Slow Diffusion by Singlet State NMR Spectroscopy

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Slow Diffusion by Singlet State NMR Spectroscopy

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ABSTRACT

Small diffusion coefficients can be measured by using populations of singlet states that have a relaxation time constant T_s that can be much longer than the longitudinal relaxation time T_1. Spatial information can be encoded with pulsed field gradients in the manner of stimulated echo sequences. Singlet states can be excited via double-quantum coherences to enhance the efficiency of phase encoding and decoding.

Diffusion Ordered NMR Spectroscopy

- DOSY -

Nuclear magnetic resonance (NMR) has long been known as a flexible tool to study transport phenomena such as diffusion, flow, convection, or electrophoretic mobility [1, 2]. Information about the localization of molecules can be encoded and decoded by pulsed field gradients (PFG) before and after a delay where translational motion can occur. A pulsed field gradient can be characterized by a product $\kappa = \gamma p s G_{max} \delta$, where γ is the gyromagnetic ratio, p the coherence order, G_{max} the peak intensity of the gradient, and δ its duration. s is a dimensionless shape factor ($0 < s \leq 1$). When the signal S is observed as a function of the gradient strength and compared to a signal S_0 obtained with very weak gradients, all other parameters remaining the same, the decay of the ratio obeys a Gaussian function:

$$S/S_0 = exp(-D\kappa^2\Delta')$$

where D is the diffusion coefficient and Δ' the effective interval between encoding and decoding by the pulsed field gradients. The analysis of such Gaussian decays allows one to determine D. The resulting 2D representation with the isotropic chemical shift along the x axis and the diffusion coefficient along the y axis is referred as “diffusion ordered NMR spectroscopy” [2].

Measurements of slow diffusion are limited by the relaxation time constants (T_1 or T_2)

Depending on the details of the pulse sequences, one must take into account attenuation factors that depend on various delays where transverse and longitudinal magnetization components suffer from T_2 or T_1 relaxation.

In the most elementary spin-echo (SE) experiments, T_2 relaxation limits the interval where diffusion can be observed to $\Delta \approx T_2$.

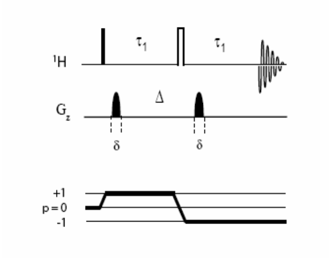


Figure 1. The simple spin echo (SE) sequence.

In stimulated echo experiments (STE), where the information is stored in the form of longitudinal magnetization, the window can be extended to $\Delta \approx T_1$, which allows one to probe slower transport processes since $T_1 \geq T_2$.

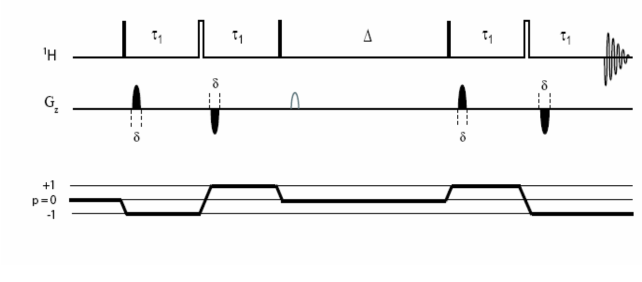


Figure 2. Standard stimulated echo sequence with bipolar pulse pairs (BPPSTE), often used for "diffusion-ordered spectroscopy" (DOSY).

Singlet States

Recently, Carravetta et al. [3, 4] have shown that nuclear spin order can be stored as *singlet states* which relax with a time constant T_s that can be an order of magnitude longer than T_1.

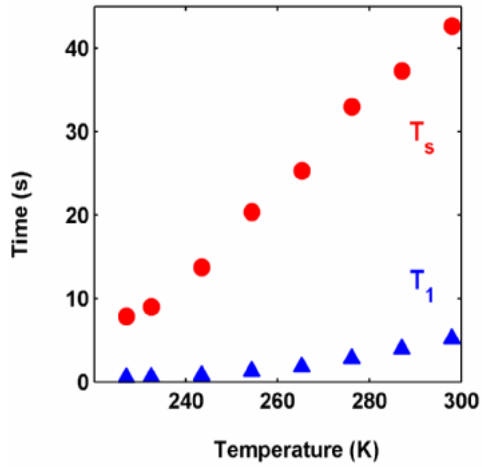
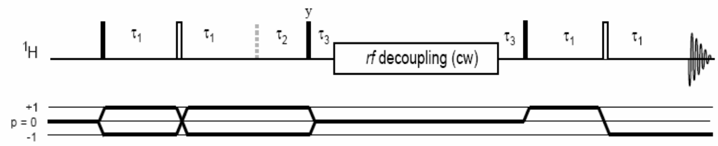
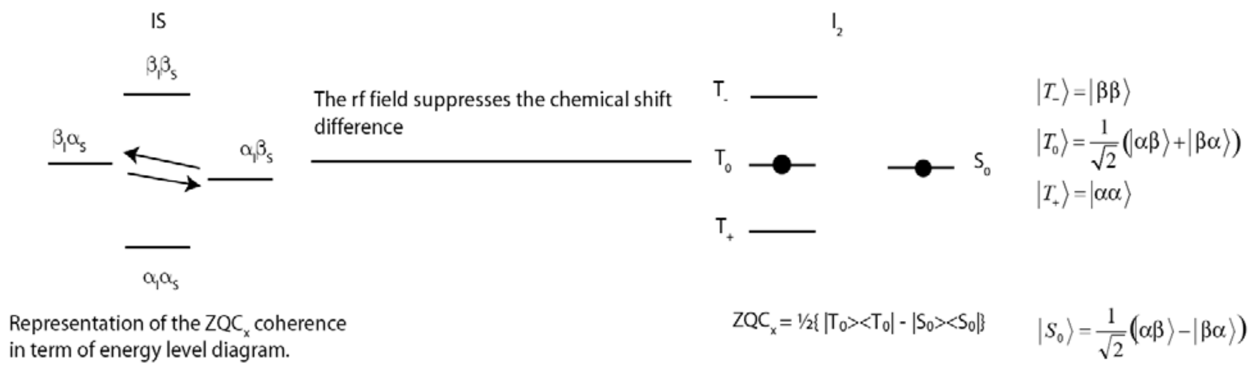


Figure 3. Method of Carravetta et al. [3] for the excitation and detection of long-lived singlet states in scalar-coupled two-spin systems with a coupling J_{IS} and chemical shifts ω_I and ω_S. The optional sandwich [τ_1 - π - τ_1] at the end allows one to convert anti-phase into in-phase magnetization. The intervals must be $\tau_1 = 1/(4J_{IS})$, $\tau_2 = \pi/|\omega_I - \omega_S|$, and $\tau_3 = \tau_2/2 = \pi/(2|\omega_I - \omega_S|)$. Filled and open rectangles represent $\pi/2$ and π pulses respectively.





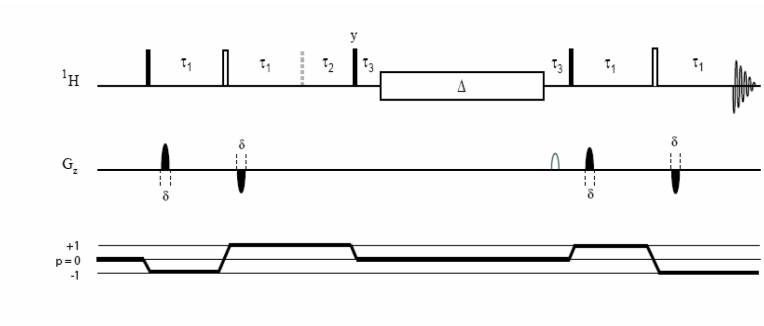
The expectation values of the operators $|T_0><T_0|$ and $|S_0><S_0|$ amount to *populations* of the central triplet and singlet states. The former have a life-time of the order of T_1, while the latter have a singlet-state life-time T_s. The long life-times of singlet states makes them attractive for the study of slow transport processes.

Singlet-state-single-quantum-DOSY

- SS-SQ-DOSY -

The key idea is shown in Figure 4, which results from a simple combination of Figures 2 and 3. A singlet state is populated at the beginning of the diffusion interval Δ in Fig. 4. The spatial information is encoded and later decoded by a bipolar pair of pulsed field gradients. The signals are attenuated in proportion to $\exp\{-D4k^2\Delta'\}\ \exp\{-\Delta/T_s\}$. Thus the main difference lies in the fact that T_1 is replaced by the much longer singlet-state relaxation time T_s.

Figure 4. "Singlet-state-single-quantum-DOSY" - The information about spatial localization is stored in the form of singlet state populations with a relaxation time T_s in the interval Δ. The intervals τ_1, τ_2 and τ_3 are defined as in sequence (a).

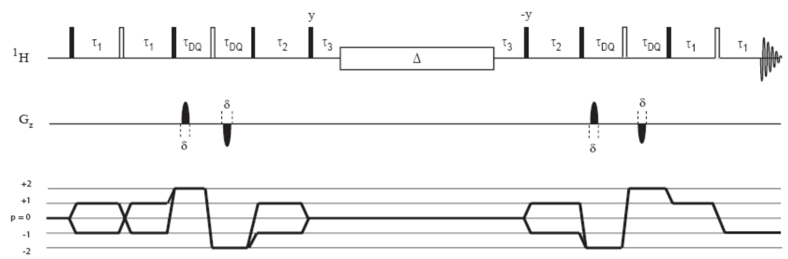


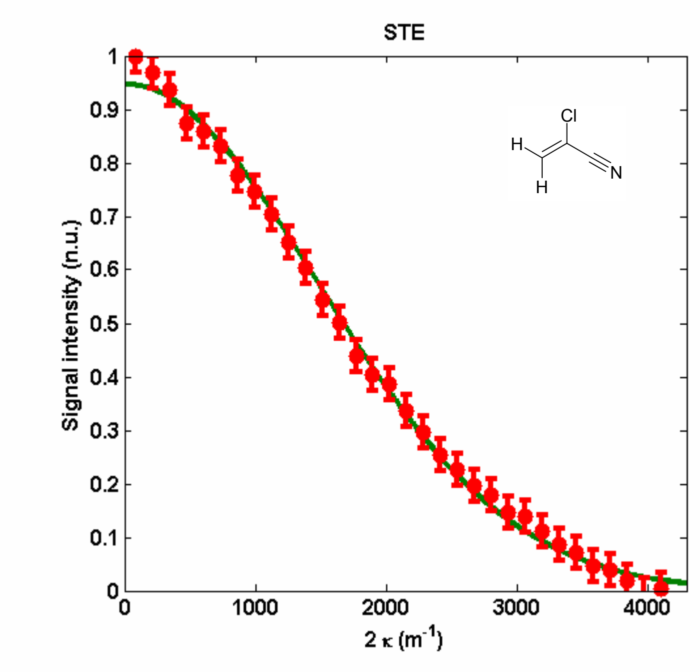
Singlet-state-double-quantum-DOSY

- SS-DQ-DOSY -

Single-quantum coherences generated at the end of the second τ_1 interval, $\sigma = 2I_xS_z + 2I_zS_x$, are temporarily converted into double-quantum coherences $\sigma = -(2I_xS_y + 2I_yS_x) = i(I_+S_+ - I_-S_-) = -2DQC_y$. The bipolar pulsed field gradients are applied to double-quantum coherences. *Thus, compared to Figure 4, it is possible to determine diffusion constants that are four times smaller*, or to obtain the same effect with field gradients that are half as strong or half as long.

Figure 5. "Singlet-state-double-quantum-DOSY" - The intervals τ_1, τ_2 and τ_3 must be like in sequence (a)





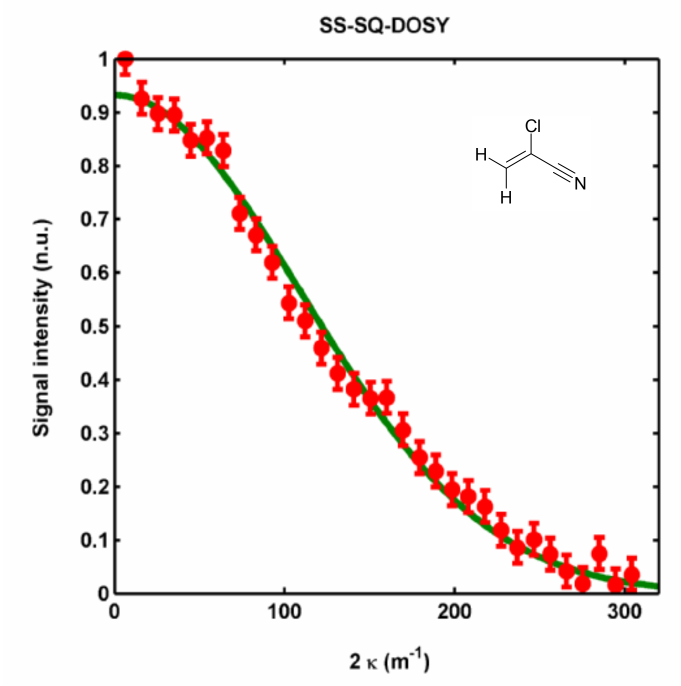


Figure 6. Gaussian decays of proton signal intensities of 10 mM 2-Chloroacrylonitrile in DMSO-D6/D_2O = 1:3, measured at 300 MHz and ***T* = -18.8 °C** (254 K) obtained with the **bipolar pulse pairs stimulated echo of Fig. 2** with **Δ' = 0.21 s, *δ* = 2 ms**. The parameter κ is defined by $\kappa = \gamma p s G_{max}\delta$. Note the scales of the horizontal axes

Figure 7. Gaussian decays of proton signal intensities of 10 mM 2-Chloroacrylonitrile in DMSO-D6/D_2O = 1:3, measured at 300 MHz and ***T* = -18.8** °C (254 K) obtained with the **singlet-state sequence of Fig. 4** with **Δ' = 19.5 s, *δ* = 155** μs. The parameter κ is defined by $\kappa = \gamma p s G_{max}\delta$. Note the scales of the horizontal axes

CONCLUSIONS

It has been shown that slow transport phenomena can be characterized by combining methods for the measurement of diffusion coefficients with the excitation and detection of singlet states. The transient excitation of double-quantum coherences allows one to use weaker gradients. In 2-Chloroacrylonitrile, the life-times T_s of the singlet states were found to be about an order of magnitude longer than the longitudinal relaxation times T_1 over a wide range of temperatures.

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