

Creating Long-Lived Spin States at Variable Magnetic Field by Means of Photo-Chemically Induced Dynamic Nuclear Polarization

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Materials

N-acetyl-L-histidine (NHis) was used as received from ABCR GmbH (99%). 2,2'-dipyridyl was received from Aldrich (99%). Since it is a good chelating agent and known to be contaminated by paramagnetic metal ions it was purified according to the following procedure. Dipyridyl was dissolved in CCl_4 and metal ions were extracted three times by an alkaline aqueous solution of EDTA. The purified dipyridyl then was dried under vacuum. The DL-[$\alpha,2,4\text{-D}_3$]-histidine (His-D3) was prepared according to Ref. 1 from L-histidine received from Aldrich (99.5%). The 0.5 M solution of His in D_2O (Deutero, 99.9%) at pH~5.5 was degassed by repeated freezing and thawing under vacuum in a glass ampoule. The degassed solution was flame sealed under vacuum in the ampoule and heated to 150 °C for two days. The received solution contained 95% deuterated His and was diluted to prepare the solution for the experiments.

Two solutions were used in this study. The first solution contains 3 mM partially deuterated histidine (DL-[$\alpha,2,4\text{-D}_3$] histidine) and 5 mM 2,2'-dipyridyl in D_2O at pH 13.3. The second solution contains 20 mM N-acetyl-L-histidine and 2 mM 2,2'-dipyridyl in D_2O at pH 5.6.

Sample irradiation

For all experiments a XeCl excimer laser (Lambda Physics Compex EMG 101 MSC, wave length 308 nm) was used as a source of light. Output energy directly after the laser was 150-170 mJ per pulse. To direct light to the NMR probehead a liquid light guide (Lumatec GmbH, series 250, 5 mm diameter, and 1500 mm length) was used with a quartz lens and a mirror in front of it to focus the laser beam. Laser energy directly after the liquid light guide was 40-50 mJ/pulse. In the NMR probehead a quartz rod (7 mm) polished from the bottom and cut by a 40 degree angle from the top was implemented (see Figure S1). This setup allows irradiating a standard NMR sample tube (5 mm outer diameter) from the side. Laser energy after the quartz rod was 20-25 mJ/pulse. Our estimates show that at least half of the light is absorbed by the central part of the sample solution (about 100 μl). All solutions used had an optical density of about 0.7 at 4 mm pathway, which means 70% absorption of the light. Since histidine has a negligibly small extinction coefficient at 308 nm, only the DP molecules absorbed light.

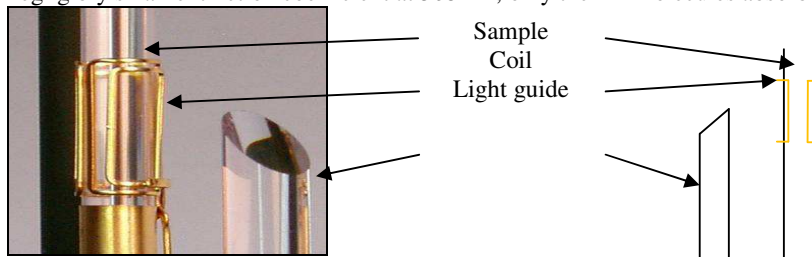


Figure S1. Light irradiation of the sample in the NMR probehead: photo (left) and scheme (right); sample, NMR saddle-shape coil and top of the light guide are shown.

For protocol (a) we used a constant repetition rate (100 Hz) of the laser during 1 second; altogether 100 laser shots were used. For protocol (b) we kept the total number of laser shots constant (100) and varied the repetition rate from 200 to 5 Hz, which gave us different irradiation time (τ_p) from 0.5 to 20 seconds.

The value of 10 mJ/pulse corresponds to 1.6×10^{16} photons; i.e., 1.1×10^{16} photons are absorbed by the sample after each laser flash. At 2 mM concentration of DP and irradiated volume of 100 μl there are approximately 1.2×10^{17} DP molecules in the irradiated volume. Thus, in roughly 10 shots all the DP molecules pass through the photo-excitation cycle. The quantum yield of quenching of the DP triplet by His at pH 13.3 is close to unity (as follows from the quenching rate constant $7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [2], His concentration of 20 mM and triplet lifetime of 14

μs [³]). Thus, after 10 laser shots approximately 10 % of the His molecules go through the excitation cycle and acquire CIDNP. After 100 shots roughly all of them get polarized, and an NMR enhancement close to the maximal achievable value is reached. 100 shots can be applied in 1 second; therefore the maximal allowed enhancement can be estimated fast. Since the rate of the LLS relaxation is small an enhancement of approximately 100-200 is reached in our experiments at low fields. It is important to note that when the same His molecule goes several times through the radical stage its CIDNP does not grow considerably. This is because the polarization created during the previous cycle is rapidly destroyed by fast relaxation at the radical stage. Therefore it is of no use to repeat excitation for longer periods of time.

LLS at variable magnetic field

In this section we will consider (i) how the LLS is selectively populated (or depopulated) over a wide field range, (ii) what the CIDNP spectrum looks like once the system is polarized at low field and the NMR spectrum is taken at high field and (iii) how the relaxation time of the LLS depends on the magnetic field. For the sake of simplicity and clarity, we will consider here only a scalar coupled two-spin $\frac{1}{2}$ system, which describes the two polarized $\beta\text{-CH}_2$ protons and for which the analytical treatment is possible.

Selective population of LLS over a wide field range. Let us show that the CIDNP technique allows one to populate (or depopulate) selectively the singlet spin state over a wide field range.

At zero field the eigen-states of the Hamiltonian of the two-spin system are characterized by the total spin, i.e., one singlet and three triplet states are the eigen-states. Here, the three degenerate triplet sub-states always have the same

population, $P_T = \frac{P_{T_+} + P_{T_0} + P_{T_-}}{3}$, which is in general different from that of the singlet state, P_S . Such a pattern is

known as the zero-field multiplet effect⁴⁻⁶ and it exists because of the isotropy of space (absence of a preferred direction) resulting in a population of states with respect to their total momentum. The rule for the sign of $(P_S - P_T)$ is known^{5,6}:

$$\text{sign}(P_S - P_T) = \text{sign}(a_1 a_2) \mu$$

Here a_1 and a_2 are the hyperfine coupling constants (HFCCs) of the spins in the radicals while μ stands for the spin multiplicity of the radical pair precursor (being equal to +1 for an initially triplet-correlated radical pair and -1 for an initially singlet-correlated radical pair). As the magnetic field increases the degeneracy of the three triplet states is lifted and in general they no longer have equal population. However, for selectively populating and investigating LLS by means of CIDNP it is sufficient that the average population of the three triplet states, $|T_+\rangle, |T_0\rangle, |T_-\rangle$, which is

$P_T = \frac{P_{T_+} + P_{T_0} + P_{T_-}}{3}$, differs from P_S . This is because there are two distinctly different time constants in the

relaxation: short times, during which the three triplet states become equally populated (times comparable to T_1), and much longer times comparable to T_{LLS} . As a consequence, at times comparable to T_1 all three triplet states acquire nearly equal populations (assuming that the thermal polarization is much smaller than CIDNP) and only much later the LLS has relaxed. Thus, at $T_1 < t < T_{LLS}$ all hyperpolarization present in the system is proportional to $(P_S - P_T)$. So, after a waiting period of T_1 the polarization is determined by a single quantity $(P_S - P_T)$ and there is only preferential population (or de-population) of the singlet state with respect to the triplet states.

In the field dependence of CIDNP there are different regions. At first, as the field increases all three triplet states acquire different populations, which results in the net polarization of the system due to the fact that $P_{T_+} \neq P_{T_-}$.

The maximum of the net CIDNP, defined as $\langle I_z \rangle = P_{T_+} - P_{T_-}$ is reached at fields, which are comparable to the effective

HFC field⁷ in the radical pair, a_{eff} (typically, a few mT). At the same time, the inequality $P_S \neq \frac{P_{T_+} + P_{T_0} + P_{T_-}}{3}$ still

holds. As the field increases to values that are much higher than a_{eff} , the states are selected with respect to their z-projection according to the properties of the radical pair Hamiltonian. As a consequence, $P_S = P_{T_0}$ and $P_S \neq P_T$.

When the field B falls into a range where $B \gg a_{eff}$ and $\Delta g B \ll a_{eff}$ one obtains $P_{T_+} = P_{T_-} \neq P_{T_0} = P_S$ and therefore zero

net CIDNP, $\langle I_z \rangle = 0$, and again $P_S \neq P_T$. Here Δg stands for the difference in g-factor for the radicals constituting

the radical pair. Finally, once $\Delta g B$ becomes larger than a_{eff} , the difference $(P_S - P_T)$ becomes small. The

corresponding magnetic fields are in the order of several Tesla for organic radicals. Magnetic field dependences of polarization and state populations are shown in Fig.S2a and Fig.S2b, respectively. Interestingly, the polarization of

the type $(P_S - P_T)$ is noticeably larger than the net polarization, $\langle I_z \rangle$, except for very high fields. Thus, for a two-spin

system the part of CIDNP, which corresponds to selective population (or depopulation) of the singlet state, can be the strongest polarization in the molecule.

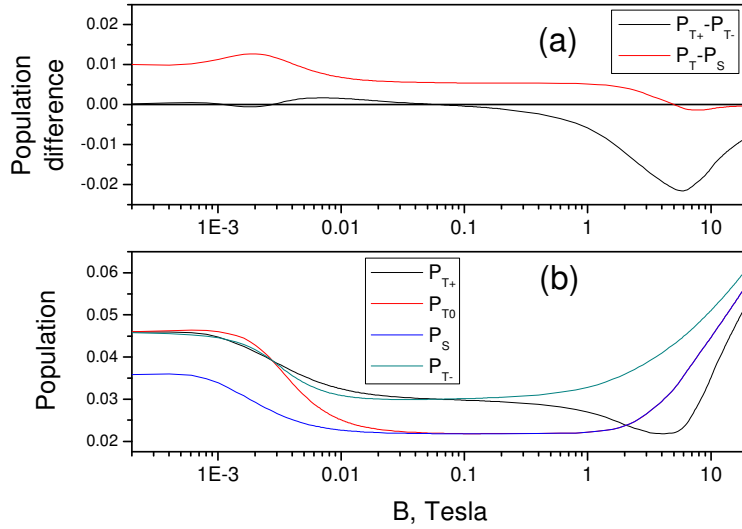


Figure S2. Field dependence of polarization (a) and populations of the spin states (b) for a two-spin system polarized by means of CIDNP. Method of calculation is discussed in Refs.^{6,8}. Parameters of calculation are taken from Ref.⁸: $g_1=2.00226$ (radical 1, modeling radical of N-acetyl-histidine) and $g_2=2.0030$ (radical 2, modeling radical of 2,2'-dipyridyl). Hyperfine couplings: $a_1=1.53$ mT for each of the protons shown, $a_2=-1.1$ mT for each of the aromatic protons, effective semiclassical hyperfine field of the other nuclei $a_{eff}=0.2$ mT – for radical 1; effective hyperfine field $a_{eff}=0.7$ mT – for radical 2. Other parameters: cage lifetime $\tau_d=0.5$ ns; recombination of the radical pair is diffusion-controlled; shown are state populations per one recombining pair.

Thus, in a wide field range CIDNP can directly provide strongly selective population of the singlet state of a pair of protons. It is important to emphasize that the singlet state (i) is long-lived being immune to the intramolecular dipolar interactions and (ii) can be a spin eigen-state of the molecule in a certain field window. Once the strength of the scalar interaction between the two spins, J , is larger than the difference, $\delta\nu$, in their Zeeman interactions with the magnetic field B , the singlet state is a spin eigen-state. For the histidine β -CH₂ protons the corresponding field range is fairly broad extending up to approximately 1 Tesla. This window of magnetic fields approximately coincides with that of forming large (P_S-P_T) polarization.

In this context it is also important to discuss the NMR enhancement provided by CIDNP patterns of such type. As follows from Fig.S2a the polarization (P_S-P_T) is about 1%. Boltzmann spin polarization of protons at 300 K and a magnetic field of 7 T (300 MHz frequency for protons) is about 5×10^{-5} . Thus, as compared to the 300 MHz NMR at thermal equilibrium CIDNP can provide a substantial NMR enhancement of approximately 200.

Pattern of the CIDNP spectrum. Another question of importance for the analysis of the relaxation behavior, is how the presence of the preferentially populated singlet state at low field reveals itself in the NMR spectra detected at high field. At low field the population pattern corresponding to selection with respect to the total momentum is characterized by zero net polarization of the spins. Only multiplet polarization is formed representing the entanglement of spins. As a result, polarization disappears when integration over the whole NMR spectrum is performed; hence it becomes necessary to analyze the individual NMR lines. In order to understand properly the CIDNP spectral pattern it is necessary (i) to consider the effects of field switching on the populations of spin states and (ii) to take into account the non-trivial dependence of the line intensities on the detection RF pulse length.

Hereafter by net and multiplet polarization we mean the expectation values of the corresponding spin operators, namely, $\hat{I}_{1z}, \hat{I}_{2z}, \hat{I}_{1z}\hat{I}_{2z}$. The net polarization of the i -th spin is defined as follows

$$\langle I_{1z} \rangle = \text{Tr}\{\hat{I}_{1z}\rho\}, \quad \langle I_{2z} \rangle = \text{Tr}\{\hat{I}_{2z}\rho\}$$

whereas the multiplet polarization of two spins is equal to

$$\langle I_{1z}I_{2z} \rangle = \text{Tr}\{\hat{I}_{1z}\hat{I}_{2z}\rho\}.$$

Here ρ is the density matrix of the two spins. Net polarization of each spin describes its magnetization along the z -axis, while multiplet polarization stands for the non-equilibrium mutual orientation (or entanglement) of the spins.

Effects of field switching. Effects of field switching become important because CIDNP is formed at low field, whereas the spectrum can only be detected with sufficient resolution at the high field of the NMR spectrometer. During field switching additional spin dynamics can be effective, which has to be taken into account. Here we will consider only two limiting cases, which correspond (a) to a very fast (sudden) field jump and (b) to very slow (adiabatic) field variation. In the two-spin $1/2$ system the states $|T_+\rangle = |\alpha\alpha\rangle$ and $|T_-\rangle = |\beta\beta\rangle$ are eigen-states of the system at any magnetic field and, consequently, their populations do not change during the switching at any

switching speed. In contrast, the states characterized by $\langle I_z \rangle = 0$ are coupled and vary with the field. At high field (difference in their Zeeman interactions with the field far exceeds their scalar coupling strength, J) the eigen-states are $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$, whilst at zero field the eigen-states are $|S\rangle$ and $|T_0\rangle$. Schemes of energy levels at high and low fields with their populations are given in Figure S3.

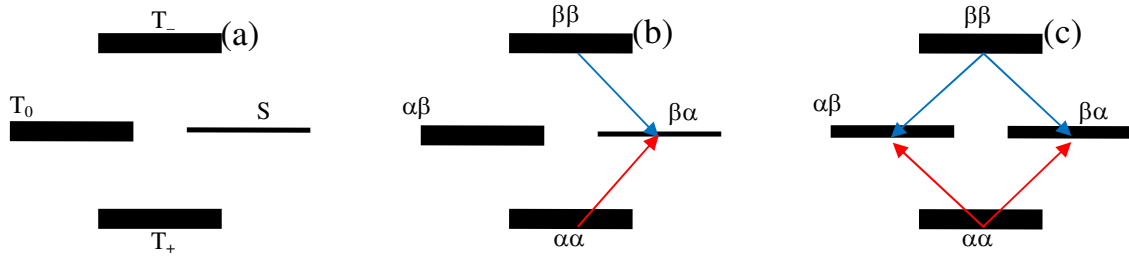


Figure S3. Populations of the spin eigen-states near zero field (a) and after switching to high field in the adiabatic (b) and sudden (c) regime. NMR transitions at high field are shown by arrows (red – absorptive and blue – emissive).

In the case of adiabatic switching the populations of the coupled spin states follow the states as they vary with the field. As a consequence, for a two-spin system the populations of the $|S\rangle$ and $|T_0\rangle$ states go selectively into the populations of the corresponding high-field states, $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ (correlation of states takes place, see Fig.S3b). Thus, the field switching only affects the two levels characterized by the zero z-projection of the total spin. In the sudden switching case the spin Hamiltonian changes abruptly so that there is no spin dynamics taking place during switching. As a consequence, the density matrix of the system remains unchanged but populations are redistributed among the eigen-states of the new (high-field) Hamiltonian. The corresponding population pattern is shown in Fig.S3c. The criterion of the adiabaticity is roughly formulated as follows: $\tau_f > 1/J$. However, if the field is not varied linearly with time or there are level-crossings at intermediate fields (which is the case if three or more coupled spins are involved) the criterion has to be modified considerably.

In the case of the β -CH₂ protons the singlet state is under-populated whereas the three triplet states are over-populated prior to the field jump.

In the case of sudden field switching the density matrix has no time to change and the resulting polarization values are the same at high and low fields. As a consequence, the two protons would have zero net polarization and a multiplet polarization, $\langle I_{1z} I_{2z} \rangle$, equal to $(P_S - P_T)/4$. In the case of adiabatic switching correlation of states becomes necessary. As a consequence, the expectation values of the spin operators are as follows^{6,8}:

$$\langle I_{1z} \rangle = \frac{P_S - P_T}{2} = -\langle I_{2z} \rangle; \quad \langle I_{1z} I_{2z} \rangle = \frac{P_S - P_T}{4}.$$

Here spin “1” is the one having the larger chemical shift on the σ -scale. Thus, not only multiplet polarization is formed, but the spins also acquire net magnetization of the same amplitude but opposite sign (resulting in zero total net CIDNP). Numerical calculations show that for the β -CH₂ protons the experimental field variation (even for the fastest switching available) is very close to the adiabatic regime because of a large J -coupling constant (about 14-15 Hz) and a relatively small difference in the NMR frequencies of the two spins. Thus, the typical population pattern for the spin system polarized at low field after field switching is as follows:

$$P_{\alpha\alpha} = P_T; \quad P_{\alpha\beta} = P_S; \quad P_{\beta\alpha} = P_T; \quad P_{\beta\beta} = P_T$$

and $P_S < P_T$.

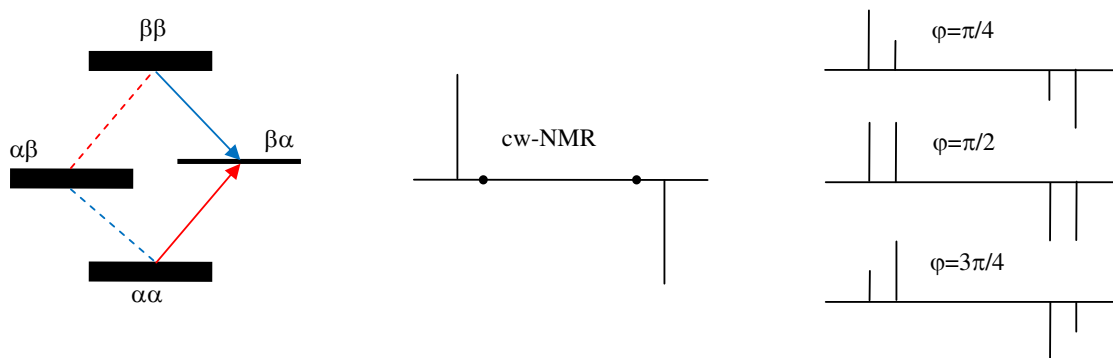


Figure S4. Populations of the spin eigen-states after adiabatic switching from zero field with parallel transitions shown in the same color; cw-NMR spectrum and Fourier transform NMR spectra at detection flip angles equal to $\pi/4$, $\pi/2$, $3\pi/4$.

Flip angle dependence of the NMR spectrum. One should also keep in mind that in the presence of non-thermal polarization the NMR spectra exhibit a rather unusual dependence on the flip angle, φ , of the detection RF-

pulse. Once polarization comes from preferred population (or depopulation) of the singlet state with subsequent adiabatic field switching the line intensities L are modified as follows⁸:

$$\begin{aligned} L_{\beta\alpha \rightarrow \beta\beta} &= -\frac{\sin \varphi}{2} \sin^2 \frac{\varphi}{2} (P_s - P_T); & L_{\alpha\alpha \rightarrow \alpha\beta} &= -\frac{\sin \varphi}{2} \cos^2 \frac{\varphi}{2} (P_s - P_T); \\ L_{\alpha\beta \rightarrow \beta\beta} &= \frac{\sin \varphi}{2} \cos^2 \frac{\varphi}{2} (P_s - P_T); & L_{\alpha\alpha \rightarrow \beta\alpha} &= \frac{\sin \varphi}{2} \sin^2 \frac{\varphi}{2} (P_s - P_T). \end{aligned}$$

The corresponding system of energy levels and their populations as well as the CIDNP spectra are shown in Figure S4.

Thus, the presence of an over-populated (or under-populated) LLS contributes to all NMR lines and the full NMR spectrum of the polarized spin system must be correctly interpreted for analyzing its relaxivity. If there is also net polarization present in the system, i.e., the populations of the triplet states at low field are different, there will be a contribution to all the NMR lines proportional to $\sin \varphi$. Analysis of the NMR lines as a function of the relaxation period at low field therefore allows one to identify both rapidly and slowly relaxing modes and determine their relaxation times. If the spin system is strongly coupled even at high field (which is the case for the β -CH₂ protons) the formulae have to be modified as proposed by Ernst et al.⁹ but the general tendency remains the same. When more than two spins are coupled and higher-spin orders are involved the general result for $L_{i \rightarrow j}$ is considerably complicated¹⁰; hence, one has to analyze spectra for a set of flip angles to obtain full information about the spin system.

Field dependence of relaxation. In general, the relaxation of the two-spin system can be described by using the approach developed by Freeman et al.¹¹ who calculated the rates of the relaxation transitions between the levels for two mechanisms (dipole-dipole relaxation and relaxation due to fluctuating local fields) at arbitrary field strength in the fast motional limit. The strength of the external magnetic field can be characterized by a single parameter, the mixing angle θ , which is defined as follows:

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

At high field (weakly coupled spins) the mixing angle turns to zero (or to π depending on the sign of J), whereas at zero field (strongly coupled spins) it is equal to $\pi/4$. The eigen-states of the spin system at arbitrary field can also be expressed in terms of θ :

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

The characteristic relaxation rates in the spin system are given by the eigen-values of the matrix \hat{W} composed of the rates of all the transitions. In Ref.¹¹ such a matrix has been determined for the dipolar relaxation mechanism:

$$\hat{W} = R_1 \begin{pmatrix} -3/5 & (1 + \sin 2\theta)/10 & (1 - \sin 2\theta)/10 & 2/5 \\ (1 + \sin 2\theta)/10 & \begin{pmatrix} -(1 + \sin 2\theta)/5 \\ -\cos^2 2\theta/15 \end{pmatrix} & \cos^2 2\theta/15 & (1 + \sin 2\theta)/10 \\ (1 - \sin 2\theta)/10 & \cos^2 2\theta/15 & \begin{pmatrix} -(1 - \sin 2\theta)/5 \\ -\cos^2 2\theta/15 \end{pmatrix} & (1 - \sin 2\theta)/10 \\ 2/5 & (1 + \sin 2\theta)/10 & (1 - \sin 2\theta)/10 & -3/5 \end{pmatrix}.$$

The relaxation rates of the system (eigen-values of \hat{W}) are as follows:

$$\begin{aligned} W_1 &= 0, & W_2 &= -R_1 = -1/T_{1d}, \\ W_{3,4} &= -\frac{20 + 2 \cos 4\theta \pm \sqrt{2(81 - 80 \cos 4\theta + \cos 8\theta)}}{60} R_1. \end{aligned}$$

All non-zero values are negative describing decrease of polarization in the system. The physical meaning of the W_i quantities can be understood once the corresponding eigen-vectors are also specified. For the first two eigen-values, V_i , the vectors are quite simple giving

$$V_1 = \begin{pmatrix} 1/2 \\ 1/2 \\ 1/2 \\ 1/2 \end{pmatrix}, \quad V_2 = \begin{pmatrix} 1/\sqrt{2} \\ 0 \\ 0 \\ -1/\sqrt{2} \end{pmatrix}.$$

The first eigen-value, which is equal to zero, thus describes the fact that the total population of all four states is preserved. The second value, equal to R_1 describes the relaxation of the net polarization of the two spins, $\langle I_z \rangle = (P_{\alpha\alpha} - P_{\beta\beta})/2$, i.e., the longitudinal relaxation of two spins. The remaining two eigen-vectors are relatively cumbersome at arbitrary θ value, however, the corresponding vectors are very simple at zero field ($\theta = \pi/4$):

$$V_3 = \begin{pmatrix} 1/\sqrt{6} \\ -1/\sqrt{3} \\ 0 \\ 1/\sqrt{6} \end{pmatrix}, \quad V_4 = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}.$$

Although the state relaxing at a rate $-W_3=3R_1/5$ cannot be straightforwardly identified the conclusions for the last vector are obvious: it describes the relaxation of the singlet-state population with the corresponding eigen-value, W_4 , going to zero. Hence, W_4 describes the field-dependent relaxation of the LLS. Thus, we can define the relaxation rate of the LLS

$$R_{LLS} = -W_4 = \frac{20 + 2 \cos 4\theta - \sqrt{2(81 - 80 \cos 4\theta + \cos 8\theta)}}{60} R_1.$$

The field dependence manifests itself for R_{LLS} via the field-dependent mixing angle θ . At zero field R_{LLS} goes to zero in accord with the existence of the LLS. At high field $R_{LLS}=R_1/3$, i.e., some character of the LLS is still present. The high-field results for the relaxation behavior are simple and the relaxation rates are equal to

$$W_1 = 0, \quad W_2 = -R_1 = -1/T_{1d}, \quad W_3 = -2R_1/5, \quad W_4 = -R_1/3.$$

corresponding to the following eigen-vectors:

$$V_1 = \begin{pmatrix} 1/2 \\ 1/2 \\ 1/2 \\ 1/2 \end{pmatrix}, \quad V_2 = \begin{pmatrix} 1/\sqrt{2} \\ 0 \\ 0 \\ -1/\sqrt{2} \end{pmatrix}, \quad V_3 = \begin{pmatrix} 1/2 \\ -1/2 \\ -1/2 \\ 1/2 \end{pmatrix}, \quad V_4 = \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \\ 0 \end{pmatrix}.$$

Thus, the total net polarization in the system relaxes with the rate of R_1 ; the difference of the individual net polarizations relaxes with $R_1/3$ and the multiplet polarization decays with a time constant of $2R_1/5$. The solutions for the eigen-vectors V_3 and V_4 at arbitrary field strength are rather cumbersome and will not be given here.

The experimental dependences were fitted with the formula derived for W_4 . For systems with more coupled spins analytical results can be obtained¹²⁻¹⁴ only for low fields (close to zero) or very high fields but not in the intermediate field range. For modeling field-dependent relaxation data for such systems it is necessary to perform a numerical analysis of the relaxation rates using the same strategy as described here (computation of the relaxation matrix and its eigen-values).

References

- (1) Matthews, H. R.; Matthews, K. S.; Opella, S. J. Selectively Deuterated Amino Acid Analogues. Synthesis, Incorporation into Proteins and NMR Properties. *Biochim. Biophys. Acta* **1977**, *497*, 1-13.
- (2) Tsentalovich, Y. P.; Morozova, O. B.; Yurkovskaya, A. V.; Hore, P. J.; Sagdeev, R. Z. Time-Resolved CIDNP and Laser Flash Photolysis Study of the Photoreactions of N-Acetylhistidine with 2,2'-Dipyridyl in Aqueous Solution. *J. Phys. Chem. A* **2000**, *104*, 6912-6916.
- (3) Tsentalovich, Y. P.; Morozova, O. B.; Yurkovskaya, A. V.; Hore, P. J. Kinetics and mechanism of the photochemical reaction of 2,2'-dipyridyl with tryptophan in water: Time-resolved CIDNP and laser flash photolysis study. *J. Phys. Chem. A* **1999**, *103*, 5362-5368.
- (4) Kaptein, R.; Den Hollander, J. A. Chemically Induced Dynamic Nuclear Polarization. X. Magnetic Field Dependence. *J. Am. Chem. Soc.* **1972**, *94*, 6269-6280.
- (5) Tarasov, V. F.; Shkrob, I. A. Low-Field CIDNP in Intracellular Radical Disproportionation. Violation of Equivalency in J-Coupled Nuclear Spin Systems. *J. Magn. Reson. Ser. A* **1994**, *109*, 65-73.
- (6) Ivanov, K. L.; Vieth, H.-M.; Miesel, K.; Yurkovskaya, A. V.; Sagdeev, R. Z. Investigation of the Magnetic Field Dependence of CIDNP in Multi-Nuclear Radical Pairs. Part II. Photoreaction of Tyrosine and Comparison of Model Calculation with Experimental Data. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3470-3480.
- (7) Schulten, K.; Wolynes, P. G. Semiclassical Description of Electron Spin Motion in Radicals Including the Effect of Electron Hopping. *J. Chem. Phys.* **1978**, *68*, 3292-3297.
- (8) Ivanov, K. L.; Lukzen, N. N.; Vieth, H. M.; Grosse, S.; Yurkovskaya, A. V.; Sagdeev, R. Z. Investigation of the Magnetic Field Dependence of CIDNP in Multinuclear Radical Pairs. 1. Photoreaction of Histidine and Comparison of Model Calculation with Experimental Data. *Mol. Phys.* **2002**, *100*, 1197-1208.
- (9) Schäublin, S.; Hoehener, A.; Ernst, R. R. Fourier Spectroscopy of Nonequilibrium States, Application to CIDNP (Chemical Induced Dynamic Nuclear Polarization), Overhauser Experiments, and Relaxation Time Measurements. *J. Magn. Reson.* **1974**, *13*, 196-216.
- (10) Ivanov, K. L.; Miesel, K.; Vieth, H. M.; Yurkovskaya, A. V.; Sagdeev, R. Z. 2D NMR Nutation Analysis of Non-Thermal Polarization of Coupled Multi-Spin Systems. *Z. Phys. Chem.* **2003**, *217*, 1641-1659.
- (11) Freeman, R.; Wittekoek, S.; Ernst, R. R. High-Resolution NMR Study of Relaxation Mechanisms in a Two-Spin System. *J. Chem. Phys.* **1970**, *52*, 1529-1544.

- (12) Vinogradov, E.; Grant, A. K. Hyperpolarized Long-Lived States in Solution NMR: Three-Spin Case Study in Low Field. *J. Magn. Reson.* **2008**, *194*, 46-57.
- (13) Grant, A. K.; Vinogradov, E. Long-Lived States in Solution NMR: Theoretical Examples in Three- and Four-Spin Systems. *J. Magn. Reson.* **2008**, *193*, 177-190.
- (14) Karabanov, A. A.; Bretschneider, C.; Köckenberger, W. Symmetries of the Master Equation and Long-Lived States of Nuclear Spins. *J. Chem. Phys.* **2009**, *131*, 204105/1-204105/10.