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Short Communication

Multiple Quantum ^{1}H-NMR of Ferrocene in Isotropic Solution*

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Summary. Excitation of multiple quantum coherence in the C_5 symmetrical A_5-spin system of ferrocene was possible by multiexponential relaxation of degenerated NMR transitions. The mechanism of the excitation was analyzed by means of a tensor operator formalism. Symmetry selection rules were postulated for the relaxation pathways.

Keywords. Relaxation; Multiple-quantum NMR spectroscopy.

Mehrquanten-^{1}H-NMR-Spektroskopie von Ferrocen in isotroper Lösung (Kurze Mitt.)

Zusammenfassung. Multiexponentielle Relaxation degenerierter NMR-Übergänge ermöglicht auch im C_5-symmetrischen A_5-Spinsystem des Ferrocens die Anregung von Mehrquantenkohärenz. Der Mechanismus der Anregung wird anhand eines Tensoroperator-Formalismus untersucht. Für die Relaxationspfade wird eine Symmetrieauswahlregel postuliert.

Introduction

It has been established that multiple quantum coherence can be excited in the absence of spin-spin coupling from degenerate one quantum coherences undergoing multi-exponential relaxation or from states of longitudinal spin order [1–8]. So far experimental evidence for multiple quantum coherence in singlet spectra has only been given for three level systems, namely methyl groups [1–3, 5–8] and nuclei with $I = 3/2$ [4].

In this paper an example of excitation of multiple quantum coherences up to an order of 5 in the A_5 spin systems of the organometallic π-complex ferrocene will be shown. This particular compound has been chosen because the fast rotation around the C_n-axis on the one hand and the heavy metal on the other hand ensure anisotropic rotation of the spin system which is a prerequisite for multi-exponential relaxation [5].

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* Dedicated to Professor Dr. Karl Schlögl on occasion of his 65th birthday

Results and Discussion

The physical mechanism of multiple quantum excitation may be understood as a generalization of the case discussed for methyl groups in Ref. [6]. It is necessary to describe the spin dynamics of the A_5 spin system in a symmetry adapted base. In the case of ferrocene the rotation of the two rings around their common axis is uncorrelated therefore a C_5 symmetry is appropriate. In a base adapted to this C_5 symmetry the spin system is represented by a set of one 6 level system with a group spin $F = 5/2$, four 4 level systems with group spins $F = 3/2$, and five 2 level systems with $F = 1/2$ as shown schematically in Fig. 1. In this spin system therefore we find 22 degenerate one quantum coherences (1QCs), 10 degenerate 2QCs, 5 degenerate 3QCs, 2 degenerate 4QCs and one 5QCs possible.

The dynamics of the $F = 3/2$ group spins are analogous to the case described for methyl groups [6] giving rise to predominantly three quantum coherence in the experiment under consideration. Here we focus our attention on the 6 level system, which is responsible for the highest orders of multiple quantum coherence. A convenient description of the density matrix is in terms of irreducible spherical tensor operators $T^{5/2}_{rp}$ (with r: rank, p: coherence level).

The matrix representations of the tensor operators used in this context are summarized in Table 1.

The matrix elements can be calculated in straightforward though arduous manner from Eq. (1) (adapted from Ref. [10]) and subsequent normalization.

$$\langle m_1 \,|\, T^{5/2}_{rp} \,|\, m_2 \rangle = \mathbb{C}\left(\frac{5}{2}, m_2, r, p, \frac{5}{2} m_1\right) \sqrt{\frac{r!\, r!\, (6+r)!}{2^r (2r)!\, (5-r)!}}. \tag{1}$$

$\mathbb{C}$ are the Clebsch-Gordan coefficients, which are defined in many fundamental textbooks on angular momentum theory, where m_1 and m_2 are the half-integer magnetic quantum numbers of the matrix elements.

A modification of the standard pulse sequence for multiple quantum spectroscopy [9] shown in Eq. (2) is used in the experiments.

$$\left[\left(\frac{\pi}{2}\right)_0 - \frac{\tau}{2} - (\pi)_\psi - \frac{\tau}{2} - \left(\frac{\pi}{2}\right)_\psi\right]_{\mathrm{TPPI}} - \left(\frac{\pi}{2}\right) - t_2\,(\text{acquisition}). \tag{2}$$

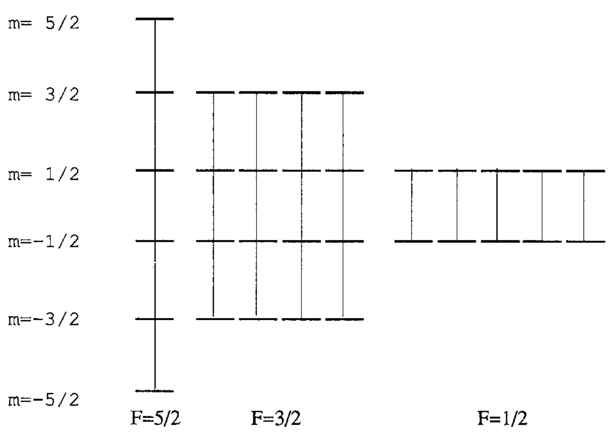

Fig. 1. Symmetry adapted energy level diagram of an A_5 spin system of C_5 symmetry

Table 1. Matrix representations of irreducible tensor operators for spin $I = 5/2$. Only operators actually used in this paper are listed. The operators for positive quantum numbers p can easily be constructed through the relation $T^{5/2}_{r,1} = -1\,\tilde{T}^{5/2}_{r,-1}$ (the tilde symbol stands for the transpose matrix)

$$T^{5/2}_{1,0} = \frac{1}{\sqrt{70}} \begin{pmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 \end{pmatrix} \qquad T^{5/2}_{1,-1} = \frac{1}{\sqrt{35}} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{8} & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{8} & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{pmatrix}$$

$$T^{5/2}_{2,-1} = \frac{1}{\sqrt{14}} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{5} & 0 \end{pmatrix}$$

$$T^{5/2}_{3,-1} = \frac{1}{\sqrt{30}} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{10} & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\sqrt{8} & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{10} & 0 \end{pmatrix}$$

$$T^{5/2}_{4,-1} = \frac{1}{\sqrt{14}} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\sqrt{5} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{5} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{2} & 0 \end{pmatrix}$$

$$T^{5/2}_{5,-1} = \frac{1}{\sqrt{42}} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\sqrt{10} & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{5} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{10} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

Usually the phase ψ would be set to 0 for even and to $\pi/2$ for odd quantum spectra [9]. To observe multiple quantum coherences of both odd and even orders—although with reduced amplitudes—in a single experiment ψ may be set to $\pi/4$. The evolution of the density matrix will be described with particular reference to this pulse sequence.

The multiple quantum excitation sequence starts by converting equilibrium longitudinal magnetization $T^{5/2}_{10}$ into first rank one quantum coherence $T^{5/2}_{1\pm1}$ through a $\pi/2$ RF pulse.

$$T^{5/2}_{10} \xrightarrow{\pi/2} d^1_{0,\pm1}\left(\frac{\pi}{2}\right) T^{5/2}_{1\pm1}\,. \tag{3}$$

The transfer coefficient $d^1_{0,\pm1}(\pi/2)$ is the appropriate Wigner rotation matrix element or can be calculated by using the full rotation matrix for $I = 5/2$, which is given in Table 2 for a rotation around the y-axis.

In general cross relaxation between the 5 degenerate one quantum coherences belonging to the totally symmetric A representation as described by the Redfield matrix $\Gamma_{ij,kl}$ effects mixing of all ranks within the current coherence level.

$$T^{5/2}_{1\pm1} \xrightarrow{\Gamma} \sum_{r=1}^{5} f^{\pm1}_{r,1}(\tau)\, T^{5/2}_{r\pm1}\,. \tag{4}$$

In this context a transformation of the Redfield matrix to our tensor operator base $\Gamma^p_{r,r'}$ is more convenient to handle as it directly describes relaxation and cross relaxation of the tensor representation of different ranks within a given coherence order. The n eigenvalues E_n and eigenvectors V_n of this matrix determine the relaxation functions [1].

$$f^p_{r,r'}(\tau) = \sum_n \frac{V_{r',n}}{V_{n,r}}\, \mathrm{e}^{-E_n t}. \tag{5}$$

Some restrictions however apply as to which of the multi-exponential relaxation functions $f^{\pm p}_{r,1}$ are vanishing as will be shown below.

Proceeding in the pulse sequence a further $\pi/2$ RF pulse now can generate multiple quantum coherence of orders between the rank of each tensor and its negative.

$$T^{5/2}_{r\pm1} \xrightarrow{\pi/2} \sum_{p=-r}^{r} d^r_{p,1}\left(\frac{\pi}{2}\right) T^{5/2}_{rp}\,. \tag{6}$$

In fact by using $\pi/2$ flip angles for the last two pulses only the highest possible coherence order for each rank can pass through the pulse sequence. This can easily be shown by calculating the transfer coefficient resulting from the superposition of the pathways via $+p$ and $-p$ quantum coherence (following the procedure given in Ref. [1]).

At this stage in a multiple quantum experiment separation of coherence orders in the ω_1 dimension is achieved by applying time proportional phase incrementation (TPPI) [9] to the excitation pulse sandwich. Then in the course of the pulse sequence the transformations of Eqs. (6) and (4) occur in reverse order and opposite direction leading to observable first rank one quantum coherence signal during the detection period $T^{5/2}_{1\pm1}$ with a multi-exponential envelope given by $\sum_{r=1}^{5} f_{1,r}(\tau)$.

In Fig. 2 the multiple quantum spectrum of a solution of ferrocene in hexadeuterobenzene acquired with the pulse sequence of Eq. (2) is shown. The absence of multiple quantum coherences of coherence levels higher than 5 is additional evidence for the rotation of the two aromatic ring systems being uncorrelated. Also only odd order coherence levels are observed, though the pulse sequence permits odd an even orders to pass. This finding can give some insight on the structure of the relaxation matrix. This is particularly useful as for the general case of a 5 by 5 matrix no explicit analytical solutions exist. From the experimental results, however, it seems that only three distinct eigenvalues are relevant when starting from first rank one quantum coherence (and there is no obvious way to start from any other).

Table 2. Rotation matrix for spin $I = 5/2$ density operators (for a rotation by an angle β around the y axis) with $c = \cos(\beta/2)$ and $s = \sin(\beta/2)$

c^5	$\sqrt{5}\,c^4 s$	$\sqrt{10}\,c^3 s^2$	$\sqrt{10}\,c^2 s^3$	$\sqrt{5}\,c\,s^4$	s^5
$-\sqrt{5}\,c^4 s$	$c^5 - 4c^3 s^2$	$\sqrt{2}\,c^2 s(2c^2 - 3s^2)$	$\sqrt{2}\,c\,s^2(3c^2 - 2s^2)$	$4c^2 s^3 - s^5$	$\sqrt{5}\,c\,s^4$
$\sqrt{10}\,c^3 s^2$	$-\sqrt{2}\,c^2 s(2c^2 - 3s^2)$	$c^5 - 6c^3 s^2 + 3c\,s^4$	$3c^4 s - 6c^2 s^3 + s^5$	$\sqrt{2}\,c\,s^2(3c^2 - 2s^2)$	$\sqrt{10}\,c^2 s^3$
$-\sqrt{10}\,c^2 s^3$	$\sqrt{2}\,c\,s^2(3c^2 - 2s^2)$	$-(3c^4 s - 6c^2 s^3 + s^5)$	$c^5 - 6c^3 s^2 + 3c\,s^4$	$\sqrt{2}\,c^2 s(-2c^2 + 3s^2)$	$\sqrt{10}\,c^3 s^2$
$\sqrt{5}\,c\,s^4$	$-4c^2 s^3 + s^5$	$\sqrt{2}\,c\,s^2(3c^2 - 2s^2)$	$\sqrt{2}\,c^2 s(2c^2 - 3s^2)$	$c^5 - 4c^3 s^2$	$\sqrt{5}\,c^4 s$
$-s^5$	$\sqrt{5}\,c\,s^4$	$-\sqrt{10}\,c^2 s^3$	$\sqrt{10}\,c^3 s^2$	$-\sqrt{5}\,c^4 s$	c^5

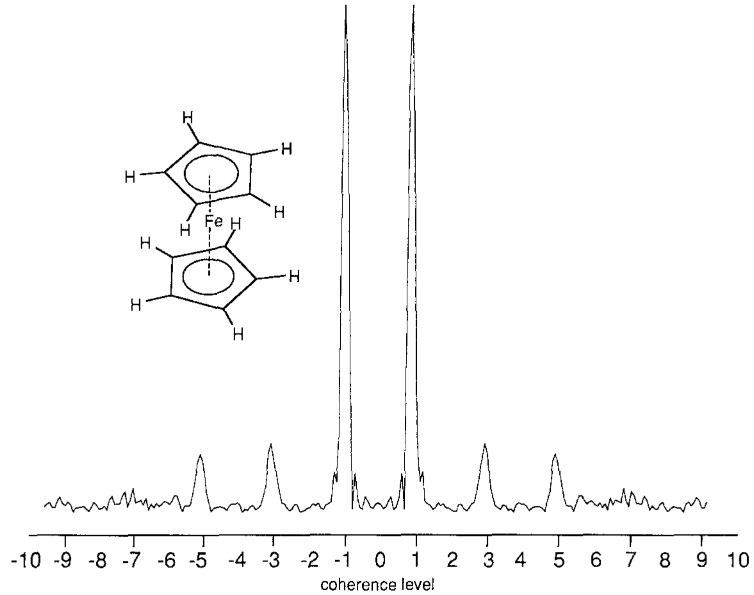

Fig. 2. Multiple quantum ^{1}H spectrum of ferrocene obtained with the pulse sequence in Eq. (1). The TPPI increments are $\pi/20$, $\tau = 80$ ms, 128 phase increments with 32 scans each at a repetition interval of 8 s were acquired. Phase cycling: CYCLOPS and axial peak suppression. No composite pulses were used as the radio frequency was applied on resonance. A symmetrized absolute value spectrum is shown

The relaxation functions $f^{\pm 1}_{1,r}(\tau)$ and their symmetrical counterparts $f^{\pm 1}_{r,1}(\tau)$ reflect the eigenvalues of the relaxation matrix. The absence of signals for multiple quantum coherences of even orders strongly suggests a generalization of a relation that has been found in the $I = 1$ and $I = 3/2$ spin systems [1].

$$f^{\pm p}_{r,r\pm(2n+1)} = 0, \qquad n = 0, 1, 2 \ldots \tag{7}$$

This is equivalent to the "symmetry selection rule" that tensor operators of odd and even ranks do not mix in the absence of symmetry breaking interactions, a condition which is safely fulfilled in the highly symmetric molecular system investigated here. As can be readily seen in the matrix representations of Table 1 this means that cross relaxation occurs only between tensors of equal symmetry with respect to the center of the matrix (see Table 1).

So far no detailed mathematical analysis of the relaxation behavior for this complex spin systems has been attempted as the expressions become rather unwieldy even under simplifying assumptions such as exclusively dipolar relaxation and neglecting cross relaxation between different group spins.

In this paper the excitation mechanism for the highest order of multiple quantum coherence so far reported for a simple singlet NMR spectrum in isotropic solution has been investigated using a spherical tensor operator formalism. The postulated symmetry selection rule is supposed to raise further interest in the relaxation behavior of highly symmetric spin systems.

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