm). At the same time, the vicinal spin–

spin coupling constants ensure efficient CIDNP transfer within the timing scheme chosen guaranteeing that the criterion Eq. (9) is fulfilled.

4 Discussion and Conclusions

Taking the CIDNP formed in photo-reactions of adenosine monophosphate, N-acetyl tryptophan and undecanone as examples we demonstrated that CIDNP (or more generally speaking, all dynamic spin polarization phenomena of liquid samples) formed at low magnetic fields is strongly affected by scalar coupling of the nuclear spins in the diamagnetic reaction products, leading to a redistribution of polarization. We observed indirect polarization of nuclei that have no HFI in the radical stage and therefore are not polarizable at high magnetic field.

On the other hand, the condition of strong coupling alone does not assure the polarization transfer and we revealed that the timing scheme (the duration of the irradiation, waiting and transfer times) of the field-cycling experiment plays a very important role in the low-field CIDNP patterns and the efficiency of polarization redistribution. Accordingly, the criterion of polarization transfer was modified in the present work. It is important to emphasize that the polarization transfer due to strong coupling of spins as a coherent process is more efficient than the slower cross-relaxation as a stochastic process. While for the two-spin system an analytical treatment of kinetics and the comparison with the experimental data was feasible, the CIDNP transfer effects were also observed and qualitatively discussed for more complex spins systems. As is demonstrated on the example of the cyclic ketone the CIDNP transfer can proceed over a long distance without direct coupling. In general, in low-field polarization experiments one can expect long-distance polarization transfer between remote nuclei if they are linked by a network of strongly coupled spins. If, however, the chain of strong interactions is broken (for instance, by introducing a link interacting only weakly with its neighbors) the long-range polarization transfer will no longer occur.

As far as determination of HFI from low-field CIDNP data is concerned, one has to perform it with caution because the polarization of the individual nuclei is not straightforwardly related to their HFI at the radical stage. Only the total CIDNP, since it is not affected by the transfer, can be directly compared with the predictions of standard theoretical simulations, while in the analysis of the low-field CIDNP of individual spins the couplings among the spins and the field variation effects inevitably have to be taken into consideration.

Channelling polarization to desired target nuclei may become a tool for enhancing the notoriously low sensitivity of NMR spectroscopy. It can be utilized, for instance, in field cycling NMR studies of biopolymers to redistribute polarization of specific subsets of the nuclear spin system (directly polarized by CIDNP or other dynamic nuclear polarization techniques) over the molecule.

As a closing remark we want to point out that the polarization transfer phenomena considered here are not unique to CIDNP and are expected to arise also in other low-field experiments on hyperpolarized spin systems. For example, the mechanism discussed above can also explain the ALTADENA experiments with unprecedented long-range polarization transfer that have recently been reported [13].

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