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2D NMR Nutation Analysis of Non-Thermal Polarization of Coupled Multi-Spin Systems

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Dedicated to Prof. Dr. Hans-Heinrich Limbach on the occasion
of his 60th birthday

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A new, convenient method of analyzing the spin polarization of a non-equilibrium system of N coupled nuclei is described and applied to photo-reactions exhibiting chemically induced dynamic nuclear polarization (CIDNP). It is based on the Fourier analysis of the variation of NMR line intensities as a function of the radio frequency excitation pulse length. A relationship between the spectral components at various harmonic order and the alignment in the spin multiplet is established. In application to the Norrish type I photolysis of cyclodecanone we demonstrate that at low magnetic field the rate determining step in the reaction kinetics depends on the mutual orientation of at least four pairs of non-equivalent spins.

1. Introduction

NMR spectroscopy owes its appeal as a versatile analytic method to the high content of information that is reflected in the position, the shape and intensity pattern of the spectral lines as well as in the time evolution of the spin observables. Matching this diversity a large variety of experimental techniques has been developed. Both aspects, developing new techniques and utilizing the potential of NMR for solving problems in analytical chemistry, have been a focus of Hans-Heinrich Limbach's interest for several decades. In this contribution we will deal with the intensity distribution in spectra of dynamically polarized spin systems. While at thermal equilibrium the spectral intensities

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correspond to the number of spins contributing to a particular line, for situations off equilibrium the response of the spin system to non-selective pulse excitation is more complex and the different pattern of polarization has also to be considered. As a rule the mechanism and the efficiency of forming the spin polarization are closely related to the magnetic parameters and the dynamics of the involved species. In many cases, the observed intensity distribution is usable as a fingerprint of intermediate stages in the polarization process. The analysis by evaluating the population numbers of the spin eigenstates by means of Fourier Transform NMR (FT-NMR) faces difficulties. First, only for small excitation pulse rotation angles $\varphi = \gamma B_1 \tau$ (γ gyromagnetic ratio, B_1 amplitude of excitation pulse, and τ pulse duration) the spectral intensities of lines are proportional to the population differences of the involved pair of levels as obtained by slow passage NMR techniques (cw-NMR). This holds true even for weakly coupled spins. Using a small excitation angle inevitably leads to a small FID amplitude and thus to a low S/N ratio. T_1 relaxation toward thermal equilibrium prohibits consecutive acquisition and accumulation of a series of signals excited at such a small angle, unless prior to each acquisition a full polarization cycle is executed. Second, spin-spin coupling is often so small or motional line broadening so large that resolution of neighboring lines is impossible. In such cases the data are insufficient for the full analysis. An alternative approach is to study the variation of the spectral intensity pattern as a function of the rotation angle φ. In the present paper we show how this approach leads to full characterization of the multi-nuclear spin order in molecules that contain several coupled nuclei and illustrate the method by a prominent experimental example.

Rotation angle dependent FT-NMR spectra, often termed nutation patterns, have been studied experimentally and theoretically in a sizable number of works [1–8]. In most cases the consideration was restricted to two-spin $1/2$ systems because they show a relatively simple nutation that contains only $\sin\varphi$ and $\sin 2\varphi$ terms. For larger spin groups the interpretation of experimental nutation patterns and the evaluation of the relevant system parameters is rather sophisticated. A spin system of N coupled spins $1/2$ shows, in general, a superposition of N terms with different angular variations. In the present article we suggest a general method to analyze the nutation patterns of such multinuclear spin systems. The approach follows the observation [3] that in a two spin system the $\sin\varphi$ term carries the net magnetization of the nuclei, while the $\sin 2\varphi$ term represents their non-equilibrium average mutual orientation. A generalization of this idea to systems of N coupled spins is to record a series of spectra measured at stepwise increased rotation angle and decompose this set by Fourier analysis into N harmonics. One can then represent the result as a 2D spectrum where the second dimension corresponds to the harmonic order of the periodic nutation pattern. In this case the k-th harmonic component will reflect the mutual orientation of k nuclear spins (k-th spin order).

Typical examples of a process generating nuclear spin polarization far off equilibrium are Para-Hydrogen Induced Polarization (PHIP) [9] and Chemically Induced Dynamic Nuclear Polarization (CIDNP) [10, 11]. PHIP (sometimes the acronyms ALTADENA [12] and PASADENA [13] are used) is observed in hydrogenation reactions. It has its origin in the singlet multiplicity of the precursor para-H_2 molecule and thus gives rise to singlet correlation of the corresponding pair of protons in the reaction products. CIDNP arises at reactions with paramagnetic intermediates and results from reactivity differences of radical pairs that depend upon the nuclear spin states [11, 14, 15] and leads to the formation of high spin order. This polarization reveals itself in anomalous intensities of the lines in the NMR-spectra of diamagnetic reaction products. The intensity pattern is correlated with the magnetic properties of the paramagnetic state, such as hyperfine coupling constants, electronic exchange interaction, external magnetic field strength, and g-factors of the radical centers and thus provides information on the transient radicals. In many cases the radical pairs recombine rapidly by means of hydrogen or electron transfer. As a consequence, the CIDNP arising in these reactions contains evidence on the elementary transfer event and allows to obtain detailed data on the reaction process that are often unavailable by other techniques. Non-equilibrium nuclear spins systems of various kind can be also prepared by applying suitable rf-pulse sequences; [1] in this way such diverse phenomena as spin waves in linear chains of nuclear spins [16] and algorithms in NMR quantum computation [17] have been studied.

In the present article we consider in detail the theoretical treatment of the two-dimensional harmonic analysis of CIDNP spectra of three coupled nuclei and describe briefly the extension to N spins, before we apply our approach to the analysis of the complicated CIDNP patterns arising in the course of the photolytic reaction of cyclic ketones.

2. 2D harmonic analysis of spin order in polarized systems of coupled nuclei

2.1 General case of the polarized system of N-spins

Here we shall present the analysis of the nutation patterns of thermally non-equilibrium system of N weakly coupled spins 1/2. We shall restrict ourselves to the so-called first order non-equilibrium states [1] where coherent superposition of states is absent and the nuclear density matrix, $\hat{\sigma}$, is diagonal in the eigenbasis of the Hamiltonian. In principle, in the case of N coupled polarized nuclei the total polarization, *i.e.* the distribution of population over the multilevel system, is determined (when using the basis of products of single-spin operators) not alone by all net polarizations

$$\left\langle \hat{I}_{\alpha z} \right\rangle = \mathrm{Tr}\left\{ \hat{I}_{\alpha z} \hat{\sigma} \right\}, \quad (\alpha = 1, \dots , N) \tag{2.1}$$

and the average mutual orientation of each pair of spins (multiplet polarization)

$$\left\langle \hat{I}_{\alpha z}\hat{I}_{\beta z}\right\rangle = \mathrm{Tr}\left\{\hat{I}_{\alpha z}\hat{I}_{\beta z}\hat{\sigma}\right\}, \quad (\alpha,\beta = 1,\ldots,N,\ \alpha\neq\beta)\,, \tag{2.2}$$

but also by higher order entanglement. Here, $\hat{I}_{\alpha z}$ is the operator of the projection of spin α on the Z axis. Correspondingly, it is necessary to determine besides $\langle\hat{I}_{\alpha z}\rangle$ and $\langle\hat{I}_{\alpha z}\hat{I}_{\beta z}\rangle$ also the following expectation values:

$$\begin{aligned}
&\left\langle \hat{I}_{\alpha z}\hat{I}_{\beta z}\hat{I}_{\gamma z}\right\rangle = \mathrm{Tr}\left\{\hat{I}_{\alpha z}\hat{I}_{\beta z}\hat{I}_{\gamma z}\hat{\sigma}\right\}, \qquad \alpha,\beta,\gamma = 1,\ldots,N, \qquad \alpha\neq\beta\neq\gamma \\
&\left\langle \hat{I}_{\alpha z}\hat{I}_{\beta z}\hat{I}_{\gamma z}\hat{I}_{\delta z}\right\rangle = \mathrm{Tr}\left\{\hat{I}_{\alpha z}\hat{I}_{\beta z}\hat{I}_{\gamma z}\hat{I}_{\delta z}\hat{\sigma}\right\}, \quad \alpha,\beta,\gamma,\delta = 1,\ldots,N, \quad \alpha\neq\beta\neq\gamma\neq\delta, \\
&\qquad \ldots \\
&\left\langle \hat{I}_{1z}\hat{I}_{2z}\ldots\hat{I}_{Nz}\right\rangle = \mathrm{Tr}\left\{\hat{I}_{1z}\hat{I}_{2z}\ldots\hat{I}_{Nz}\hat{\sigma}\right\}.
\end{aligned} \tag{2.3}$$

For the k-th order multiplet effect (average mutual orientation of k spins) there are C_N^k different combinations of the form (2.3) (here C_N^k are the binomial coefficients). To tackle the problem of determination of the quantities (2.1), (2.2), (2.3) we suggest the method presented below.

As we deal exclusively with weakly-coupled systems of spin $1/2$ nuclei the eigenstates of the Hamiltonian can be characterized by the set of magnetic quantum numbers of the individual nuclei (namely, their projections on the Z axis). Also, we will assume that the rf-excitation is homogeneous and non-selective with respect to all ^{1}H $\Delta\langle I_z\rangle = \pm 1$ transitions. For systems of N weakly-coupled non-selectively excited spins $1/2$ the flip angle dependence of the spectral line corresponding to the transition $|i\rangle \to |j\rangle$ between states $|i\rangle$ and $|j\rangle$ (the nutation pattern) is given by the following equation [1, 2]:

$$L_{i\to j}(\varphi) = \sin\varphi \sum_{(rs)} \left(\sin\frac{\varphi}{2}\right)^{2\Delta_{ij,rs}} \left(\cos\frac{\varphi}{2}\right)^{2N-2\Delta_{ij,rs}-2} L^{(0)}_{r\to s}\,. \tag{2.4}$$

In this context it is important to note that the FT-MNR signal intensity does not only depend on the population difference between states $|i\rangle$ and $|j\rangle$, but on the population differences between other states as well. Here $L^{(0)}_{r\to s} = (P_s - P_r)/2$ is the standard intensity of the fully selectively excited NMR transition $|r\rangle \to |s\rangle$ determined by the difference between their populations, $\Delta_{ij,rs}$ is the so-called “spin-flip number” [1] equal to the number of spin $1/2$ flips, required to make the state transitions $|i\rangle \to |j\rangle$ and $|r\rangle \to |s\rangle$ coincide. As a consequence, only the signals corresponding to the so-called “parallel” transitions (*i.e.* transitions that can be put into coincidence by flipping the spins) affect each other. The expression (2.4) of the N-spin non-equilibrium system can be written as a Fourier series consisting of N sine terms:

$$L_{i\to j}(\varphi) = \sum_{n=1}^{N} A^{(n)}_{i\to j} \sin n\varphi\,. \tag{2.5}$$

The amplitude of the harmonics, $A^{(n)}_{i\to j}$, are to be found as the coefficients of the Fourier series expansion of the periodic function $L_{i\to j}(\varphi)$. The expression for the NMR line intensity at the n-th harmonic, $A^{(n)}_{i\to j}$, is derived in the Appendix. One may represent the flip angle dependent FT-NMR spectrum (2.5) of a system off thermal equilibrium as a two dimensional one: the first coordinate is the spin precession frequency while the second one is the number of the harmonic, n. Hence, the original φ-dependent spectrum of the N spin system can be decomposed in two dimensions into N spectra at the different harmonics. It is important to note that the k_1-th order multiplet polarization (2.3) does not contribute to the k_2-th harmonic if $k_2 > k_1$. Therefore, the N-th harmonic contains purely N-th order multiplet polarization $\left\langle \hat{I}_{1z}\hat{I}_{2z}\ldots\hat{I}_{Nz}\right\rangle$, the $(N-1)$-th multiplet polarizations can be extracted from the $(N-1)$-th harmonic and so on. As a result, the expectation values of spin operators of different order are resolved in the second dimension. Consequently, by analyzing the CIDNP spectrum at all $1 \le n \le N$ one extracts all the quantities (2.1), (2.2), and (2.3) that provide the desired information on the radical reaction pathways and the magnetic properties (HFI constants, g-factors and electronic exchange interaction) of the reactants.

The way suggested here to determine the net and multiplet CIDNP is by no means unique. For systems of two spins 1/2 Vollenweider and Fischer [3] suggested measuring the FT-NMR spectra at $\varphi = \pi/4$ and $\varphi = 3\pi/4$, because their sum and their difference yield the net and multiplet polarization, respectively. However, to extend this approach to a larger number of spins turns out to become rather sophisticated; in general, one would have to measure at N exactly set flip angles and perform a complicated superposition of the spectra. In principle, the contributions of net and multiplet polarization can be also separated by means of a two-dimensional COSY experiment [18], as it is widely used in CIDNP investigations of protein structure [19]. In the presence of polarization additional cross-peaks arise solely from the multiplet polarization [18]. While such an analysis works well at $N = 2$, it meets a similar complication at larger N: no cross peaks arise from multiplet polarization of an order higher than two. To extract these quantities one would have to apply more pulses, thus increasing the complexity of the COSY experiment. In contrast, our present approach yields all data of interest in a straightforward way for systems with an arbitrary number of polarized nuclei. At the same time, the experiment is rather simple with just one variable rf-pulse necessary to record the data.

2.2 System of three coupled spins

As a demonstration of our approach we show an example of 2D harmonic analysis of the nutation patterns for three weakly coupled spins 1/2 (AMX-system). At thermal equilibrium the NMR spectrum shown in Fig. 1(a) consists of three quartets centered at the frequencies σ_1, σ_2, σ_3 (in units of the chemical shift), where σ_i is the chemical shift of the corresponding nucleus. The system

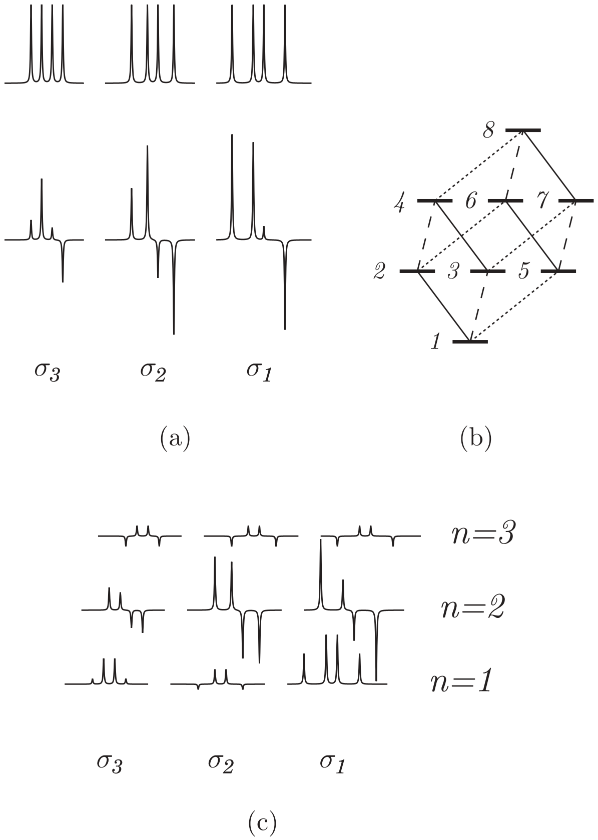

Fig. 1. 2D harmonic analysis of a three-spin system (schematic). (a): (upper trace) spectrum in thermal equilibrium and (lower trace) CIDNP spectrum measured at $\varphi = \pi/6$, with state populations calculated according to Adrian's theory [20] (see text). (b): system of eigenstates; states are enumerated according to Eq. (2.6); solid, long-dashed and short-dashed lines show the "parallel" NMR transitions. (c): harmonic spectra at $n = 1, 2, 3$. σ_i is the chemical shift of the i-th nuclei.

of eigenstates is presented in Fig. 1(b). Three groups of "parallel" transitions that affect each other in the FT-NMR [1] are shown by the solid, long-dashed, and short-dashed lines. Here we have chosen the following notation for the eigenstates:

$$\begin{aligned} &|1\rangle = |\alpha_1\alpha_2\alpha_3\rangle, \quad |2\rangle = |\alpha_1\alpha_2\beta_3\rangle, \quad |3\rangle = |\alpha_1\beta_2\alpha_3\rangle, \quad |4\rangle = |\alpha_1\beta_2\beta_3\rangle, \\ &|5\rangle = |\beta_1\alpha_2\alpha_3\rangle, \quad |6\rangle = |\beta_1\alpha_2\beta_3\rangle, \quad |7\rangle = |\beta_1\beta_2\alpha_3\rangle, \quad |8\rangle = |\beta_1\beta_2\beta_3\rangle\,. \end{aligned} \tag{2.6}$$

Let us first consider the intensities of the lines corresponding to the NMR transitions (flips) of the third spin. For instance, the expression for the

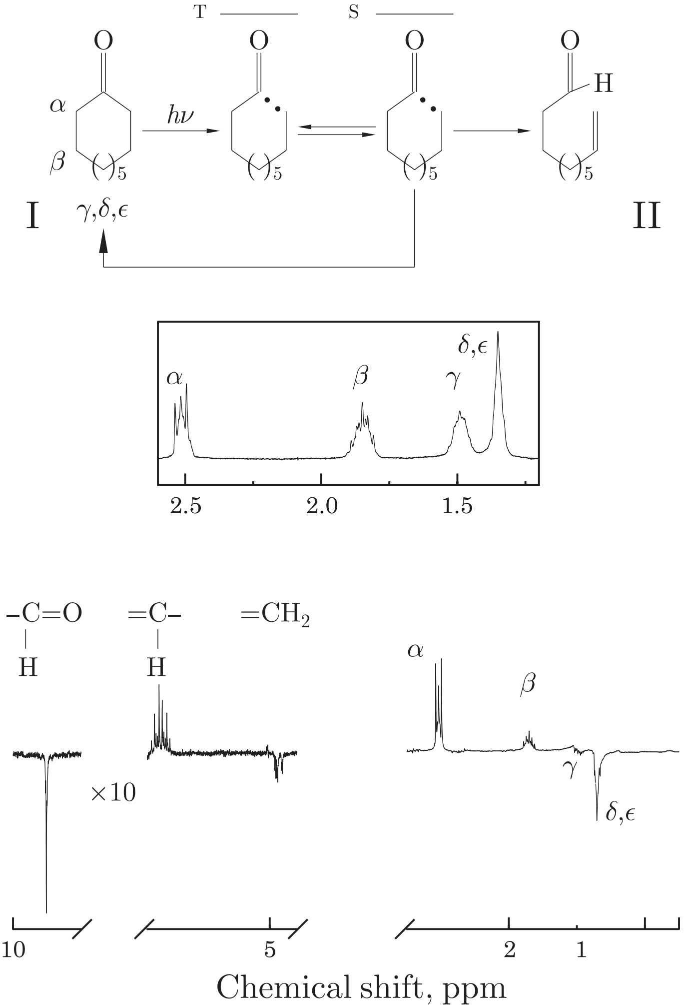

Fig. 2. Photolysis of cyclodecanone (C-10). Reaction scheme (top), thermal spectrum (insert) and CIDNP spectrum measured at $\varphi = \pi/4$ (bottom). Lines of product I at right and of product II at left part of the spectral range. α, β, γ, δ, and ϵ denote corresponding protons of ketone I.

$|\alpha_1\alpha_2\alpha_3\rangle \to |\alpha_1\alpha_2\beta_3\rangle$ ($|1\rangle \to |2\rangle$) transition intensity is as follows [1]:

$$L_{1\to 2} = \frac{1}{2}\sin\varphi\Big(\cos^4\frac{\varphi}{2}(P_1 - P_2) + \cos^2\frac{\varphi}{2}\sin^2\frac{\varphi}{2}(P_3 - P_4 + P_5 - P_6) + \sin^4\frac{\varphi}{2}(P_7 - P_8)\Big)\,. \tag{2.7}$$

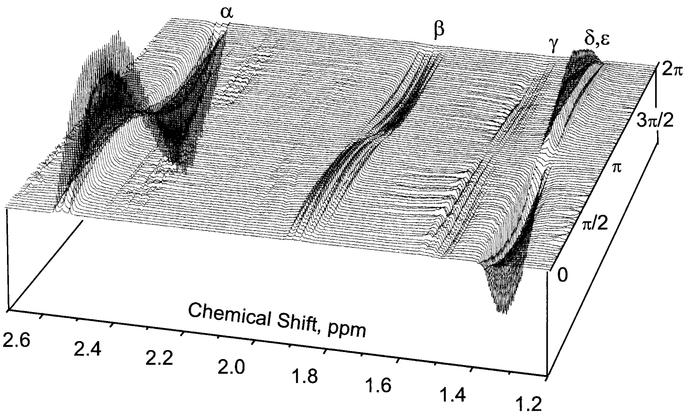

Fig. 3. CIDNP spectra of cylodecanone taken at different rotation angle φ.

One should note that in reference [1] there is a misprint (extra $\cos^2\frac{\varphi}{2}$) in the formula corresponding to (2.7). In accordance with the general formula (2.4) the intensity of the line that corresponds to the transition $|1\rangle \to |2\rangle$ does not only depend on the population difference $P_1 - P_2$ but on the population differences of “parallel” transitions ($|3\rangle \to |4\rangle$, $|5\rangle \to |6\rangle$, $|7\rangle \to |8\rangle$) as well [1]. We can write (2.7) as a sum of three Fourier harmonics:

$$L_{1\to 2} = A^{(1)}_{1\to 2}\sin\varphi + A^{(2)}_{1\to 2}\sin 2\varphi + A^{(3)}_{1\to 2}\sin 3\varphi\,. \tag{2.8}$$

The intensities of the harmonics, $A^{(n)}_{1\to 2}$, are as follows:

$$\begin{aligned} A^{(1)}_{1\to 2} &= \frac{5(P_1 - P_2 + P_7 - P_8) + 3(P_3 - P_4 + P_5 - P_6)}{32}, \\ A^{(2)}_{1\to 2} &= \frac{P_1 - P_2 - P_7 + P_8}{8}, \\ A^{(3)}_{1\to 2} &= \frac{P_1 - P_2 - P_3 + P_4 - P_5 + P_6 + P_7 - P_8}{32}, \end{aligned} \tag{2.9}$$

The operators of interest involving the third spin are given for the AMX-system as:

$$\begin{aligned} \hat{I}_{3z} &= \frac{1}{2}\mathrm{Diag}\{1,\,-1,\,1,\,-1,\,1,\,-1,\,1,\,-1\}\,, \\ \hat{I}_{1z}\hat{I}_{3z} &= \frac{1}{4}\mathrm{Diag}\{1,\,-1,\,1,\,-1,\,-1,\,1,\,-1,\,1\}\,, \\ \hat{I}_{2z}\hat{I}_{3z} &= \frac{1}{4}\mathrm{Diag}\{1,\,-1,\,-1,\,1,\,1,\,-1,\,-1,\,1\}\,, \\ \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z} &= \frac{1}{8}\mathrm{Diag}\{1,\,-1,\,-1,\,1,\,-1,\,1,\,1,\,-1\}\,. \end{aligned} \tag{2.10}$$

Here the notation of states is taken as in (2.6). The corresponding expectation values are:

$$\begin{aligned}\langle \hat{I}_{3z}\rangle &= \frac{P_1 - P_2 + P_3 - P_4 + P_5 - P_6 + P_7 - P_8}{2}\,,\\ \langle \hat{I}_{1z}\hat{I}_{3z}\rangle &= \frac{P_1 - P_2 + P_3 - P_4 - P_5 + P_6 - P_7 + P_8}{4}\,,\\ \langle \hat{I}_{2z}\hat{I}_{3z}\rangle &= \frac{P_1 - P_2 - P_3 + P_4 + P_5 - P_6 - P_7 + P_8}{4}\,,\\ \langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle &= \frac{P_1 - P_2 - P_3 + P_4 - P_5 + P_6 + P_7 - P_8}{8}\,.\end{aligned} \tag{2.11}$$

By substituting (2.11) we can rewrite (2.9) as follows:

$$A^{(1)}_{1\to 2} = \frac{\langle \hat{I}_{3z}\rangle + \langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle}{4},\quad A^{(2)}_{1\to 2} = \frac{\langle \hat{I}_{1z}\hat{I}_{3z}\rangle + \langle \hat{I}_{2z}\hat{I}_{3z}\rangle}{4},\quad A^{(3)}_{1\to 2} = \frac{\langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle}{4}\,. \tag{2.12}$$

Hence, as expected, the intensity of the third harmonics is completely determined by the triple multiplet polarization, $\langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle$. As it was in the case of two nuclei the intensity of the second harmonics depends on the multiplet polarization of two spins. Here we consider the NMR transitions of the third spin, therefore the relevant two-spin multiplet polarization is the mutual entanglement of the third spin with the two other spins, *i.e.* $\langle \hat{I}_{1z}\hat{I}_{3z}\rangle$ and $\langle \hat{I}_{2z}\hat{I}_{3z}\rangle$. The first Fourier harmonics, obviously, reflects the net polarization of the third spin. The additional term containing the triple multiplet polarization is not essential here and can be easily removed by adding up the intensities of the transitions $|1\rangle \to |2\rangle$, $|3\rangle \to |4\rangle$, $|5\rangle \to |6\rangle$, $|7\rangle \to |8\rangle$ (all flips of the third spin), see text below. The respective sign of the contributions to the multiplet polarization, $\langle \hat{I}_{1z}\hat{I}_{3z}\rangle$ and $\langle \hat{I}_{2z}\hat{I}_{3z}\rangle$, to each line at the second harmonics depends on the projections of the first and the second nuclei. A similar analysis can be done for the other transitions of the third spin: $|3\rangle \to |4\rangle$, $|5\rangle \to |6\rangle$, $|7\rangle \to |8\rangle$. For all other transitions of the third spin the intensities of the harmonics are given by:

$$\begin{aligned}A^{(1)}_{3\to 4} &= \frac{\langle \hat{I}_{3z}\rangle - \langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle}{4},\quad A^{(2)}_{3\to 4} = \frac{\langle \hat{I}_{1z}\hat{I}_{3z}\rangle - \langle \hat{I}_{2z}\hat{I}_{3z}\rangle}{4},\quad A^{(3)}_{3\to 4} = -\frac{\langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle}{4}\,,\\ A^{(1)}_{5\to 6} &= \frac{\langle \hat{I}_{3z}\rangle - \langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle}{4},\quad A^{(2)}_{5\to 6} = -\frac{\langle \hat{I}_{1z}\hat{I}_{3z}\rangle - \langle \hat{I}_{2z}\hat{I}_{3z}\rangle}{4},\quad A^{(3)}_{5\to 6} = -\frac{\langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle}{4}\,,\\ A^{(1)}_{7\to 8} &= \frac{\langle \hat{I}_{3z}\rangle + \langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle}{4},\quad A^{(2)}_{7\to 8} = -\frac{\langle \hat{I}_{1z}\hat{I}_{3z}\rangle + \langle \hat{I}_{2z}\hat{I}_{3z}\rangle}{4},\quad A^{(3)}_{7\to 8} = \frac{\langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\rangle}{4}\,.\end{aligned} \tag{2.13}$$

Hence, the third harmonics at any line immediately yields direct information about the triple multiplet effect, $\left\langle \hat{I}_{1z}\hat{I}_{2z}\hat{I}_{3z}\right\rangle$. From the second harmonics one may easily extract $\left\langle \hat{I}_{1z}\hat{I}_{3z}\right\rangle$ and $\left\langle \hat{I}_{2z}\hat{I}_{3z}\right\rangle$:

$$\left\langle \hat{I}_{1z}\hat{I}_{3z}\right\rangle = 2\left(A^{(2)}_{1\to 2}+A^{(2)}_{3\to 4}\right) = 2A^{(2)}_{\alpha_1\alpha_3\to\alpha_1\beta_3}, \tag{2.14}$$

$$\left\langle \hat{I}_{2z}\hat{I}_{3z}\right\rangle = 2\left(A^{(2)}_{1\to 2}+A^{(2)}_{5\to 6}\right) = 2A^{(2)}_{\alpha_2\alpha_3\to\alpha_2\beta_3}.$$

Such a way of extracting the desired quantities is, in fact, the averaging over the states of the “extra” nuclei as is indicated by the symbol on the right hand side of Eq. (2.14). The total intensity of the spectrum at $n=1$ allows one to determine the net polarization of the corresponding spin. For instance, summing all line intensities of the third spin transitions at $n=1$ we obtain $\left\langle \hat{I}_{3z}\right\rangle$:

$$\left\langle \hat{I}_{3z}\right\rangle = A^{(2)}_{1\to 2}+A^{(2)}_{3\to 4}+A^{(2)}_{5\to 6}+A^{(2)}_{7\to 8}\,. \tag{2.15}$$

This result is independent of any multiplet CIDNP contribution.

The remaining 8 NMR lines corresponding to flips of the first and second spins can be analyzed in the same way and the three residual quantities of interest, $\langle \hat{I}_{1z}\rangle$, $\langle \hat{I}_{2z}\rangle$, $\langle \hat{I}_{1z}\hat{I}_{2z}\rangle$, can thus be extracted.

The CIDNP spectrum of three coupled spins 1/2 at $\varphi=\pi/6$ is shown in Fig. 1(a), bottom. In this example we used the following population numbers of the nuclear states (2.6): $P_1=P_{\alpha\alpha\alpha}=\sqrt{7}$, $P_2=P_{\alpha\alpha\beta}=\sqrt{5}$, $P_3=P_{\alpha\beta\alpha}=\sqrt{3}$, $P_4=P_{\alpha\beta\beta}=1$, $P_5=P_{\beta\alpha\alpha}=1$, $P_6=P_{\beta\alpha\beta}=1$, $P_7=P_{\beta\beta\alpha}=\sqrt{3}$, and $P_8=P_{\beta\beta\beta}=\sqrt{5}$. They correspond to CIDNP resulting from geminate radical pair recombination in liquid solution, and were calculated according to Adrian’s model [20]. For this model calculation we assumed that (1) in the radical pair all three nuclei belong to the first radical, (2) the relationship between their HFI constants is $a_1=3a_3$, $a_2=2a_3$, (3) the external magnetic field B_{pol} is much larger than a_1, a_2, a_3 and (4) $2(g_1-g_2)B_{\text{pol}}=a_3$ (where g_1, g_2 are the g-factors of the first and second radical, respectively). The 2D NMR spectrum of the three coupled spins 1/2 is shown in Fig. 1(c). The intensity integrated over all transitions of each spin at $n=1$ is equal to its net polarization (2.15). The spectrum at $n=2$ yields the second order multiplet CIDNP (2.14), *i.e.*, the three quantities $\left\langle \hat{I}_{1z}\hat{I}_{2z}\right\rangle$, $\left\langle \hat{I}_{1z}\hat{I}_{3z}\right\rangle$, and $\left\langle \hat{I}_{2z}\hat{I}_{3z}\right\rangle$. At $n=3$ we obtain the pure spectrum of the third-order multiplet CIDNP (2.12).

Systems with a larger number of weakly-coupled polarized spins can be analyzed in the same way. The k-th order multiplet polarization does not manifest itself in the harmonics of any order higher than k. By analyzing subsequently the spectra at N harmonics from $n=N$ to $n=1$ one obtains the values of the multiplet effects of all orders and all net polarizations. All contributions of higher order multiplet polarization to lower order harmonics can be easily removed by proper averaging over the corresponding nuclei as we showed in (2.15).

3. 2D nutation analysis of the CIDNP spectra of multinuclear systems

As a rule CIDNP (non-Boltzmann population of the nuclear spin states of diamagnetic reaction products) is formed in reactions that involve radical intermediates. In many cases electronic singlet–triplet inter-system crossing is the kinetic bottleneck of radical pair recombination [11]. The rate of the singlet–triplet conversion is governed by magnetic interactions (Zeeman interaction and HFI) and depends on the nuclear configuration of the radicals. Therefore, diamagnetic reaction products are either depleted or enriched by one or another nuclear spin state, *i.e.* the reaction product acquires nuclear polarization that can be much larger than Boltzmann polarization [11]. CIDNP investigations allow one to determine the radical reaction pathways and to measure the magnetic interactions in transient short-lived radical species that are often beyond the reach of EPR spectroscopy.

3.1 Experimental

Usually CIDNP experiments are carried out in the probe of the NMR spectrometer at a fixed strength of the external magnetic field B_0. Quite often, such a practice is not favorable for studying reaction dynamics because CIDNP exhibits a well pronounced dependence on the external magnetic field strength determined by the magnetic parameters of the radical species. In many cases the strength of the NMR spectrometer field is not suitable for CIDNP measurements. To avoid such limitation and measure, in particular, polarization patterns near $B = 0$, we make in the present work use of the field cycling high resolution NMR spectrometer recently built at the FU Berlin [5, 6]. A detailed description of the experimental setup is given elsewhere [5, 6, 21]. The mechanical field cycling set-up allows the detection of high resolution NMR-spectra under permanent slow sample-rotation (0–150 Hz) at 7 T and polarization at any desired magnetic field strength between earth magnetic field and 7 T. At a field below 0.1 T, where a high homogeneity of the magnetic field across the sample volume is required, the low field strength is set by control of the electric current through a pair of additional Helmholtz coils placed under the cryomagnet. A CIDNP experiment that employs mechanical field cycling contains three consecutive steps: (1) CIDNP generation by means of photoreactions at the desired field B_{pol}; (2) transfer of polarized reaction products to the observation field B_0 of the NMR spectrometer (switching of the external magnetic field from B_{pol} to B_0); (3) measurement of the FT-NMR at $B = B_0$. In the current experiments CIDNP was generated at an external field near $B_{\text{pol}} = 0$ (“zero-field”). After the adiabatic transfer (≈ 500 ms) into the cryomagnet (step 2), the length of the rf-excitation pulse in the NMR detection (step 3) was varied in order to obtain the nutation patterns shown in Fig. 3. Since the field change occurs adiabatically, the populations of the individual nuclear spin eigenstates are conserved. For the NMR-detection the rf-amplitudes were adjusted, sufficiently high for exciting the whole spectrum homogeneously, but low enough to allow small steps in φ for resolving harmonics of high order.

During step 1 the sample is irradiated by a XeCl eximer laser at 308 nm with a repetition rate of 50 Hz and energy of up to 100 mJ/pulse through a flexible liquid light guide with a 90° prism on the top. This provides constant irradiation conditions, and in previous investigations the technique allowed the detailed determination of CIDNP field dependencies in photo-reactions of amino acids, dipeptides [6–8, 21, 22] as well as in rigid and flexible biradicals [21, 23]. The samples containing ≈ 0.06 M of cyclodecanone (Aldrich) in $CDCl_3$ (Aldrich) were prepared to yield an optical density of 0.7 at 308 nm for the 4-mm optical pathway inside the NMR sample tube. All samples were purged with pure nitrogen gas and sealed in a standard 5 mm Pyrex NMR tube. In order to prevent vortex formation and sample shaking during the transfer, a Teflon plug was inserted into the tube on top of the liquid. All chemicals were used as received.

3.2 2D nutations analysis of the CIDNP in the photo-reactions of cyclic ketones

In order to illustrate the applicability of the suggested approach to the analysis of multi-nuclear spin systems, we choose a reaction where hydrogen atom transfer plays a key role for the product formation and strong CIDNP is formed. It is the Norrish type I reaction of the cyclic aliphatic ketone cyclodecanone ($C_{10}H_{18}O$). The scheme of the photolysis is shown in Fig. 2. This reaction proceeds via α-cleavage of the C–C bond in the triplet excited state of the carbonyl compound, resulting in the formation of a triplet acyl-alkyl biradical. The reaction is convenient for the analysis of its nutation patterns, as it occurs with restoration of the initial compound I. Another reaction product seen in the CIDNP spectrum is dec-9-enal (product II in Fig. 2) formed via H-atom abstraction from β position at the alkyl end of the biradical by the acyl group [24]. Since the reactive state of the biradical is the singlet state, the singlet–triplet conversion of the biradical is a necessary reaction step. This transition is spin forbidden, but it becomes allowed due to weak magnetic interactions in the intermediate: the difference in Zeeman frequencies of the two unpaired electrons and their hyperfine interaction with the magnetic nuclei.

The main peculiarity of reactions involving biradicals in comparison with ordinary radical pairs in solution is that the radical centers do not have the possibility to diffuse apart but stay linked by the polymethylene chain. As a result the electronic exchange interaction J, which determines the splitting between singlet and triplet states, is non-zero during the lifetime of the biradical. The presence of an external magnetic field leads to the splitting of the triplet sublevels according to the projections of the electronic and nuclear spins and affects the rate of the singlet–triplet interconversion. Three different magnetic field ranges with respect to the size of the exchange integral have to be considered. Near the magnetic field of electronic level crossing, $B_{\text{pol}} = 2|J|/\gamma_{\text{electron}}$, the conditions for the singlet–triplet transition are the most favorable [11]. In our case the electron–nuclear $T_{-\alpha}$–S_{β} transition (S, $T_{+,-,0}$ denote the electronic spin states, α and β the projections of the nuclear spin) becomes efficient, leading to a depletion of α and enrichment of β spins in the products. Accordingly, a characteristic maximum of emissive nuclear spin polarization was detected in the field dependence of unsaturated aldehydes, formed in the photoreaction of the homologous series of cyclic aliphatic ketones [25]. At high magnetic field as is typical for NMR spectrometer magnets ($B_{\text{pol}} \gg 2|J|/\gamma_{\text{electron}}$) another polarization pathway becomes dominant. Here, CIDNP is formed by S–T_0 transitions and the polarization pattern is in accordance with the spin density distribution in the biradicals. The main part of the hyperfine interaction with the protons is associated with the alkyl end of the biradical and can be estimated using the corresponding values of the analogous monoradicals (-2.2 mT and 2.8 mT in α and β position to the alkyl end, respectively) [26]. Thus, only protons in α- and β-CH_2 positions are polarized with the sign of polarization corresponding to the sign of the HFI constants [27–29]. From the analysis of polarization patterns and their field dependence one obtains information about exchange and hyperfine interaction as well as about molecular and spin dynamics [30, 31]. In the range of weak magnetic field, where the B_{pol} is lower than the value of individual hyperfine coupling constants, all electron and nuclear spin states are strongly coupled by hyperfine interaction. The selectivity of the singlet–triplet transitions is governed by hyperfine interaction and determined by the magnitude of the total nuclear spin, but not by its projection as it is at high magnetic field. The singlet–triplet transitions occur in a way that the total (electron plus nuclear) spin is conserved, therefore electronic transitions are accompanied by nuclear spin flips. Since the selection rules for transitions at low field are associated with the total nuclear spin it is reasonable to expect the formation of high order multiplet CIDNP in this field region.

The nuclear spin polarization, which is formed in the singlet–triplet conversion of short lived intermediate biradicals, is conserved in the diamagnetic reaction products for a time of the order of T_1 (nuclear longitudinal relaxation time) and can therefore be detected as anomalous intensities in the NMR spectra taken immediately after the reaction. The aldehyde proton of dec-9-enal has a very long relaxation time (of about 50 seconds), therefore it acquires rather strong polarization upon long light irradiation. In contrast, the protons of the cycloketone have a much shorter relaxation time, their polarization stays smaller and was not studied in detail before. Due to the short field cycling time of our set-up which is much shorter than T_1 of the ketone protons we were able to detect CIDNP not only for the aldehyde proton of product II, but also for all the protons of the initial ketone and for the three protons attached to the carbon atoms in the double bond of II. The NMR spectrum of cyclodecanone at thermal equilibrium and the CIDNP spectrum detected at low magnetic field of 2 mT are shown in Fig. 2 with the assignment of lines. Due to molecular conformational motion of the cyclic molecule the lines of protons in α- and β-CH_2 positions are broadened and the spin-spin couplings of γ δ and ϵ protons are only partially resolved. In contrast to the high field CIDNP, in the low field region all lines of the ketone show polarization. In the NMR spectrum taken 1 second after laser irradiation at $B_{\text{pol}} = 2$ mT the lines corresponding to α-CH_2 protons exhibit very strong absorption, while for β-CH_2 an absorptive signal of weaker intensity is detected. In spite of the fact that for the δ- and ϵ-CH_2 positions of the biradical the HFI constants are negligibly small (less than 0.1 mT) the strongest emissive polarization is detected for these protons and a weak emissive signal for γ-CH_2 protons. This observation leads us to conclusion that not only α- and β-CH_2, but all protons of the biradical are involved in the singlet–triplet conversion at this magnetic field. The symmetry of the polarization pattern of cyclodecanone looks very similar to the CIDNP pattern detected for the amino acids tyrosine [8] and histidine [7] at very low magnetic field. Here, all the protons are substantially polarized, but in a way that the total polarization integrated over the whole spectrum is equal to zero. This similarity allows us to suggest that in the photo-reaction of cyclodecanone we detect mutual entanglement of nearly all protons in the diamagnetic products irrespective of the size of the hyperfine interaction coupling constant. The aliphatic region of the CIDNP spectra taken at different rotation angle φ is shown in Fig. 3.

For the analysis of the multi-spin order in the polarization of cyclodecanone we choose the signal of the α-CH_2 protons because it has the largest intensity in the CIDNP spectrum. Up to a harmonic order of ten signals well above the noise level are detected, with the trend that at even orders the intensity is higher than at neighboring odd orders. In Fig. 4 the spectra corresponding to the harmonic orders from 1 to 6 are shown. The occurrence of so many harmonics confirms the suggestion that all protons in the molecule are entangled with each other. The spectral shape at the first harmonic almost coincides with that of NMR at thermal equilibrium. In the spectra at the higher harmonics the lines that are non-resolved in ordinary NMR split in emissive and absorptive components. The same analysis is made for the β-CH_2 protons of cyclodecanone, and intensities above the noise level are found for the first six harmonics (not shown). The absorptive spectrum at $n = 1$ (net CIDNP spectrum) is actually the same as the spectrum at thermal equilibrium. At $n > 1$ the spectra reflect the mutual ordering of spins and exhibit "antiphase" structure inherent to the multiplet polarization. Likewise, the harmonic spectra of the spin group of the methylene protons of the unsaturated aldehyde (II) corresponding to the first 5 harmonics for the $=CH_2$ protons as shown in Fig. 5 exhibit strong multiplet order up to $n = 3$ and of smaller size up to $n = 5$. The net CIDNP spectrum ($n = 1$) of the these protons is emissive, while the spectra of higher order harmonics have an antiphase nature. This result unambigu-

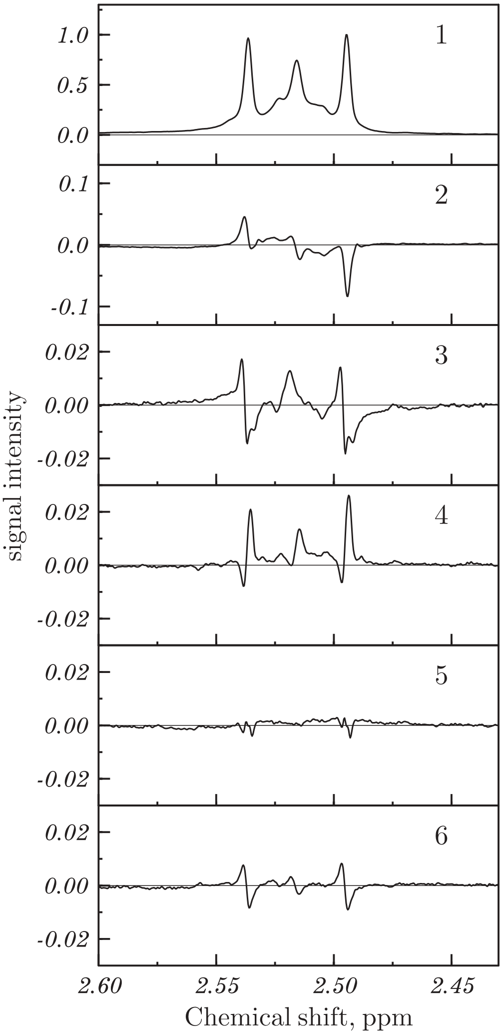

Fig. 4. CIDNP spectra of α-CH_2 protons of cyclodecanone at different harmonics. Numbers indicate the order of the harmonics.

ously supports the conclusion that not only back cyclization of the biradical with the restoration of the initial compound, but also the reaction of the hydrogen atom transfer from the β position of the alkyl end to the acyl moiety of the biradical occurs with the formation of polarization of high multiplet order. The quantitative analysis of the full CIDNP nutation behavior at low magnetic field is under way in our laboratories and will be published in a separate paper.

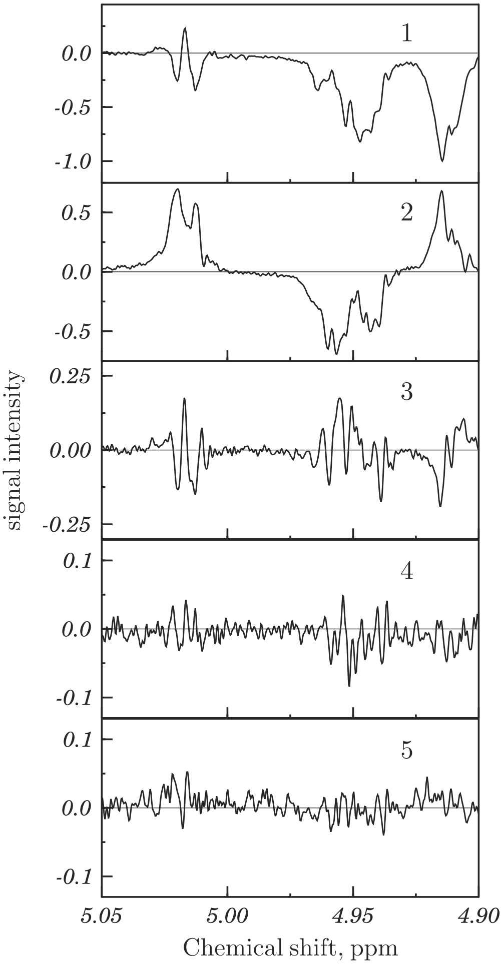

Fig. 5. CIDNP spectra of $=CH_2$ protons of product II at different harmonics. Numbers indicate the order of the harmonics.

4. Conclusion

The main concern of this article is to introduce Fourier decomposition of coherent spin motion of *N* coupled nuclei under excitation by a non-selective rf pulse as a method for analyzing the spin order of multi-spin systems. In this way we obtain a two dimensional representation of spectra, where the first dimension is the usual NMR frequency while the second dimension is related to the number of spins that are entangled. As we demonstrated this technique allows the extraction of all the quantities required for a full characterization of the spin polarization (namely, nuclear net polarizations and multiplet polarizations of all orders) of non-equilibrium systems.

To illustrate the method it was applied to the study of the low-field CIDNP formed in the photolysis of cyclodecanone having an acyl-alkyl biradical as short-lived intermediate. For two products of this reaction, the starting cyclic ketone and the unsaturated aldehyde formed via intramolecular hydrogen atom abstraction in the biradical stage, the 2D analysis of the nutation pattern is carried out. Because of "antiphase" structure in spectra at higher harmonic order neighboring lines become better resolved. In a straightforward way the contributions from net and multiplet polarization to the total CIDNP are separated. We anticipate exhaustive quantitative analysis of net and multiplet CIDNP generated by means of singlet–triplet interconversion not only for flexible biradicals, but also for photoinduced hydrogen or electron transfer reactions of many biologically relevant systems. Strong nuclear polarization has been detected in recent low-field CIDNP experiments on amino acids, peptides and proteins [5–8]. Already from a qualitative analysis of the nutation pattern it is obvious that spin orders of $N > 2$ contribute to spin polarization at low magnetic field. Our results demonstrate that in spin-selective chemistry at low field the entanglement of several nuclear spins has a significant influence. The quantitative evaluation of all net and multiplet contributions to the total polarization as described in this article will provide all the information that is obtainable from dynamic polarization data and often unavailable from other experiments.

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Appendix A

Here we shall derive the expression for $A^{(n)}_{i\to j}$ (intensity of the n-th harmonics at transition $|i\rangle \to |j\rangle$).

Formula (2.4) can be rewritten as follows:

$$L_{i\to j} = 2\sum_{rs}\left(\sin\frac{\varphi}{2}\right)^{2\Delta_{ij,rs}+1}\left(\cos\frac{\varphi}{2}\right)^{2N-2\Delta_{ij,rs}-1} L^{(0)}_{r\to s} = \sum_{rs} A_{ij,rs} L^{(0)}_{r\to s}\,. \tag{A.1}$$

The new quantity, $A_{ij,rs}$, can be represented as follows:

$$A_{ij,rs} = 2\left(\sin\frac{\varphi}{2}\right)^{2\Delta_{ij,rs}+1}\left(\cos\frac{\varphi}{2}\right)^{2N-2\Delta_{ij,rs}-1} \tag{A.2}$$
$$= 2\left(\frac{e^{i\varphi/2}-e^{-i\varphi/2}}{2i}\right)^{2\Delta_{ij,rs}+1}\left(\frac{e^{i\varphi/2}+e^{-i\varphi/2}}{2}\right)^{2N-2\Delta_{ij,rs}-1} .$$

This result can be rewritten as a sum of $2N+1$ exponential terms:

$$A_{ij,rs} = \frac{1}{2i}\sum_{n=-N}^{N} a_{ij,rs}^{(n)} \exp(in\varphi) , \tag{A.3}$$

where

$$a_{ij,rs}^{(n)} = \frac{(-1)^{\Delta_{ij,rs}}}{4^{N-1}} \sum_{m=0}^{2N-2\Delta_{ij,rs}-1} (-1)^{N-m-n} C_{2\Delta_{ij,rs}+1}^{N-m-n} C_{2N-2\Delta_{ij,rs}-1}^{m} . \tag{A.4}$$

One may prove that $a_{ij,rs}^{(n)} = -a_{ij,rs}^{(-n)}$ (as a consequence, $a_{ij,rs}^{(0)} = 0$). Therefore, the expression (A.3) is a sum of N sine terms:

$$A_{ij,rs} = \sum_{n=1}^{N} a_{ij,rs}^{(n)} \sin n\varphi \tag{A.5}$$

and the general result (A.1) is recast as follows:

$$L_{i\to j} = \sum_{n=1}^{N} A_{i\to j}^{(n)} \sin n\varphi = \sum_{n=1}^{N}\sum_{rs} a_{ij,rs}^{(n)} \sin n\varphi \; L_{r\to s}^{(0)} , \tag{A.6}$$

where $a_{ij,rs}^{(n)}$ is given by (A.4).

References

1. R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford (1987).
2. S. Schäublin, A. Höhener, and R. R. Ernst, J. Magn. Reson. **13** (1974) 196.
3. J.-K. Vollenweider and H. Fischer, Chem. Phys. **108** (1986) 365; R. Hany, J.-K. Vollenweider, and H. Fischer, Chem. Phys. **120** (1988) 169.
4. V. F. Tarasov and I. A. Shkrob, J. Magn. Reson. Ser. A **109** (1994) 65.
5. S. Grosse, F. Gubaydullin, H. Scheelken, H.-M. Vieth, and A. V. Yurkovskaya, Appl. Magn. Reson. **17** (1999) 211.
6. S. Grosse, A. V. Yurkovskaya, J. Lopez, and H.-M. Vieth, J. Phys. Chem. A **105** (2001) 6311.
7. K. L. Ivanov, N. N. Lukzen, H.-M. Vieth, S. Grosse, A. V. Yurkovskaya, and R. Z. Sagdeev, Mol. Phys. **100** (2002) 1197.

8. K. L. Ivanov, H.-M. Vieth, K. Miesel, A. V. Yurkovskaya, and R. Z. Sagdeev, Phys. Chem. Chem. Phys. **5** (2003) 3470.
9. G. Buntkowsky, J. Bargon, and H.-H. Limbach, J. Am. Chem. Soc. **118** (1996) 8677.
10. J. Bargon and H. Fischer, Z. Naturforsch. A **22** (1967) 1556.
11. K. M. Salikhov, Yu. N. Molin, R. Z. Sagdeev, and A. L. Buchachenko, *Spin Polarization and Magnetic Effects in Chemical Reactions*, Elsevier, Amsterdam (1984).
12. M. G. Pravica and P. Weitekamp, Chem. Phys. Lett. **145** (1988) 255.
13. T. C. Eisenschmid, R. U. Kirss, P. Deutsch, S. I. Hommeltoft, J. Bargon, R. G. Lawler, and A. L. Balch, J. Am. Chem. Soc. **109** (1987) 8089.
14. G. L. Closs, J. Am. Chem. Soc. **91** (1969) 4552.
15. R. Kaptein and L. J. Oosterhoff, Chem. Phys. Lett. **4** (1969) 195.
16. Z. L. Madi, B. Brutscher, T. Schulte-Herbrüggen, R. Brüschweiler, R. R. Ernst, Chem. Phys. Lett. **268** (1997) 300.
17. N. Linden, B. Hervé, R. J. Carbajo, and R. Freeman, Chem. Phys. Lett. **305** (1999) 28.
18. R. Boelens, A. Podoplelov, and R. Kaptein, J. Magn. Reson. **69** (1986) 116.
19. C. E. Lyon, Ph.D. Thesis, Oxford University, UK (1999).
20. F. J. Adrian, J. Chem. Phys. **54** (1971) 3912.
21. S. Grosse, Ph.D. Thesis, Freie Universität Berlin (2000).
22. H. Fabian, S. Grosse, M. Onnen, H.-M. Vieth, and A. V. Yurkovskaya, RIKEN Rev. **44** (2002) 134.
23. M. Wegner, H. Fischer, S. Grosse, H.-M. Vieth, A. M. Oliver, and M. N. Paddon-Row, Chem. Phys. **264** (2001) 341.
24. C. Doubleday, Jr., N. J. Turro, and F. H. Wang, Acc. Chem. Res. **22** (1989) 199.
25. G. L. Closs and C. Doubleday, J. Am. Chem. Soc. **95** (1973) 2735.
26. H. Fischer and K.-H. Hellwege, *Magnetic Properties of Free Radicals*, Landolt-Börnstein, Springer, Berlin, Heidelberg, New York (1977).
27. Yu. P. Tsentalovich, A. V. Yurkovskaya, R. Z. Sagdeev, A. A. Obynochnyi, P. A. Purtov, and A. A. Shargorodskii, Chem. Phys. **139** (1989) 307.
28. A. V. Yurkovskaya, Yu. P. Tsentalovich, N. N. Lukzen, and R. Z. Sagdeev, Res. Chem. Intermed. **17** (1992) 145.
29. O. B. Morozova, A. V. Yurkovskaya, Yu. P. Tsentalovich, and H.-M. Vieth, J. Phys. Chem. A **101** (1997) 399.
30. S. V. Dvinskikh, A. V. Yurkovskaya, and H.-M. Vieth, J. Phys. Chem. **100** (1996) 8125.
31. A. Yurkovskaya, S. Grosse, S. Dvinskikh, O. Morozova, and H.-M. Vieth, J. Phys. Chem. A **103** (1999) 980.