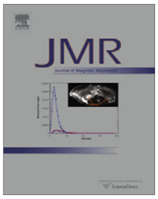
Journal of Magnetic Resonance 211 (2011) 217–220

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr



Multiple decoherence-free states in multi-spin systems

H.J. Hogben [a,*], P.J. Hore [a], Ilya Kuprov [b]

[a] Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, UK
[b] Oxford e-Research Centre, University of Oxford, 7 Keble Road, Oxford OX1 3QG, UK

ARTICLE INFO

Article history:
Received 5 May 2011
Revised 31 May 2011
Available online 13 June 2011

Keywords:
NMR
Singlet
Decoherence
Relaxation
Long-lived state

ABSTRACT

A numerical procedure is presented for mapping the vicinity of the null-space of the spin relaxation superoperator. The states populating this space, i.e. those with near-zero eigenvalues, of which the two-spin singlet is a well-studied example, are long-lived compared to the conventional T_1 and T_2 spin-relaxation times. The analysis of larger spin systems described herein reveals the presence of a significant number of other slowly relaxing states. A study of coupling topologies for n-spin systems ($4 \leqslant n \leqslant 8$) suggests the symmetry requirements for maximising the number of long-lived states.

1. Introduction

An ability to tame spin relaxation by finding the rare states that resist the gradual drift towards thermal equilibrium [1–3] is of considerable interest in magnetic resonance. The slowly relaxing states may be used to store polarisation [4–7], measure slow diffusion [8], and obtain information on molecular structure [9]. Such super-stable states were recently found to exist in dipolar-coupled spin systems [1] and have since attracted much theoretical [7,10–12] and experimental [2,7,8,11] attention. Their common property – a zero dipolar relaxation rate – can be formulated as defining the null space of the relaxation superoperator to which their associated eigenvectors belong. More generally, we are interested in finding those eigenstates of the full relaxation superoperator that have small (but not necessarily zero) eigenvalues. Analytical treatments are possible for small systems [3,10–12], but collections of more than four spins have not hitherto been studied systematically.

Drawing on our recent work on large-scale spin dynamics simulations [13–15] and construction of relaxation superoperators [16] for large spin systems, we report here a systematic mapping of the dipolar relaxation null spaces for systems with four to eight spins using the *Spinach* software library [17]. Investigation of different spin-½ coupling topologies evinces clear symmetry and coupling requirements for maximising the number of long-lived states.

The null-space analysis follows a simple procedure: build the Liouvillian and find the eigenvectors corresponding to zero or near-zero eigenvalues [12,18]. Different dipolar coupling topologies comprising at least four spins are predicted to have more than one non-trivial (i.e. other than the identity operator) long-lived state when certain symmetry requirements are met. These criteria are illustrated with three examples of commercially available molecules expected to exhibit multiple long-lived states in liquid state NMR experiments.

2. Theoretical formalism

In order to be long-lived, a state $\hat{\rho}$ or a subspace of states $K = \mathrm{span}\{\hat{\rho}_1, \ldots, \hat{\rho}_k\}$ must be invariant with respect to time evolution under the system Liouvillian $\hat{\hat{L}}$:

$$\begin{gathered}\exp\left(-\mathrm{i}\hat{\hat{L}}t\right)\hat{\rho} = \hat{\rho} \Rightarrow \left(\sum_{n=0}^{\infty}\frac{(-\mathrm{i}t)^n}{n!}\hat{\hat{L}}^n\right)\hat{\rho} = \hat{\rho} \Rightarrow \\ \hat{\rho} + \sum_{n=1}^{\infty}\frac{(-it)^n}{n!}\hat{\hat{L}}^n\hat{\rho} = \hat{\rho} \Rightarrow \sum_{n=1}^{\infty}\frac{(-it)^n}{n!}\hat{\hat{L}}^n\hat{\rho} = 0 \quad \forall t \in [0,\infty),\end{gathered} \tag{1}$$

where $\hat{\hat{L}} = \hat{\hat{H}} + \mathrm{i}\hat{\hat{R}}$, $\hat{\hat{H}}$ is the Hamiltonian commutation superoperator and $\hat{\hat{R}}$ is the relaxation superoperator. This invariance is only possible (as a consequence of the Taylor expansion uniqueness theorem) if $\hat{\rho}$ or K belongs to the null space of the Liouvillian:

$$\hat{\hat{L}}\hat{\rho} = 0 \quad \hat{\hat{L}} : K \to \{0\} \tag{2}$$

The general task of finding long-lived states in a particular system therefore amounts to finding the null space of the system Liouvillian. Control of the coherent part of the Liouvillian (contained in $\hat{\hat{H}}$) is well developed: field-shuttling, spin-locking and

---

* Corresponding author.
E-mail address: hannah.hogben@chem.ox.ac.uk (H.J. Hogben).

1090-7807/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jmr.2011.06.001

decoupling can be used to halt the evolution of states of interest under the influence of chemical shift differences or external *J*-couplings [11,12,19]. There remains the part of the Liouvillian that we cannot normally control – the incoherent relaxation processes – which has yet to be fully exploited from a practical perspective. Accordingly, we shall focus our attention on the relaxation superoperator and look for states that are immune to it. The most general formulation of spin-relaxation theory for spin systems with a one-way coupling to a classical heat bath is [20,21]:

$$\hat{\sigma}(t+\Delta t)=\hat{\sigma}(t)+\left[\sum_{n=1}^{\infty}(-i)^{n}\int_{0}^{\Delta t}\mathrm{d}t_{1}\int_{0}^{t_{1}}\mathrm{d}t_{2}\ldots\int_{0}^{t_{n-1}}\mathrm{d}t_{n}\langle\hat{\hat{H}}_{1}^{\mathrm{R}}(t_{1})\hat{\hat{H}}_{1}^{\mathrm{R}}(t_{2})\ldots\hat{\hat{H}}_{1}^{\mathrm{R}}(t_{n})\rangle\right]\hat{\sigma}(t) \tag{3}$$

where $\langle\rangle$ denotes ensemble average, $\hat{\sigma}(t)$ is the ensemble average density matrix and $\hat{\hat{H}}_{1}^{\mathrm{R}}(t)$ is the stochastic part of the Liouvillian commutation superoperator, both written in the interaction representation with respect to the coherent Liouvillian. Truncation of this series at the second order with some additional assumptions is known in magnetic resonance as Bloch–Redfield–Wangsness relaxation theory [22,23]. As most semi-classical theories do, this formalism relaxes the system to the infinite temperature state. This is easily fixed [24], but the relaxation destination is unimportant for the present treatment – we only seek to determine whether a particular state is going (or not going) to relax at all.

It is clear from Eq. (3) that a *sufficient* condition for a state to be immune to propagation under the relaxation superoperator is belonging to the null space of the stochastic Hamiltonian commutation superoperator at all times:

$$\hat{\hat{H}}_{1}^{\mathrm{R}}(t)\hat{\sigma}=0\quad\Rightarrow\quad e^{i\hat{\hat{H}}_{0}t}\hat{\hat{H}}_{1}(t)e^{-i\hat{\hat{H}}_{0}t}e^{i\hat{\hat{H}}_{0}t}\hat{\rho}=0\quad\Rightarrow\quad\hat{\hat{H}}_{1}(t)\hat{\rho}=0. \tag{4}$$

Whether or not this is also a *necessary* condition, we do not know – this seems unlikely, because terms could in principle cancel or vanish under the average in Eq. (3). This explains why singlet states are immune to dipolar relaxation (the singlet density matrix commutes with the dipolar Hamiltonian involving the two spins in question and with any operator that does not affect those spins) and provides a rapid test for the long-lived character of a state of interest. In particular any state from which all transitions under $\hat{\hat{H}}_{1}(t)$ are permutation-symmetry-forbidden is going to be long-lived. However, *all* of the long-lived states (including those where the eigenvalue is very small but non-zero) can only be discovered with certainty by mapping the null-space of the full relaxation superoperator in square brackets in Eq. (3).

Before embarking on larger systems, we shall briefly review the classic two-spin case [1]. For a dipolar-coupled pair of spins-½ the null space of the relaxation superoperator is spanned by two states. If only dipolar relaxation is considered, the eigenvalues are exactly zero and the states persist indefinitely. Any linearly independent pair of states (they do not have to be orthogonal) may be chosen as the basis of this two-dimensional null space, for example:

$$\hat{1}=\hat{P}_{T_{+}}+\hat{P}_{T_{0}}+\hat{P}_{T_{-}}+\hat{P}_{S}\quad\text{and}\quad\hat{P}_{TS}=\hat{P}_{T_{+}}+\hat{P}_{T_{0}}+\hat{P}_{T_{-}}-\hat{P}_{S} \tag{5}$$

where $\{\hat{P}_{S},\hat{P}_{T_{+}},\hat{P}_{T_{0}},\hat{P}_{T_{-}}\}$ are projectors into the singlet and the three triplet states. The identity operator $\hat{1}$ is not interesting because it commutes with any Hamiltonian and will hereafter be omitted from the discussion. The $\hat{P}_{TS}$ state is the difference between the singlet state, $\hat{P}_{S}$, and the sum of the three triplet states. Any linear combination of these states is also in the null space and is thus also long-lived. A particularly convenient (on symmetry grounds) linear combination, known as "the" singlet state may be written in the usual $\alpha\beta$ basis set as:

$$\hat{P}_{S}=\frac{1}{2}(|\alpha\beta\rangle-|\beta\alpha\rangle)(\langle\alpha\beta|-\langle\beta\alpha|), \tag{6}$$

corresponding to a projector into the two-spin zero-quantum coherence. For convenience, the normalisation factors will henceforth be omitted.

The magnetic dipolar interaction operator, which often dominates relaxation in liquid-state NMR, is bilinear in the spin operators:

$$\hat{H}_{D}=D(r)\left[3(\hat{S}_{1}\cdot u_{12})(\hat{S}_{2}\cdot u_{12})-(\hat{S}_{1}\cdot\hat{S}_{2})\right] \tag{7}$$

with $D(r)=-\mu_{0}\hbar\gamma_{1}\gamma_{2}/4\pi r_{12}^{3}$. $\hat{S}_{i}$ is a vector of the spin operators, $\{\hat{S}_{x},\hat{S}_{y},\hat{S}_{z}\}$, r_{12} is the distance between the spins and u_{12} is unit vector along the spin–spin direction. In large spin systems, because products and linear combinations of two-spin singlets are invariant under sums of dipolar operators, we would expect some of the long-lived states to be products and linear combinations of products of two-spin singlets.

Our large-scale implementation of liquid-state Bloch–Redfield–Wangsness relaxation theory is described in detail elsewhere [16]; it includes all cross-correlations and non-secular terms as well as (optionally) dynamic frequency shifts. The isotropic rotational diffusion approximation is used in this paper, but the *Spinach* library [17] can handle arbitrary user-specified correlation functions. If chemical shielding anisotropy (CSA) is present, it is also included because singlet states are not immune to CSA and DD-CSA processes [1,19].

In the simulations presented below the dipolar interactions were calculated directly from user-specified coordinates (model systems) and crystal structure geometries (real molecules). CSA tensors and scalar couplings were estimated using the DFT GIAO B3LYP/EPR-II method in Gaussian03 [25]. All interaction tensors were then fed into the relaxation theory module of the *Spinach* library [17], the resulting relaxation superoperator was diagonalised and the eigenvectors corresponding to small eigenvalues were inspected. An example of MATLAB code calling the *Spinach* library for this purpose can be found in Supplementary information along with the console output that lists all the interaction parameters.

3. Results and discussion

A systematic search to find long-lived states by mapping the null space of the full relaxation superoperator has been performed on dipolar coupled systems with three to eight spin-½ nuclei. A range of system symmetries and coupling patterns was investigated; the results are summarised in Fig. 1 in which coupling topologies are grouped according to the number of long-lived states found in them. A nearest neighbour separation of 1 Å was chosen (to give a dipolar coupling of $D\approx 120$ kHz); being just

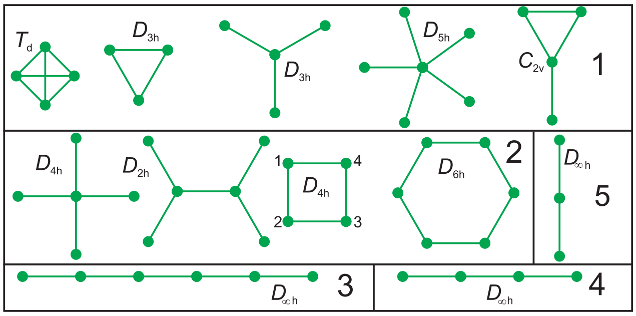


Fig. 1. Dipolar coupled spin-systems grouped according to null-space size. Nodes represent spin positions and solid lines a separation of 1 Å ($D\approx 120$ kHz).

shorter than a ^{13}C–^{1}H bond length this provides an upper bound on the dipolar interactions likely to be encountered in organic molecules. All pair-wise dipolar interactions were included in the relaxation superoperator with coupling constants and dipolar axes calculated from the geometry of the spin system.

For a dipolar coupled three-spin-system only the linear geometry returns a long-lived state as was shown analytically in Ref. [26]. For larger systems it appears that only the topologies that have a centre of inversion show any long-lived states at all. This is to be expected for the dipolar relaxation superoperator, which inherits the symmetry of Eq. (7) with respect to the permutation of the two spins. The long-lived states are not formed from combinations of singlets across the most strongly coupled pairs, i.e. those with minimum separation, but instead from the symmetric combinations of products of singlets across the spins interchanged by the inversion symmetry. For example, the square D_{4h} four-spin system yields a non-trivial null-space state:

$$4\hat{P}_S^{\{1,3\}}\hat{P}_S^{\{2,4\}} - 1 \tag{8}$$

(the numbering is shown in Fig 1). Because all linear combinations of eigenvectors with small eigenvalues do themselves have small eigenvalues, it is possible to take an alternative linear combination of the state in Eq. (8) with its identity operator partner to yield the more intuitively recognisable $\hat{P}_S^{\{1,3\}}\hat{P}_S^{\{2,4\}}$. This demonstrates the localised singlet character of the inversion-related spins, i.e. of those across the diagonal of the square which experience the weaker of the two dipolar coupling amplitudes in the system. The same state, with its triplet mixture counterpart, also forms a part of the null space of the linear four-spin system (Fig. 1), along with two further mixed states. An isolated singlet state across any pair of spins in that system does not appear anywhere in the null space and thus would not exhibit slow relaxation. This may be confirmed by substitution of the requisite states into Eq. (4) which fails to return the all-zero vector indicative of long-lived character.

Multi-spin systems are known to have a long-lived state when a localised singlet interacts only weakly with neighbouring spins [3]. Coupling topologies combining strong ($D \approx 120$ kHz) and weak ($D \approx 120$ Hz) interactions were therefore investigated with the results shown in Fig. 2 and Supplementary information Table SI.

Four-spin systems, of C_1 and D_{2h} symmetry, have been observed experimentally to display a long-lived state [27]. The nature of the observed state was proposed to be a singlet localised on one of the two pairs of strongly coupled spins stabilised by the J-coupling within the pair [18]. The results from our analysis, shown in Fig. 2, demonstrate that this is certainly possible but that a more complicated product of singlets may also be responsible for the long lifetime observed. The states in addition to the isolated singlets are either products of the strongly dipolar-coupled singlets or symmetric linear combinations across all pair-wise singlet permutations. The number of long-lived states available is maximised when sets of strongly coupled pairs are related by centres of inversion, more precisely by an inversion with respect to the midpoint of the pairs, not necessarily the centre of inversion of the whole system. The state vectors are linear combinations or products of localised singlets across all pairs of symmetry related spins, even if they have only a weak dipolar coupling. As the interactions between sets of strongly coupled pairs increases the long-lived states are increasingly perturbed and the non-symmetric linear combinations mix so as to increase the eigenvalues of the relaxation matrix, reducing the long-lived states to those shown in Fig. 1.

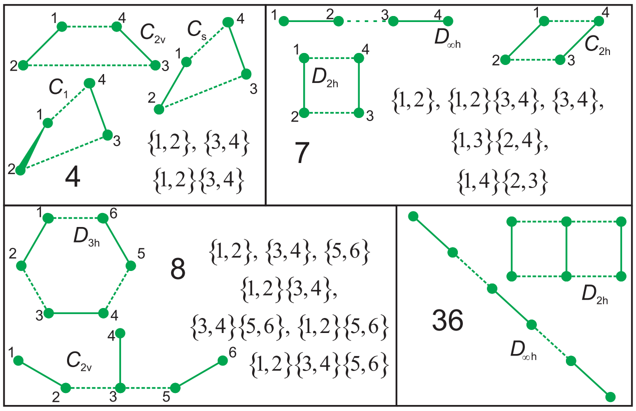


Fig. 2. Multi-spin systems with both strong ($D \approx 120$ kHz, solid lines) and weak ($D \approx 120$ Hz, dashed lines) dipolar couplings, grouped according to null-space size, n. When $n < 10$ the constituent states of each group which derive from singlet-states, $\hat{P}_S^{\{i,j\}}$, across pairs of spins $\{i, j\}$ are given. Nodes represent spin positions. All pair-wise dipolar interactions were included.

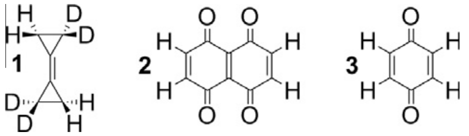


Fig. 3. Molecules expected to show long lived states.

Having established the symmetry and coupling pattern requirements for the presence of multiple long-lived states, we have investigated three apparently suitable molecules, Fig. 3. They were chosen primarily for the symmetry of their dipolar coupling networks but also for their relatively small CSA. The eigenvalues of

Table 1
Ten smallest eigenvalues (in s^{-1}) for dipolar relaxation only, dipolar and CSA relaxation and the full coherent Liouvillian for three example molecules, numbering as in Fig. 3, in a 1.0 T magnetic field. The identically zero eigenvalue always belongs to the identity operator. All simulation parameters for these systems are given in Supplementary information. The magnetic properties were calculated using Gaussian03 [25] using literature crystal structures [28–30].

Molecule	Dipolar relaxation	Dipolar and CSA relaxation	Total Liouvillian
1	0	0	0
	0.0000	0.0009	0.0684
	0.0015	0.0024	0.1271
	0.0038	0.0046	0.7623
	0.0057	0.0064	2.3863
	0.0057	0.0065	2.8843
	0.0087	0.0093	3.4775
	1.8800	1.8694	3.9168
	1.8800	1.8695	3.9168
	1.8800	1.8810	5.6113
2	0	0	0
	0.0000	0.0000	0.0000
	0.0001	0.0003	0.0643
	0.0003	0.0003	0.0644
	0.0004	0.0004	0.1581
	0.0004	0.0004	0.2967
	0.0006	0.0006	0.2988
	0.1710	0.1683	0.3294
	0.1710	0.1683	0.3778
	0.1710	0.1690	0.4549
3	0	0	0
	0.0000	0.0000	0.0000
	0.0033	0.0032	0.0648
	0.0038	0.0038	0.0946
	0.0085	0.0085	0.1612
	0.0085	0.0085	0.3264
	0.0088	0.0088	0.3382
	0.1644	0.1666	0.3904
	0.1644	0.1666	0.4158
	0.1669	0.1669	0.5289

the system Liouvillian were calculated for three cases: dipolar relaxation superoperator only, full relaxation superoperator (including CSA) only, and finally the total Liouvillian that includes also the coherent evolution for the molecule in a moderate (1 Tesla) static field. Table 1 shows the 10 smallest amplitude eigenvalues in each instance; long-lived states are defined as those that have eigenvalues more than an order of magnitude smaller than the majority.

Each molecule reveals six non-trivial long-lived states, that is, six states that would resist relaxation if coherent evolution is suppressed. In the presence of unsuppressed coherent evolution, bicyclopropylidene-d_4 (**1**) naphthalenetetrone (**2**) and *p*-benzoquinone (**3**) all have only one extremely long-lived state, which has an eigenvalue seven orders of magnitude smaller than the average. Reducing the field strength, or using other methods to limit coherent evolution, moves the eigenvalues towards the relaxation-only limit, that is, the six usable states identified in Fig 2. Molecules with more sets of inversion-related dipolar coupled pairs should exhibit even more long-lived states.

4. Conclusion

We have presented a method with which to determine the number and identity of the states in multi-spin systems that are immune or insensitive to dipolar relaxation. Using this procedure we have identified some general requirements to maximise the number of long-lived states. Firstly, for a strongly coupled spin system to exhibit long-lived states, some spin pairs must be related by an inversion symmetry. Multiple pairs of strongly dipolar-coupled spins with only weak inter-pair interactions lead to many long-lived states when there are ‘pairs of pairs’ related to each other by a centre of inversion. We have identified large slowly relaxing subspaces in several commercially available molecules. Their existence provides scope for using these and other such molecules as hyperpolarising agents in magnetic resonance experiments.

Acknowledgments

This work was funded by the EPSRC (EP/F065205/1, EP/H003789/1) and supported by the Oxford e-Research Centre.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmr.2011.06.001.

References

[1] M. Carravetta, O.G. Johannessen, M.H. Levitt, Beyond the T_1 limit: singlet nuclear spin states in low magnetic fields, Phys. Rev. Lett. 92 (2004) 153003–153006.

[2] G. Pileio, M. Carravetta, E. Hughes, M.H. Levitt, The long-lived nuclear singlet state of N-15-nitrous oxide in solution, J. Am. Chem. Soc. 130 (2008) 12582–12583.

[3] P. Ahuja, R. Sarkar, P.R. Vasos, G. Bodenhausen, Long-lived states in multiple-spin systems, ChemPhysChem 10 (2009) 2217–2220.

[4] P.R. Vasos, A. Comment, R. Sarkar, P. Ahuja, S. Jannin, J.P. Ansermet, J.A. Konter, P. Hautle, B. van den Brandt, G. Bodenhausen, Long-lived states to sustain hyperpolarized magnetization, Proc. Natl. Acad. Sci. USA 106 (2009) 18469–18473.

[5] W.S. Warren, E. Jenista, R.T. Branca, X. Chen, Increasing hyperpolarized spin lifetimes through true singlet eigenstates, Science 323 (2009) 1711–1714.

[6] P. Ahuja, R. Sarkar, S. Jannin, P.R. Vasos, G. Bodenhausen, Proton hyperpolarisation preserved in long-lived states, Chem. Commun. 46 (2010) 8192–8194.

[7] G. Pileio, M. Carravetta, M.H. Levitt, Storage of nuclear magnetization as long-lived singlet order in low magnetic field, Proc. Natl. Acad. Sci. USA 107 (2010) 17135–17139.

[8] R. Sarkar, P. Ahuja, P.R. Vasos, G. Bodenhausen, Measurement of slow diffusion coefficients of molecules with arbitrary scalar couplings via long-lived spin states, ChemPhysChem 9 (2008) 2414–2419.

[9] M.C.D. Tayler, S. Marie, A. Ganesan, M.H. Levitt, Determination of molecular torsion angles using nuclear singlet relaxation, J. Am. Chem. Soc. 132 (2010) 8225–8227.

[10] A.A. Karabanov, C. Bretschneider, W. Kockenberger, Symmetries of the master equation and long-lived states of nuclear spins, J. Chem. Phys. 131 (2009) 204105–204114.

[11] G. Pileio, M.H. Levitt, Theory of long-lived nuclear spin states in solution nuclear magnetic resonance. II. Singlet spin locking, J. Chem. Phys. 130 (2009) 214501–214514.

[12] M. Carravetta, M.H. Levitt, Theory of long-lived nuclear spin states in solution nuclear magnetic resonance. I. Singlet states in low magnetic field, J. Chem. Phys. 122 (2005) 214505–214518.

[13] I. Kuprov, N. Wagner-Rundell, P.J. Hore, Polynomially scaling spin dynamics simulation algorithm based on adaptive state-space restriction, J. Magn. Reson. 189 (2007) 241–250.

[14] I. Kuprov, Polynomially scaling spin dynamics II: further state-space compression using Krylov subspace techniques and zero track elimination, J. Magn. Reson. 195 (2008) 45–51.

[15] H.J. Hogben, P.J. Hore, I. Kuprov, Strategies for state space restriction in densely coupled spin systems with applications to spin chemistry, J. Chem. Phys. 132 (2010) 174101–174110.

[16] I. Kuprov, Diagonalization-free implementation of spin relaxation theory for large spin systems, J. Magn. Reson. 209 (2011) 31–38.

[17] H.J. Hogben, M. Krzystyniak, G.T.P. Charnock, P.J. Hore, I. Kuprov, Spinach – a software library for simulation of spin dynamics in large spin systems, J. Magn. Reson. 208 (2011) 179–194.

[18] G. Pileio, M.H. Levitt, J-stabilization of singlet states in the solution NMR of multiple-spin systems, J. Magn. Reson. 187 (2007) 141–145.

[19] P. Ahuja, R. Sarkar, P.R. Vasos, G. Bodenhausen, Molecular properties determined from the relaxation of long-lived spin states, J. Chem. Phys. 127 (2007) 134112.

[20] J.H. Freed, Generalized cumulant expansions and spin-relaxation theory, J. Chem. Phys. 49 (1968) 376–392.

[21] R. Kubo, Generalized cumulant expansion method, J. Phys. Soc. Jpn. 17 (1962) 1100–1120.

[22] A.G. Redfield, On the theory of relaxation processes, IBM J. Res. Dev. 1 (1957) 19–31.

[23] M. Goldman, Formal theory of spin-lattice relaxation, J. Magn. Reson. 149 (2001) 160–187.

[24] M.H. Levitt, L. Dibari, Steady-state in magnetic-resonance pulse experiments, Phys. Rev. Lett. 69 (1992) 3124–3127.

[25] M.J. Frisch et al., Gaussian 03, Gaussian, Wallingford, CT, 2004.

[26] A.K. Grant, E. Vinogradov, Long-lived states in solution NMR: theoretical examples in three- and four-spin systems, J. Magn. Reson. 193 (2008) 177–190.

[27] G. Pileio, M. Concistre, M. Carravetta, M.H. Levitt, Long-lived nuclear spin states in the solution NMR of four-spin systems, J. Magn. Reson. 182 (2006) 353–357.

[28] M. Traetteberg, A. Simon, E.M. Peters, A. Demeijere, Bonding properties of bicyclopropylidene – gas-phase electron-diffraction study and X-ray crystal structure analysis, J. Mol. Struct. 118 (1984) 333–343.

[29] F.H. Herbstein, M. Kapon, 1,4,5,8-Naphthalenetetrone, Acta Crystallogr. Sec. B – Struct. Sci. 38 (1982) 3123–3125.

[30] J. Trotter, Rho-benzoquinone – mean-plane Fourier, Acta Crystallogr. 14 (1961) 553.