Singlet-triplet coherences in nuclear magnetic resonance

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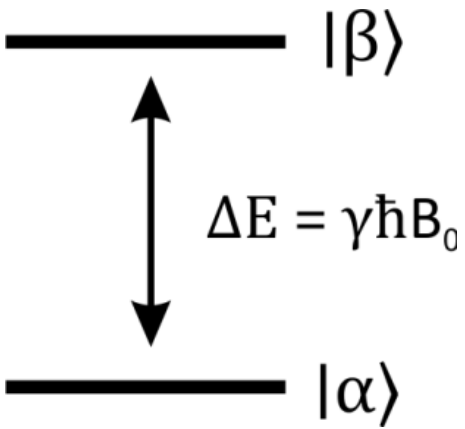
M. H. Levitt, A. V. Yurkovskaya, K. L. Ivanov

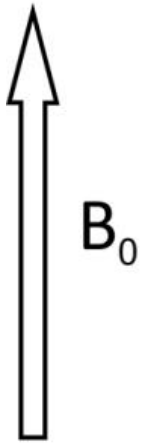
topics

- Introduction to NMR
- ST coherences in pairs of weakly coupled spins
- ST coherences in pairs of near-equivalent spins

Precession of a nuclear spin-1/2

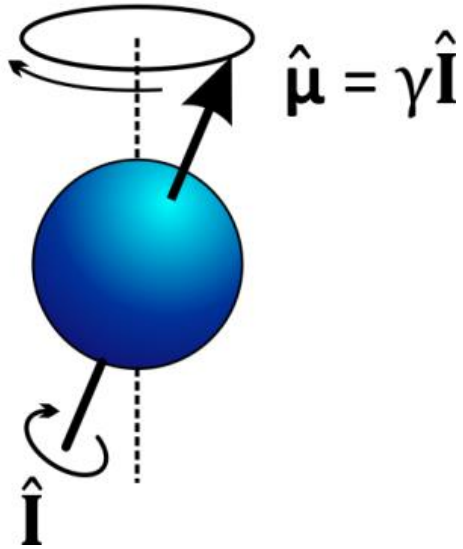
$|\psi\rangle = C_\alpha|\alpha\rangle + C_\beta|\beta\rangle$



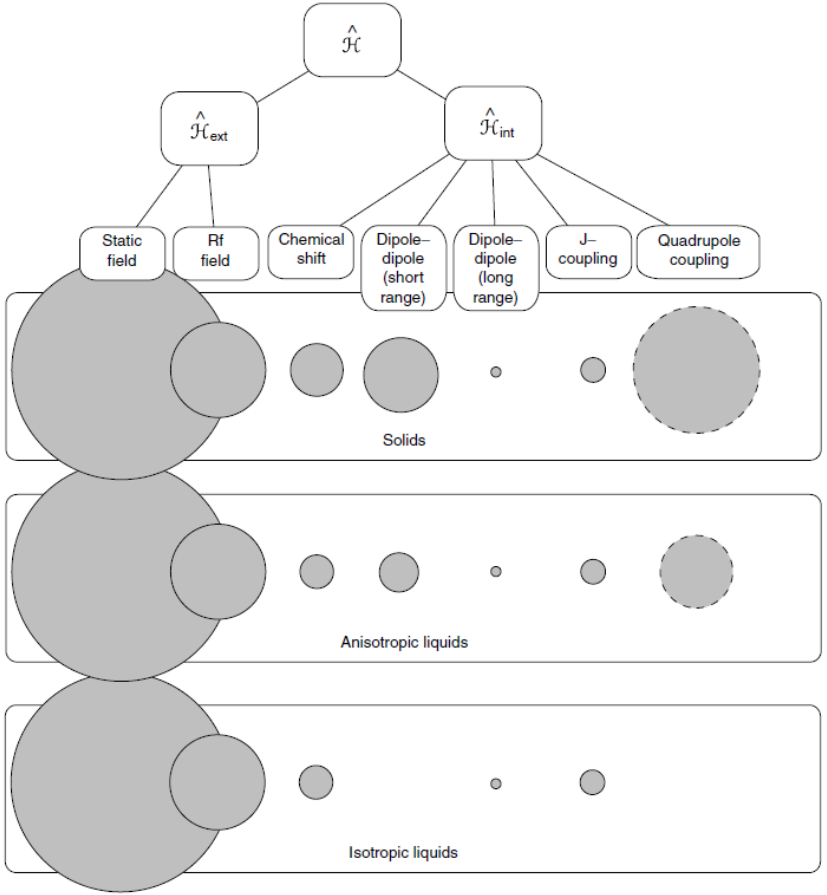


Larmor frequency

$\omega_0 = -\gamma B_0$

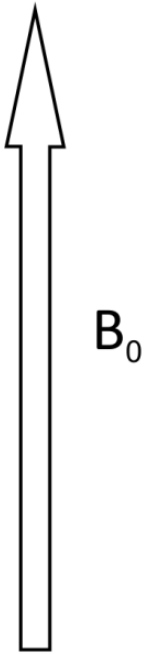


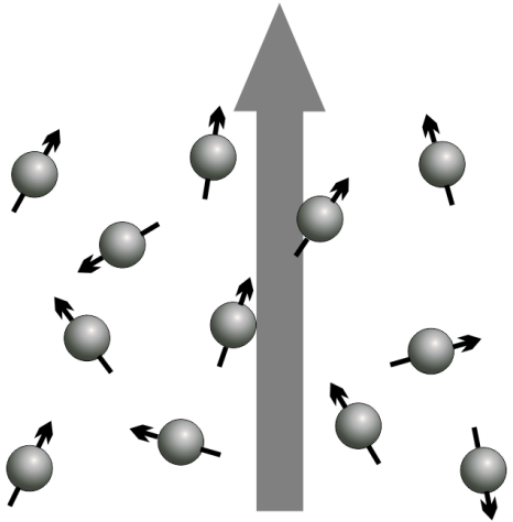
Control over nuclear spin states



M.H. Levitt, Spin dynamics: basics of nuclear magnetic resonance-2nd ed., (2008)

Nuclear paramagnetism

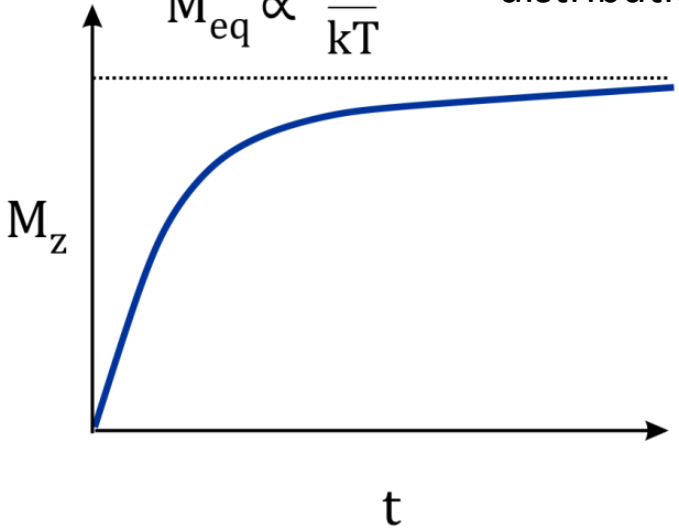




Net magnetization at thermal equilibrium

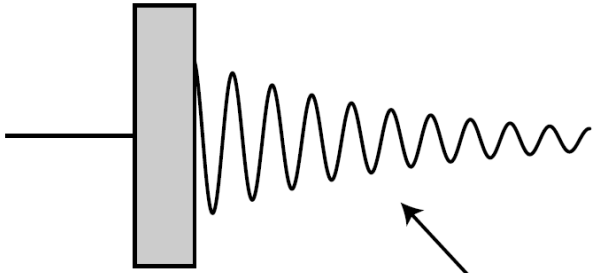
Boltzmann distribution

$$M_{eq} \propto \frac{\gamma B_0}{kT}$$



$$M_z(t) = M_{eq}(1 - \exp\{-t/T_1\})$$

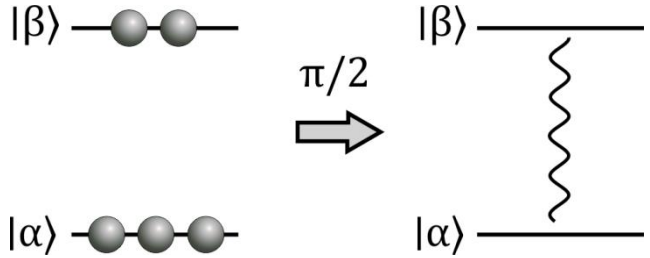
NMR coherences

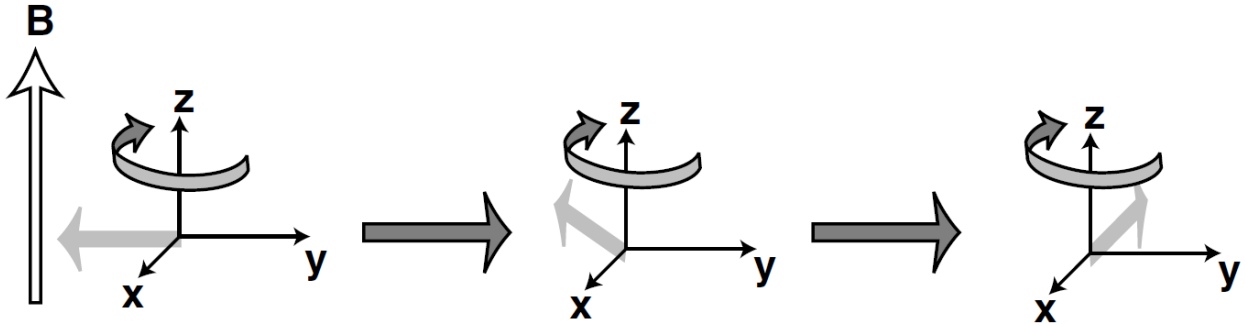


R.f. pulse

NMR signal

Decays with T_2 transverse relaxation time

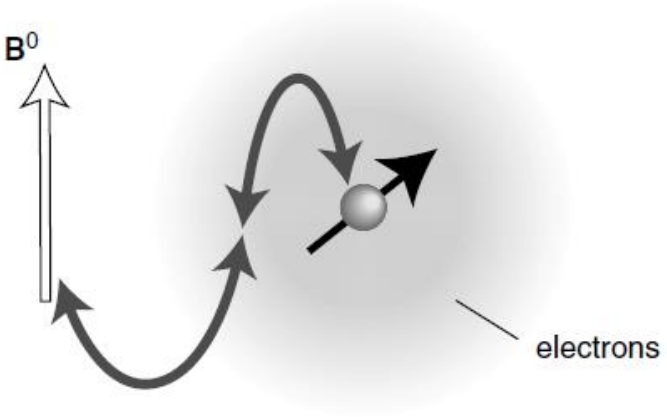




M.H. Levitt, Spin dynamics : basics of nuclear magnetic resonance-2nd ed., (2008)

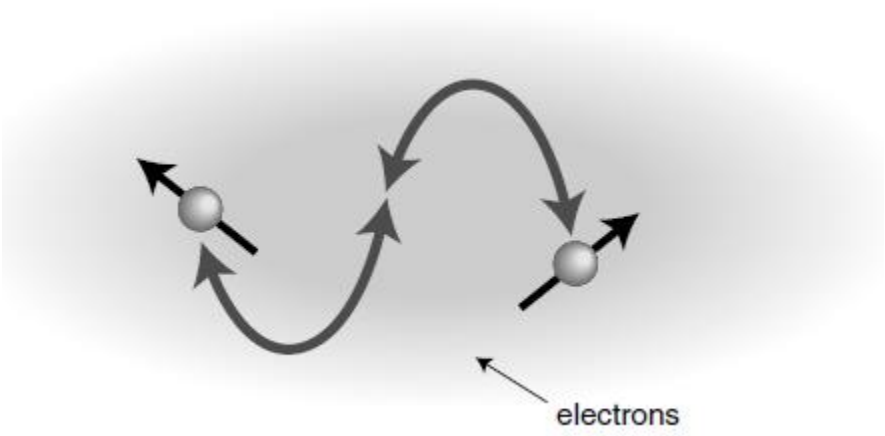
Internal interactions

Chemical shift



Electrons interact with the B_0 and induce a field on a nuclear

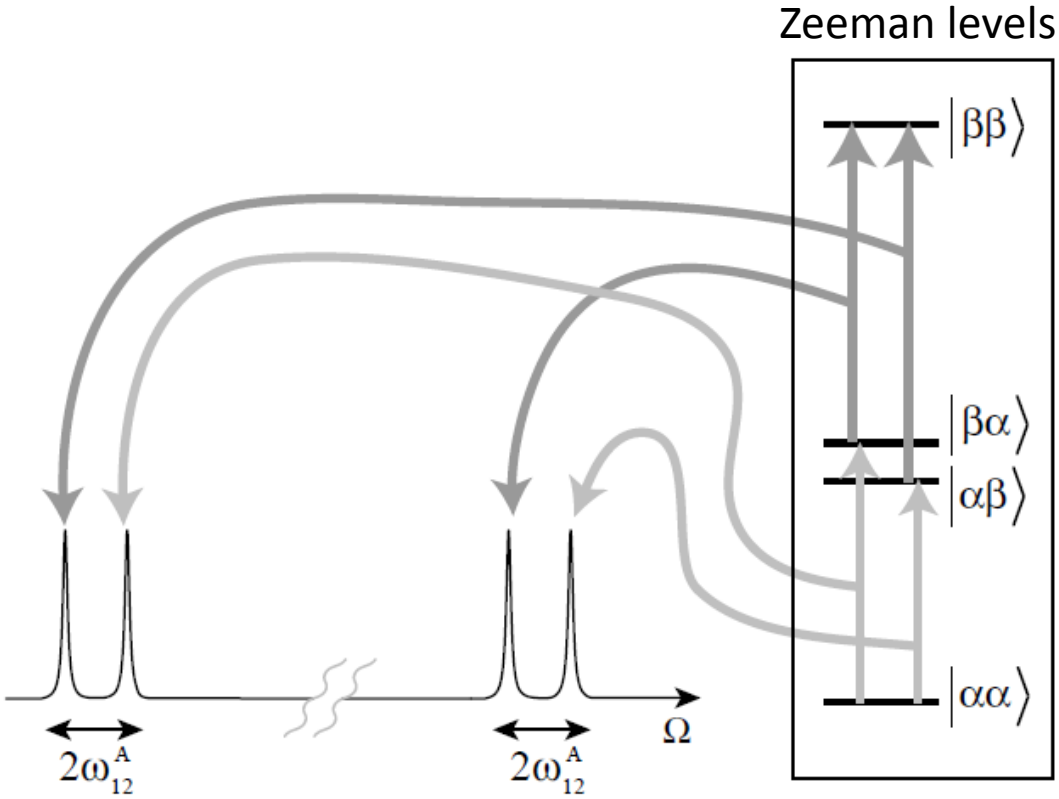
J-coupling



Nuclear spins interact indirectly via electrons

M.H. Levitt, Spin dynamics : basics of nuclear magnetic resonance-2nd ed., (2008)

Two weakly coupled spins



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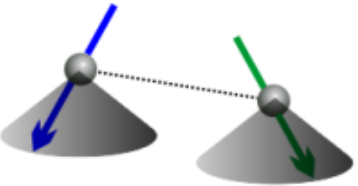
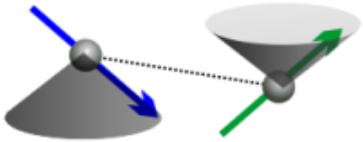
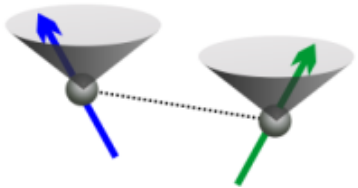
Two strongly coupled spins







$|T_-\rangle = |\beta\beta\rangle$

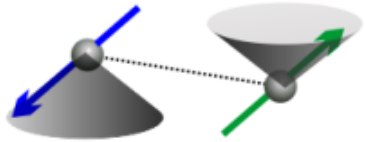
$\Delta E = \gamma\hbar B_0$

$|T_0\rangle = \dfrac{|\alpha\beta\rangle + |\beta\alpha\rangle}{\sqrt{2}}$

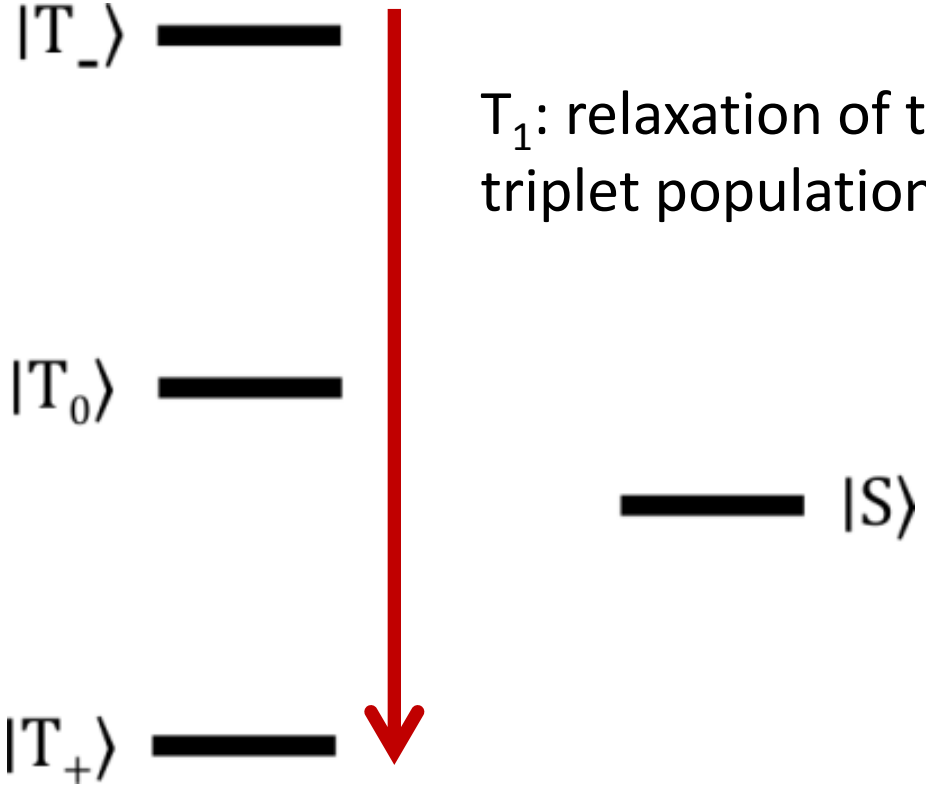
$\Delta E = \gamma\hbar B_0$

$|T_+\rangle = |\alpha\alpha\rangle$

$|S\rangle = \dfrac{|\alpha\beta\rangle - |\beta\alpha\rangle}{\sqrt{2}}$

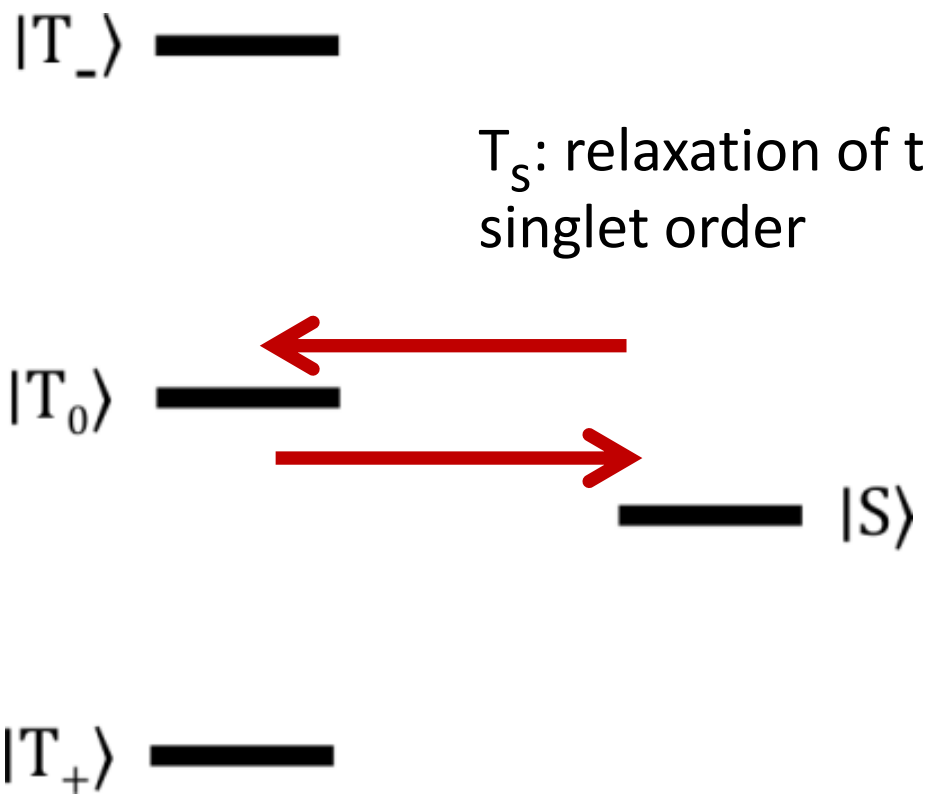


Relaxation times

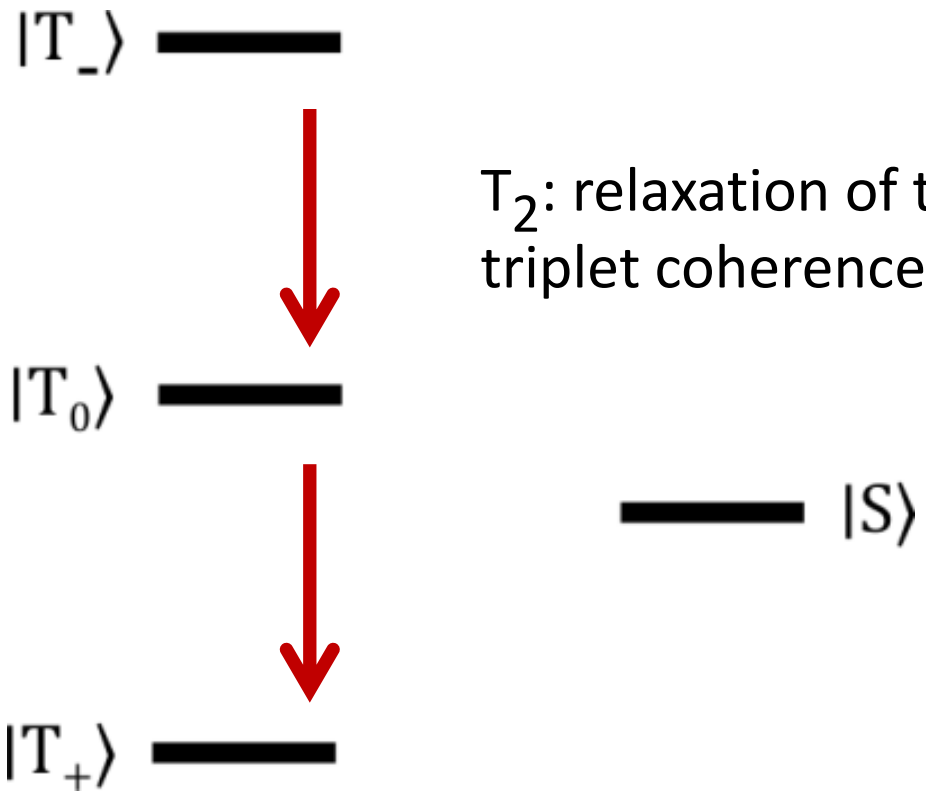


T_1: relaxation of the triplet populations

Relaxation times

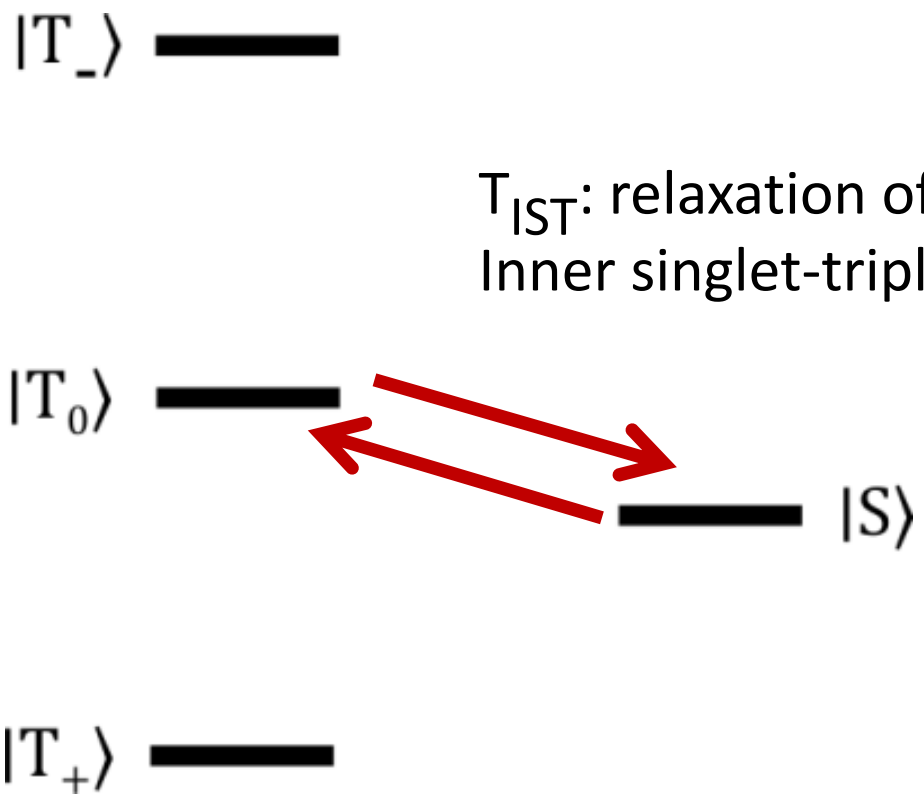


Relaxation times



T_2: relaxation of the triplet coherences

Relaxation times



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J|A|C|S
COMMUNICATIONS

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The Long-Lived Nuclear Singlet State of ^{15}N-Nitrous Oxide in Solution

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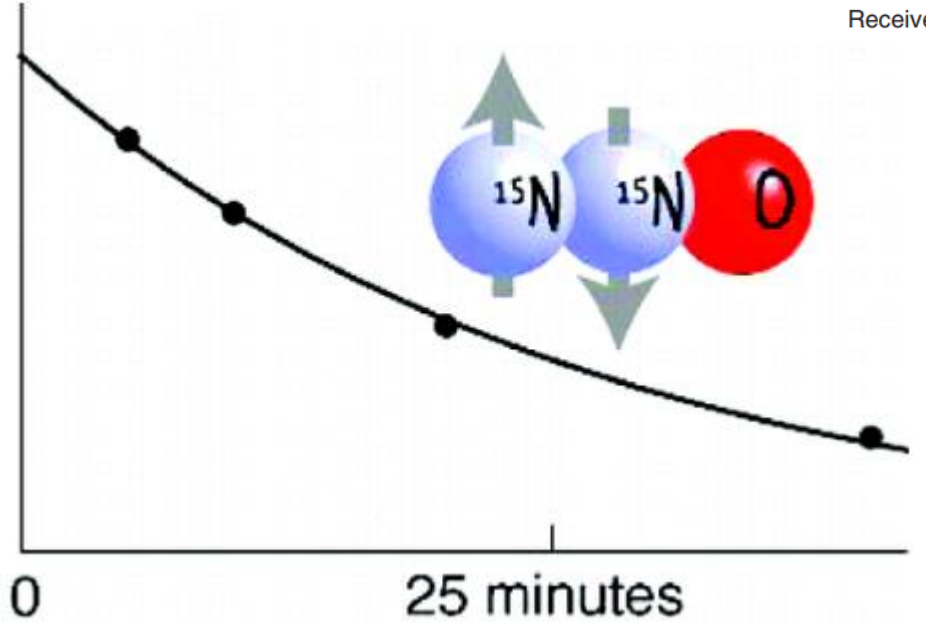
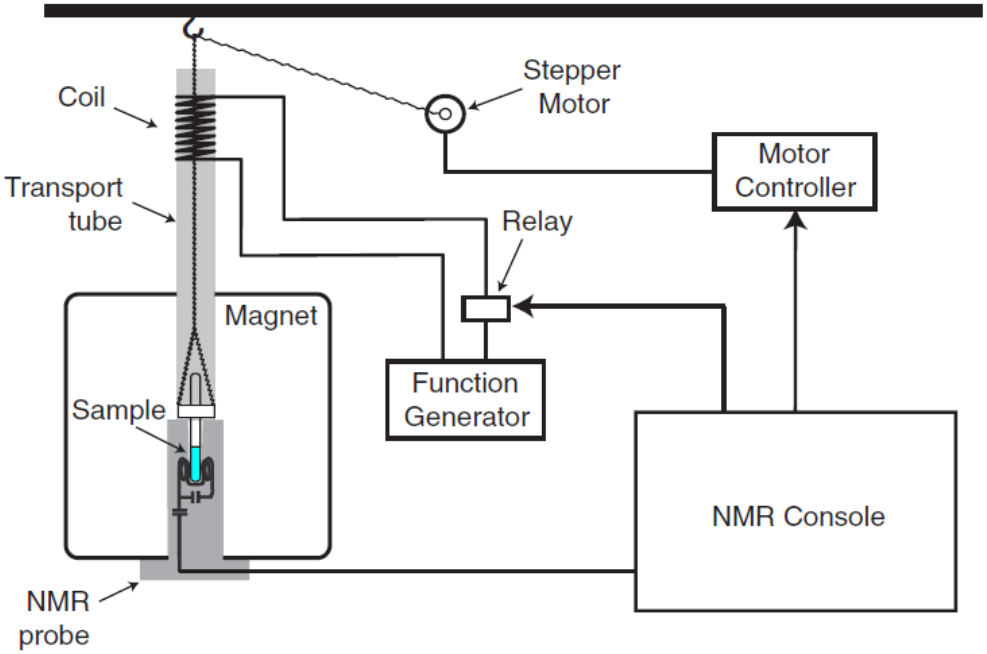
Received May 14, 2008; E-mail: mhl@soton.ac.uk

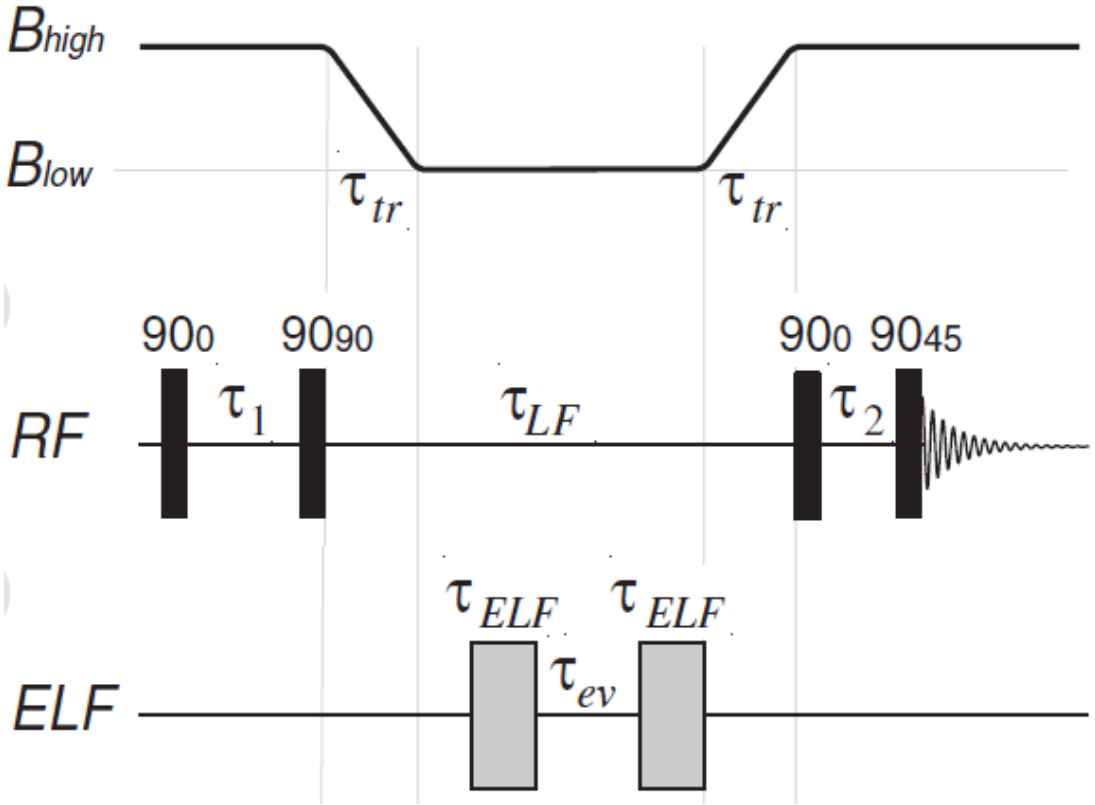


Extremely Low-Frequency Spectroscopy in Low-Field Nuclear Magnetic Resonance

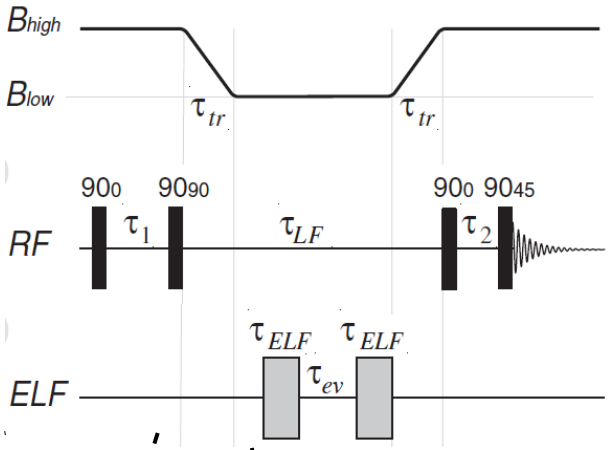
Giuseppe Pileio, Marina Carravetta, and Malcolm H. Levitt*
School of Chemistry, Southampton University, SO17 1BJ, United Kingdom
(Received 28 May 2009; published 20 August 2009)

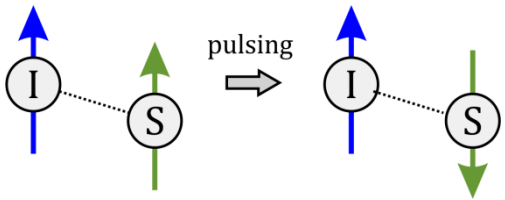


Adiabatic change of the eigen-states

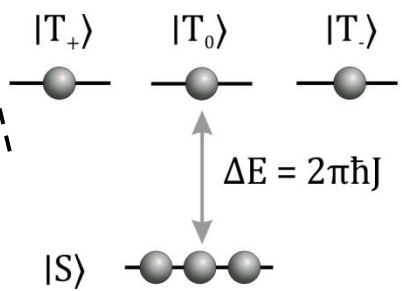


Adiabatic change of the eigen-states

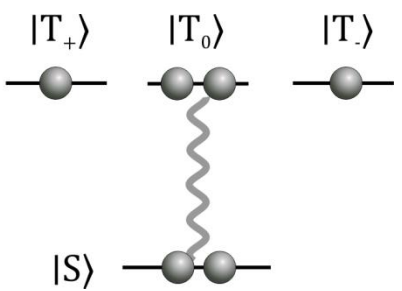




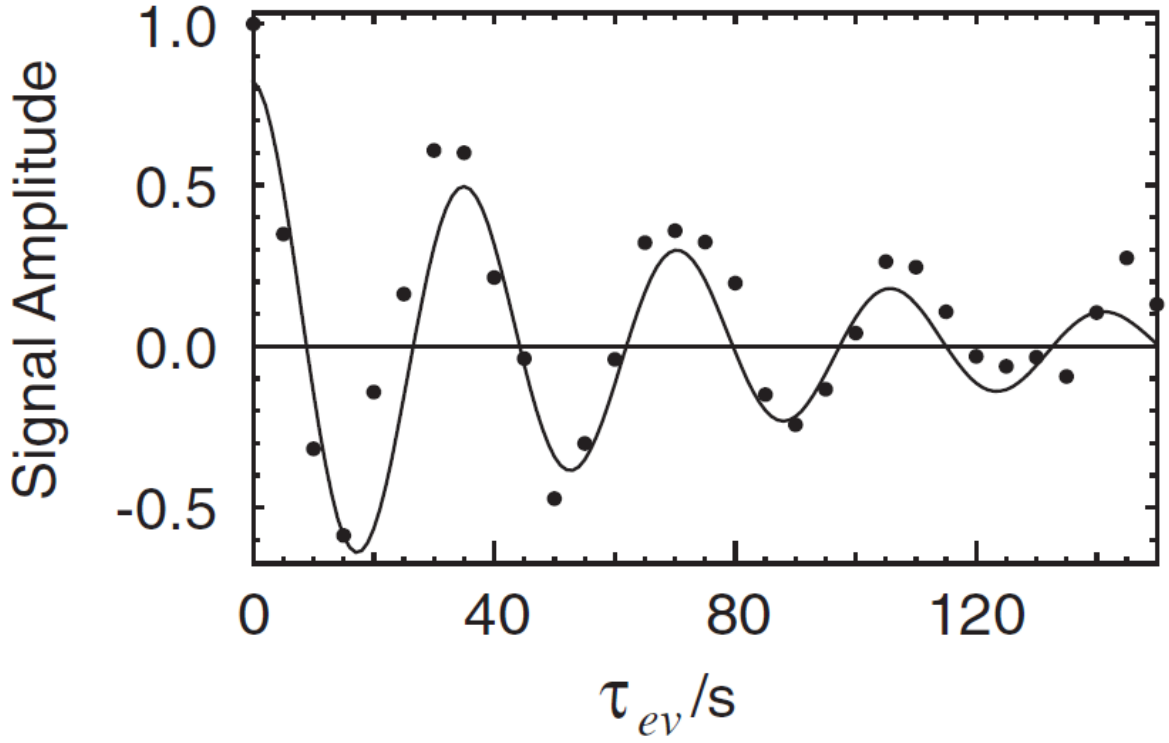
$\hat{I}_z + \hat{S}_z$ $\hat{I}_z - \hat{S}_z$



ELF $\pi/2$

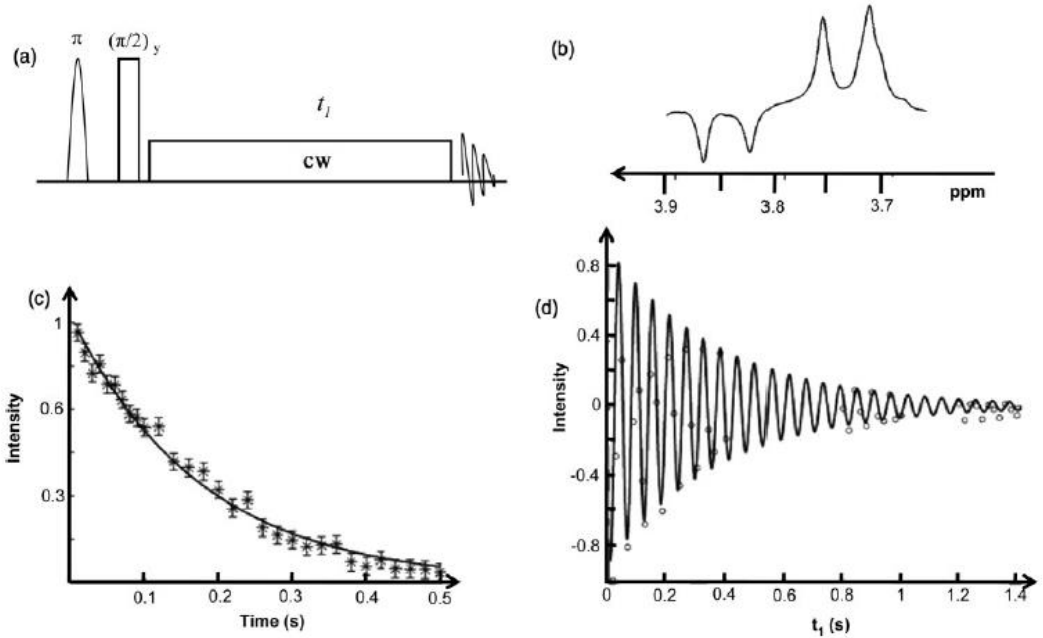


Adiabatic change of the eigen-states

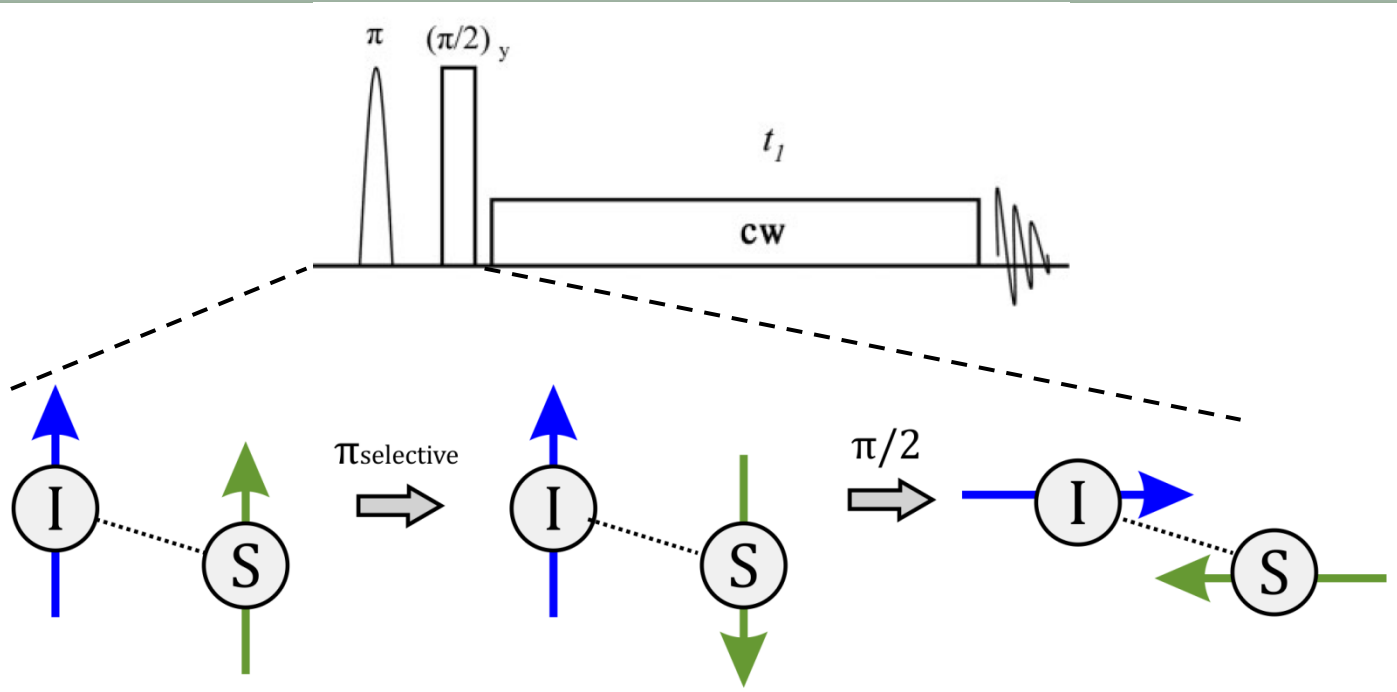


Long-Lived Coherences for Homogeneous Line Narrowing in Spectroscopy

Riddhiman Sarkar,[1] Puneet Ahuja,[1] Paul R. Vasos,[1,*] and Geoffrey Bodenhausen[1,2]

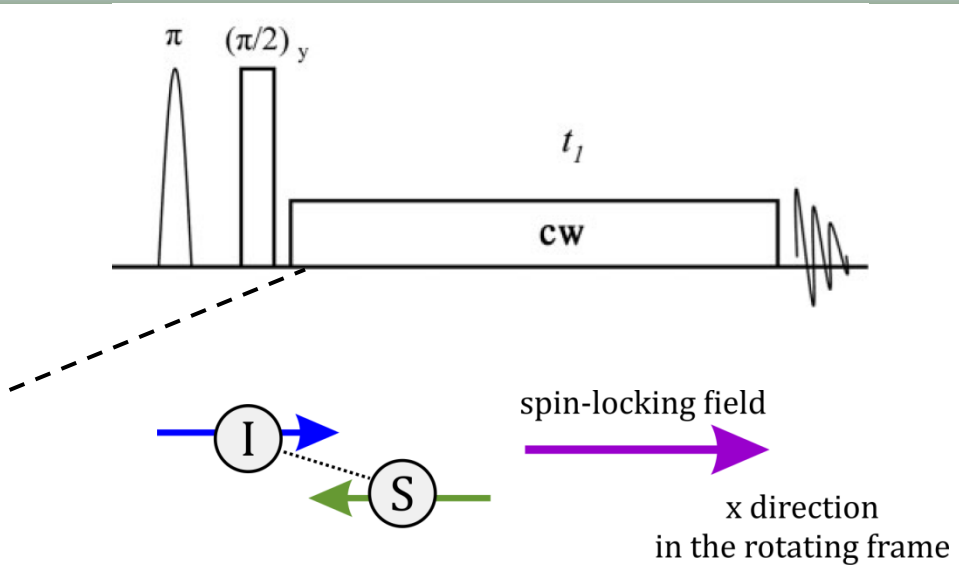


Pulse sequence for creating the ST coherence



$\hat{I}_z + \hat{S}_z$ $\hat{I}_z - \hat{S}_z$ $\hat{I}_x - \hat{S}_x$

Spin-locking field



Evolution under spin-locking RF-field results in new eigen-states: singlet and three triplet

However these triplet states have the quantization axis parallel to the x-axis of the rotating frame

$$\hat{I}_x - \hat{S}_x \xrightarrow{2\pi J\,(\hat{I}\cdot\hat{S})} \mathbf{Cos(\pi J t)}\,\{\hat{I}_x - \hat{S}_x\} + \mathrm{Sin}(\pi J t)\,\{2\hat{I}_y \hat{S}_z - 2\hat{I}_z \hat{S}_y\}$$

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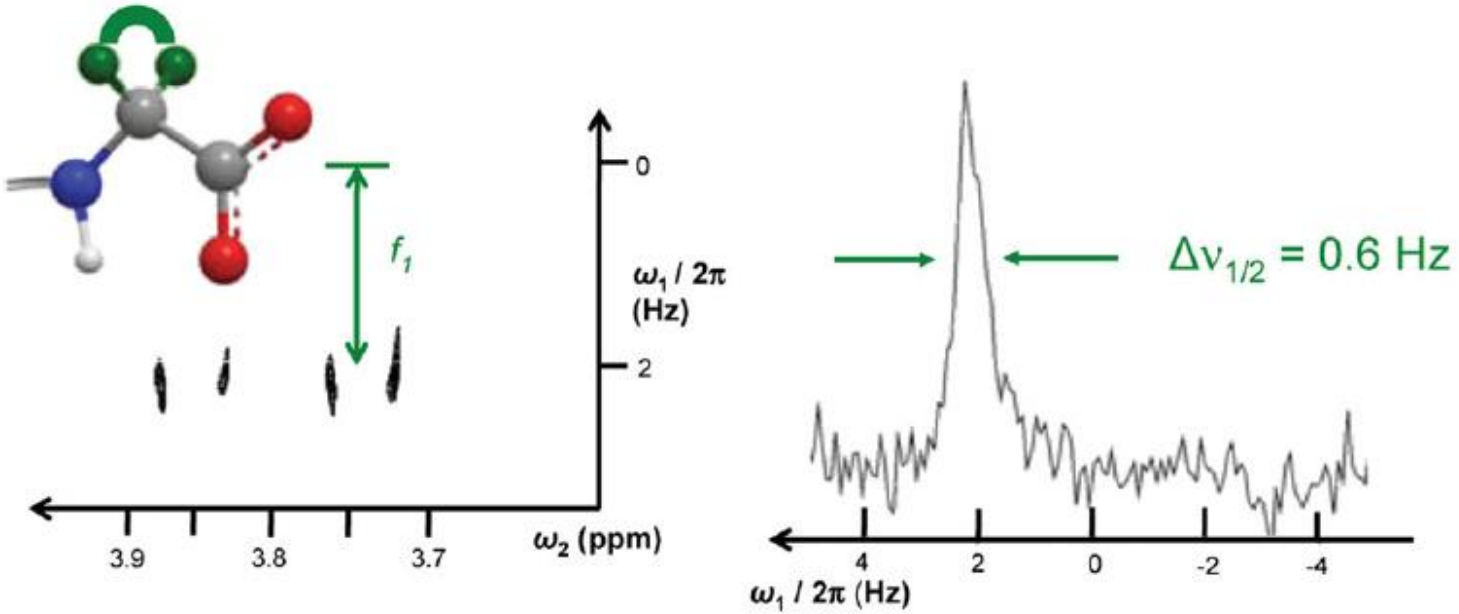

topics

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- Singlet – Triplet Coherences in pairs of near-equivalent spins

Angewandte
Communications

NMR Spectroscopy

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A Nuclear Singlet Lifetime of More than One Hour in Room-Temperature Solution**

Gabriele Stevanato, Joseph T. Hill-Cousins, Pär Håkansson, Soumya Singha Roy, Lynda J. Brown, Richard C. D. Brown, Giuseppe Pileio, and Malcolm H. Levitt**

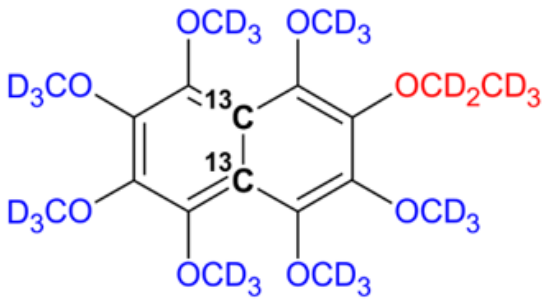
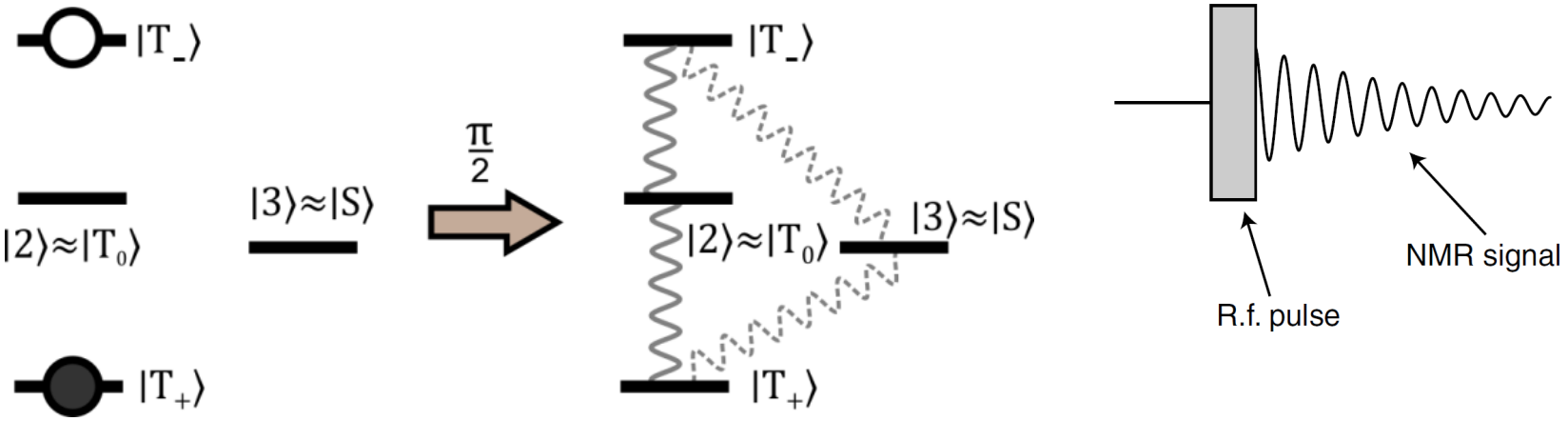


Table 1: Singlet (T_S) and magnetization (T_1) decay time for $^{13}C_2$-I in [D_6]acetone as a function of magnetic field B.

B [T]	T_S [s][a]	T_1 [s][a]	T_S [s][b]	T_1 [s][b]
0.0020 ± 10^{-4}	3950 ± 220	78 ± 3	270 ± 20	33 ± 1
0.10 ± 0.02	4030 ± 220	72 ± 2	348 ± 8	37 ± 2
0.4 ± 0.2	4250 ± 130	73 ± 2	380 ± 8	40 ± 1
0.7 ± 0.3	4240 ± 150	76 ± 2	381 ± 12	46 ± 1
1.6 ± 0.7	4050 ± 180	73 ± 2	487 ± 22	48 ± 2
3.8 ± 1.3	3310 ± 70	55 ± 2	624 ± 17	37 ± 1
5.1 ± 1.3	2590 ± 30	43 ± 1	611 ± 26	29 ± 1
7.0 ± 1.2	1610 ± 20	29 ± 1	574 ± 19	22 ± 1
8.0 ± 1.0	1240 ± 40	24 ± 1	524 ± 28	19 ± 1
9.39	950 ± 60	19 ± 1	485 ± 23	18 ± 1

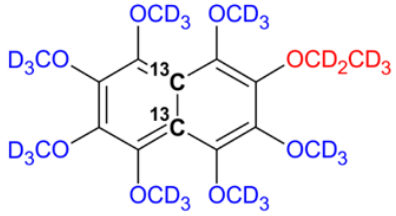
[a] Degassed sample; [b] non-degassed sample with [O_2] about 2 mM.

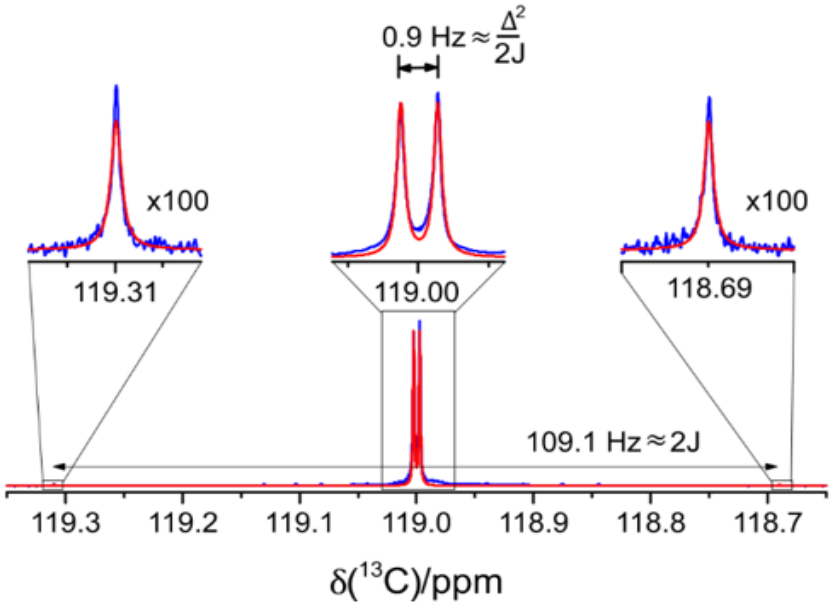
Efficiency of the coherences excitation



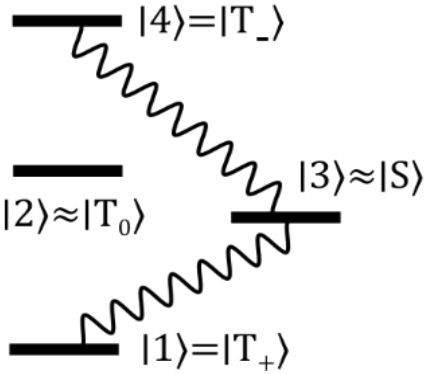
- Hard pulse excites 10 times stronger coherences within triplet manifold
- Detection further scales down the relative intensities of the OST transitions to the triplet ones by the same factor of 10
- The common reason: the OST coherences are less efficiently coupled to the probe coil

Near-equivalent spin pairs

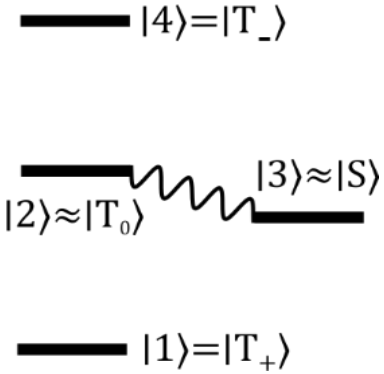




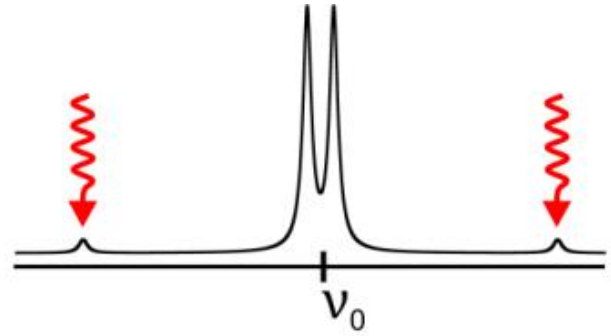
Outer **S**inglet-**T**riplet Transitions (**OST**)

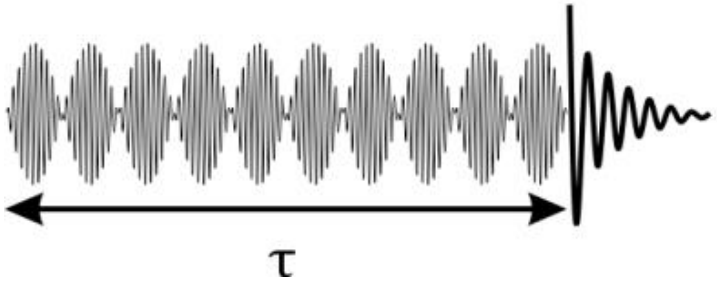


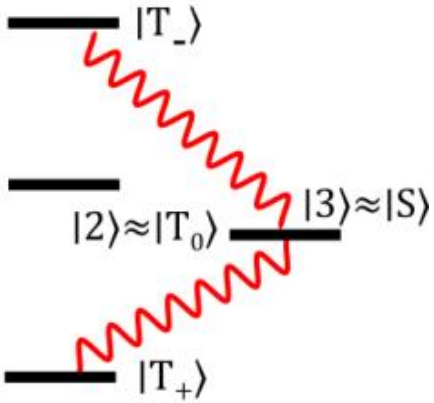
Inner **S**inglet-**T**riplet Transitions (**IST**)



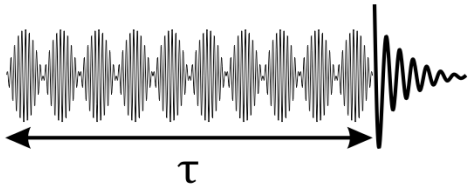
Selective excitation of the OST coherences

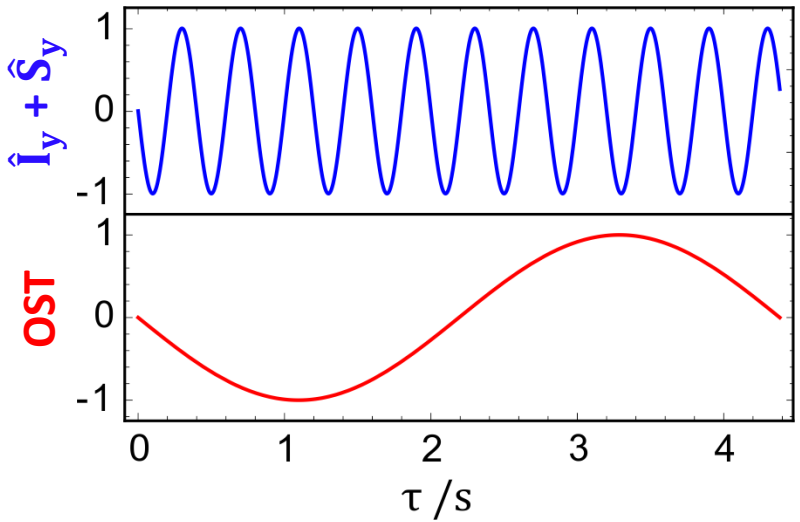


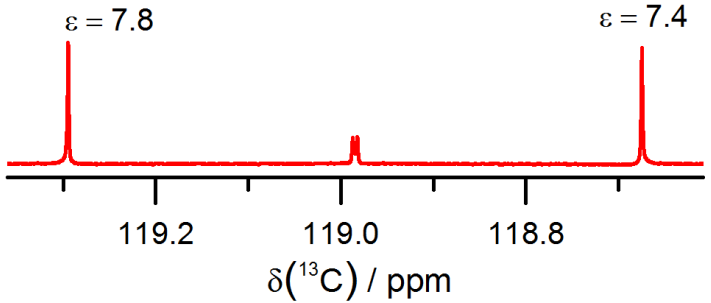


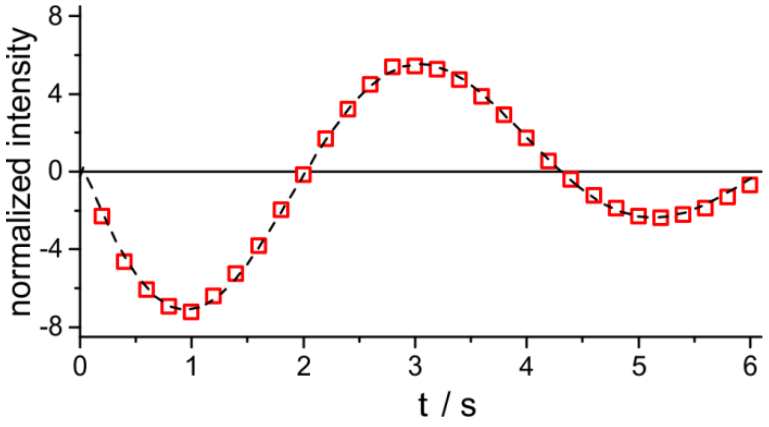


Nutation of the OST coherences

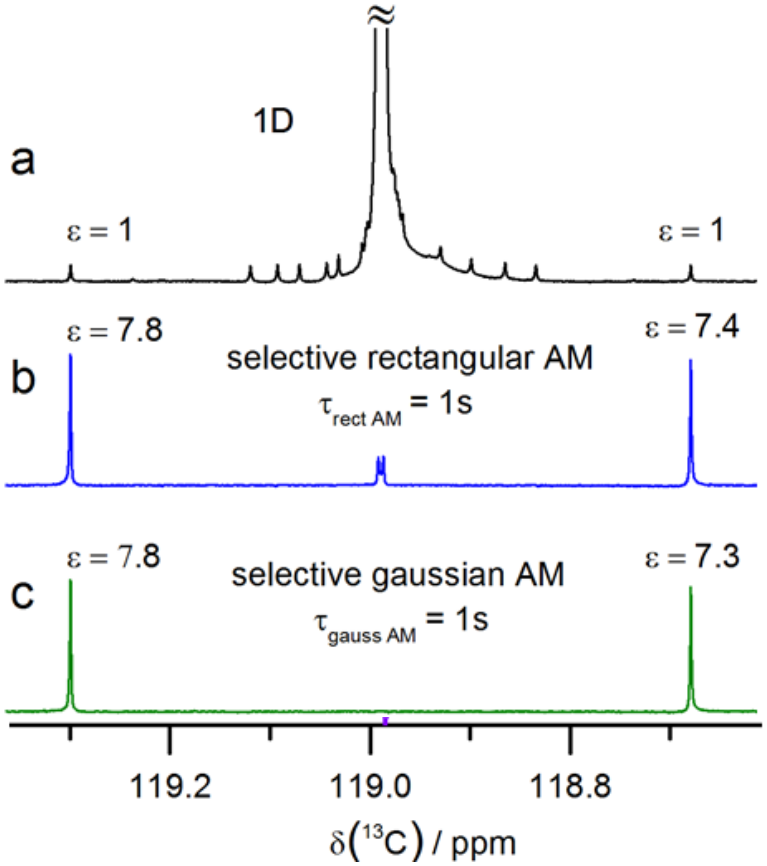


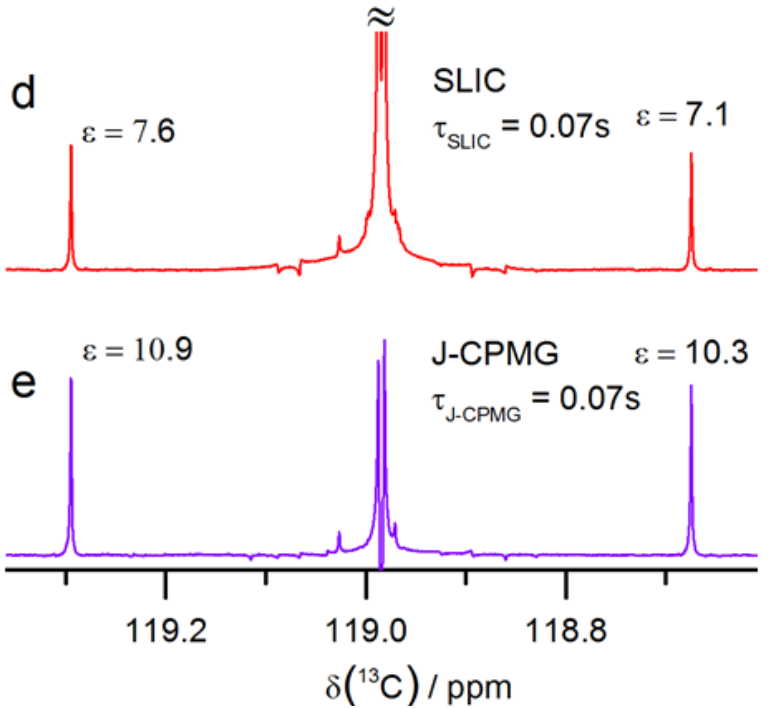




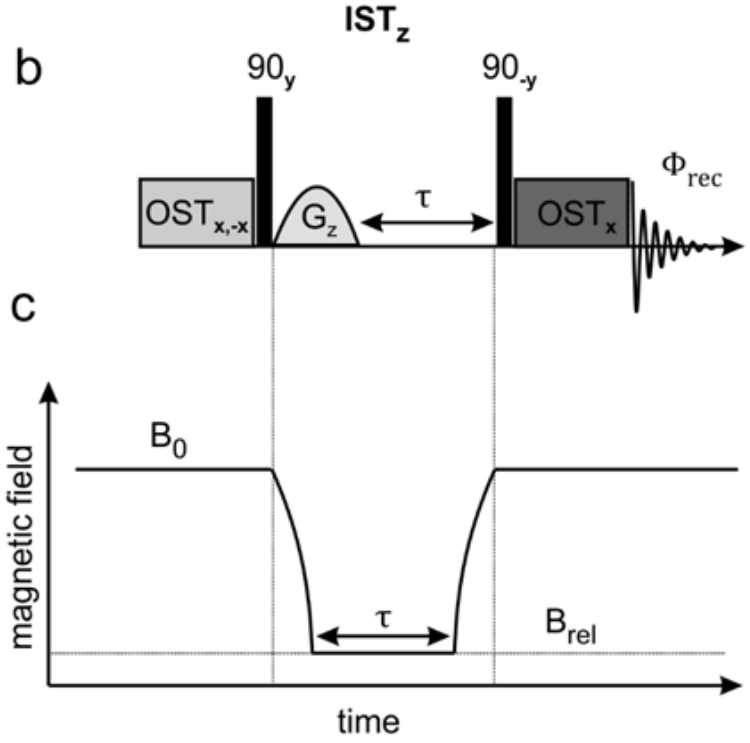


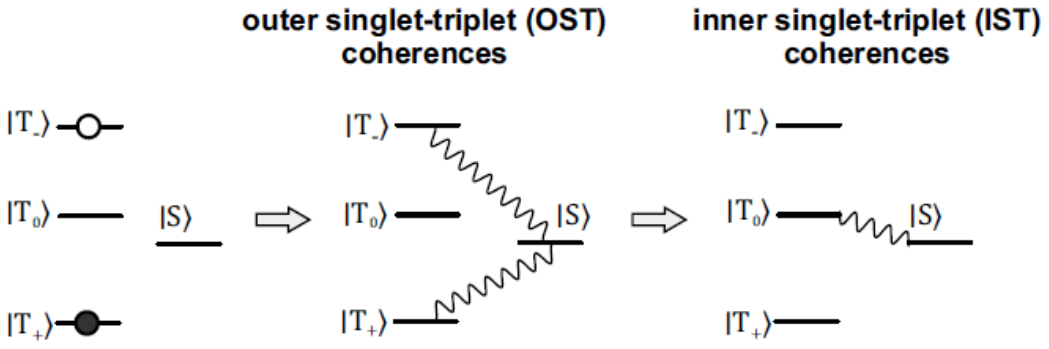
Comparison of different methods for excitation of the OST coherences



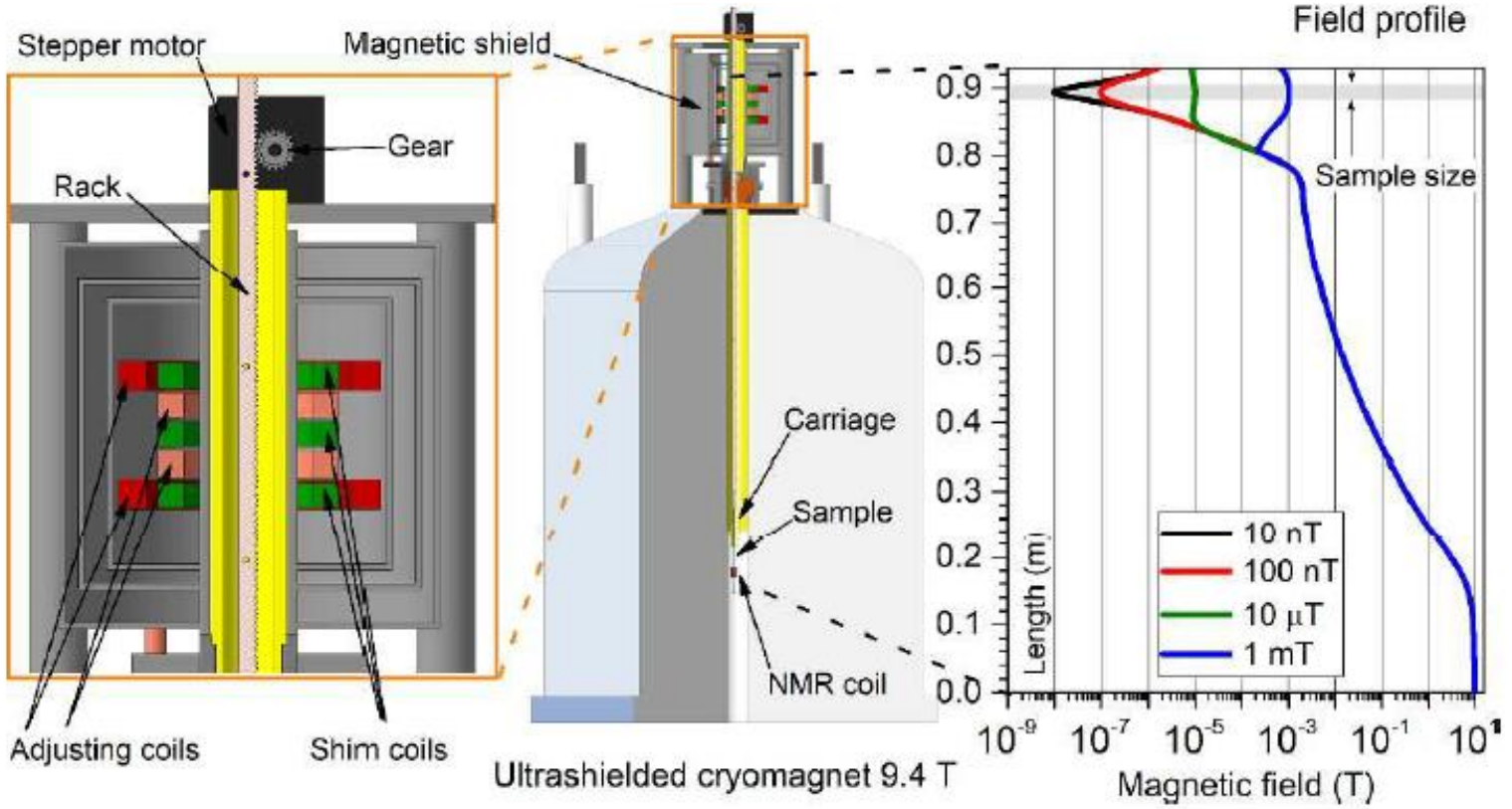


Shuttling setup for field-cycling

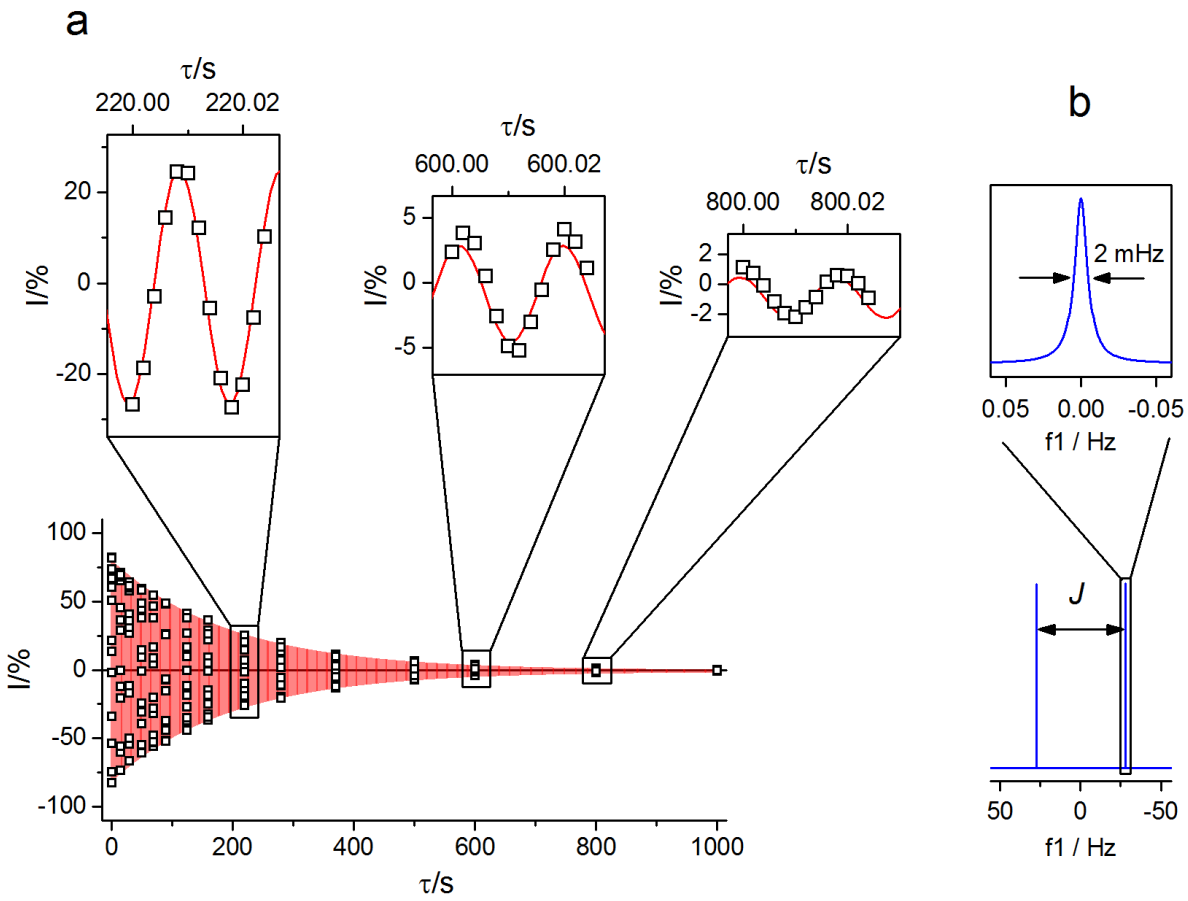




Shuttling setup for field-cycling



IST coherence in weak magnetic field



$T_{IST} = 198$ s, $T_1 = 83$ s

frequency = 54.141 Hz

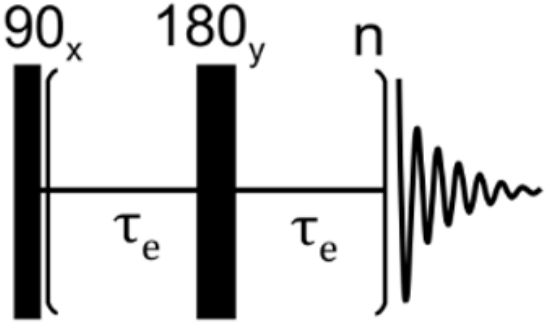
Conclusions

Remarkably long lifetime of the inner singlet-triplet coherence of about 200 s

very precise measurement of the spin-spin *J*-couplings allows extract the information about chemical environment

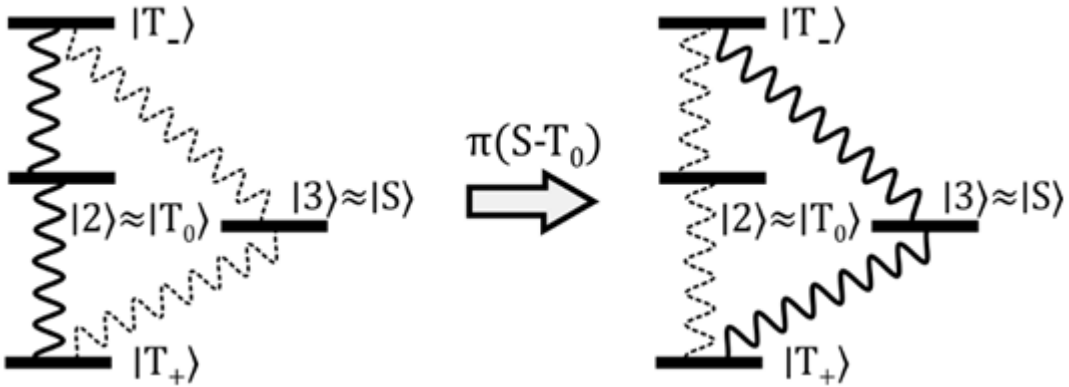
It opens the way to study molecules that are almost an order of magnitude larger than could be hitherto studied.

J-CPMG



Echo delay should be:

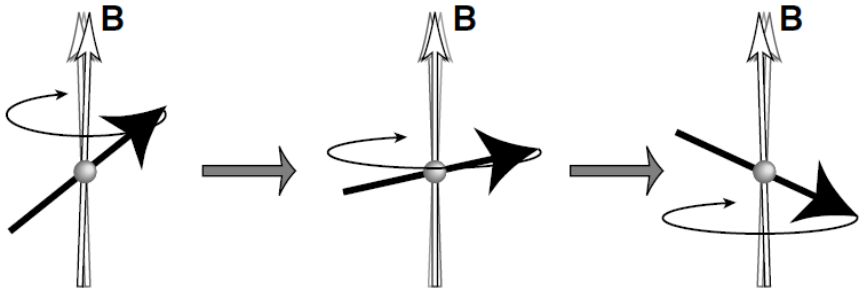
$$\tau_e = \frac{1}{4\sqrt{J^2 + \Delta^2}} \approx \frac{1}{4J}$$

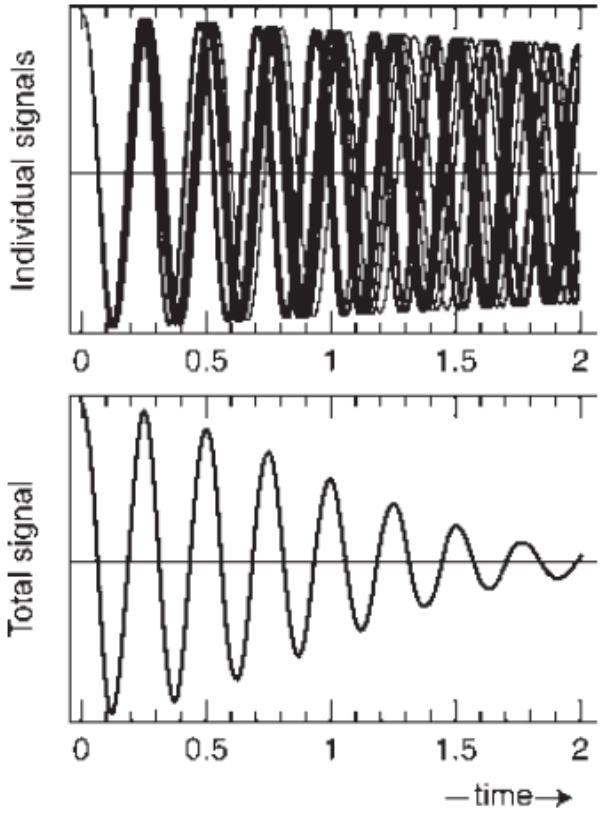


Number of echoes should be:

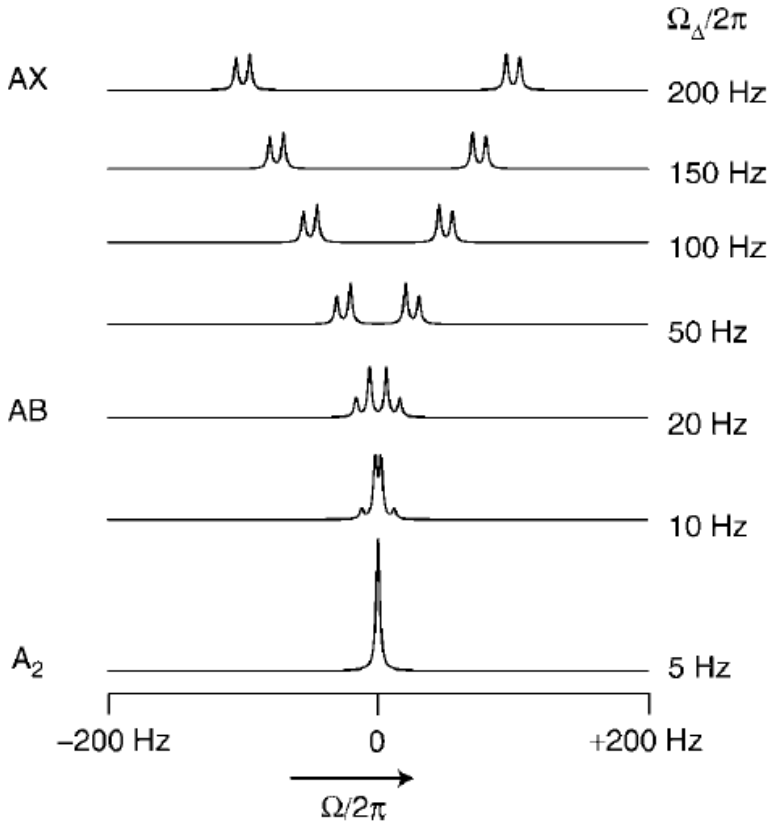
$$n = \mathrm{round}\left(\frac{\pi}{2\theta}\right)$$

Relaxation





Two strongly coupled spins



M.H. Levitt, Spin dynamics : basics of nuclear magnetic resonance-2nd ed., (2008)