Spin-Lock Induced Crossing: J-Coupling Spectroscopy at High and Low Field

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Introduction

We demonstrate a novel method of J-coupling and chemical shift measurement for strongly-coupled spin systems.

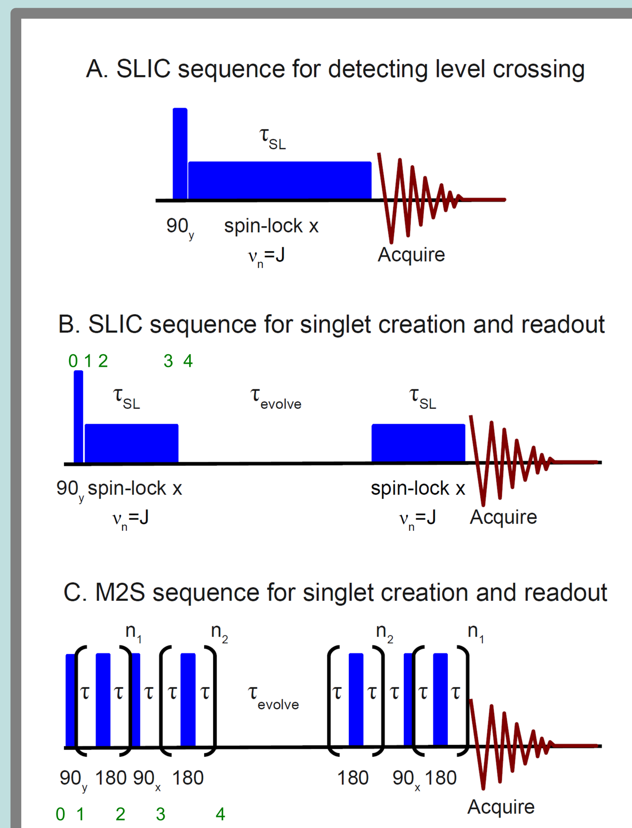
Weak spin locking is used to match the energy levels of dressed states, such as the singlet and triplet, thereby creating a "spin-lock induced crossing," or SLIC.

At the energy crossing, small chemical shift differences drive magnetization transfer between the dressed states.

We applied a SLIC sequence to pairs of nearly-equivalent spins at high field to create long-lived singlet states, and we found it to be more effective than the M2S sequence.

We also developed a SLIC sequence to measure J-coupling spectra at low magnetic field without the addition of heteronuclei.

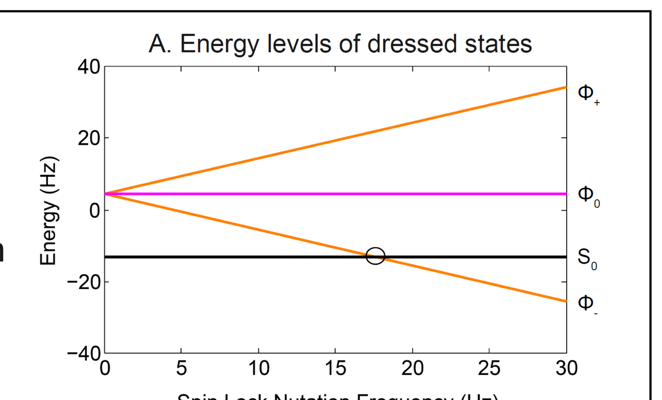
Nearly-Equivalent Spins



Two spins are "nearly-equivalent" if J >> δν.

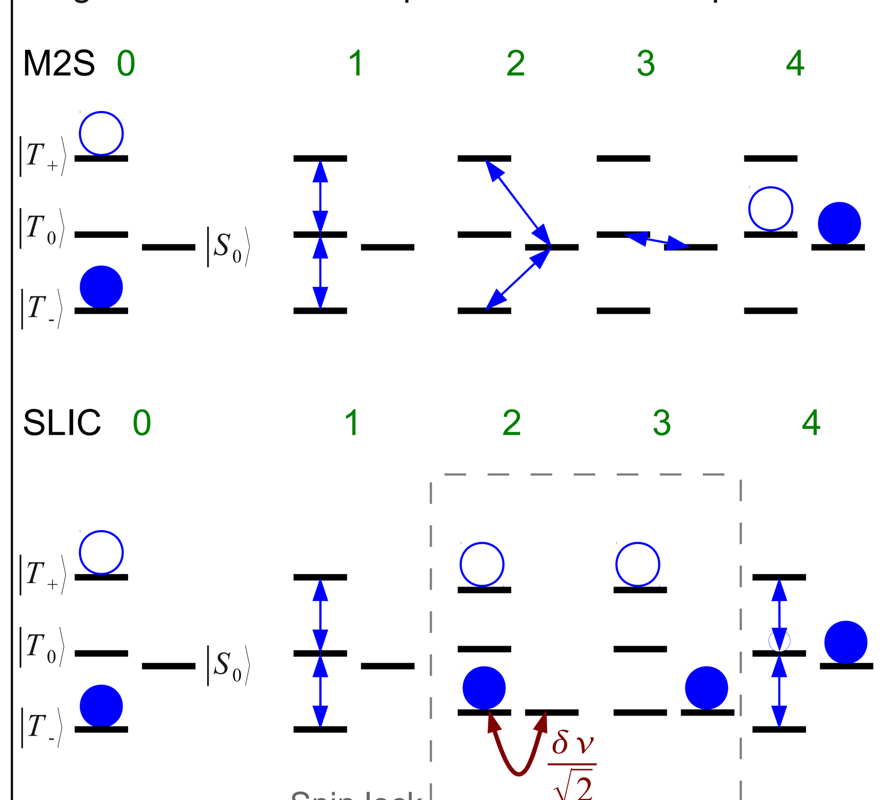
SLIC ("Spin-Lock Induced Crossing") or M2S[1] ("Magnetization to Singlet") sequences can transfer magnetization between the singlet and triplet states.

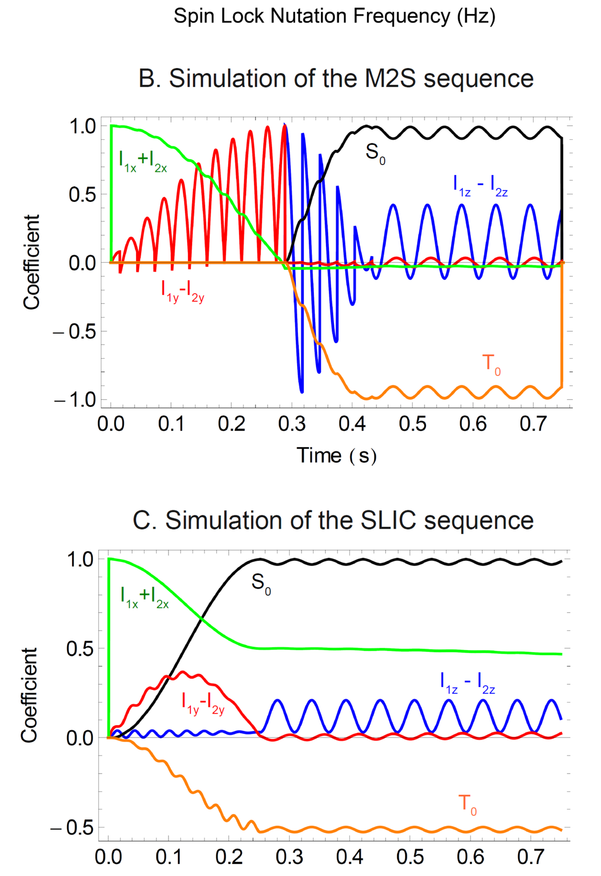
Coherence
Population
Depopulation



How the sequences work

Magnetization at the steps shown in the sequences:



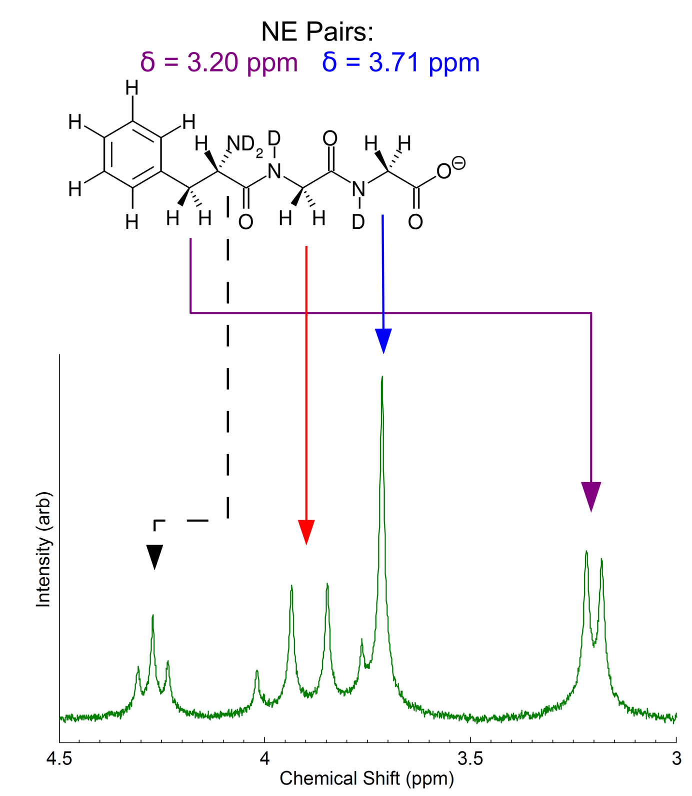


1. MCD Tayler and MH Levitt. Singlet nuclear magnetic resonance of nearly-equivalent spins. *Phys Chem Chem Phys*, 13:5556-5560, 2011.

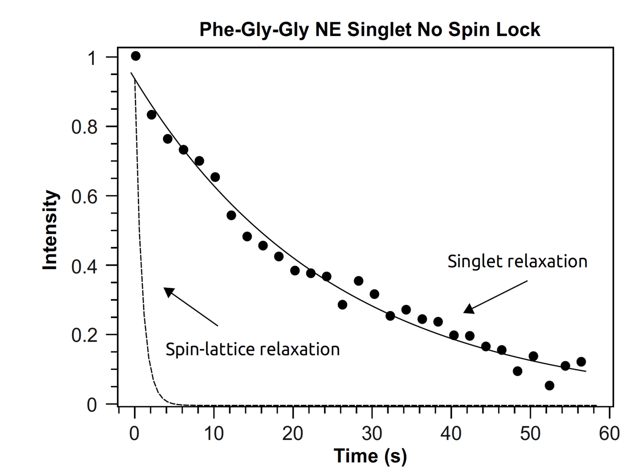
Singlets in Nearly-Equivalent Spins at 4.7 T

The tripeptide phenylalanine-glycine-glycine possesses two nearly-equivalent spin pairs. Each pair appears unresolved at 4.7 T.

For both spin pairs, SLIC can transfer magnetization to the singlet state, which has a lifetime much longer than T_1 and does not require a spin lock for preservation:



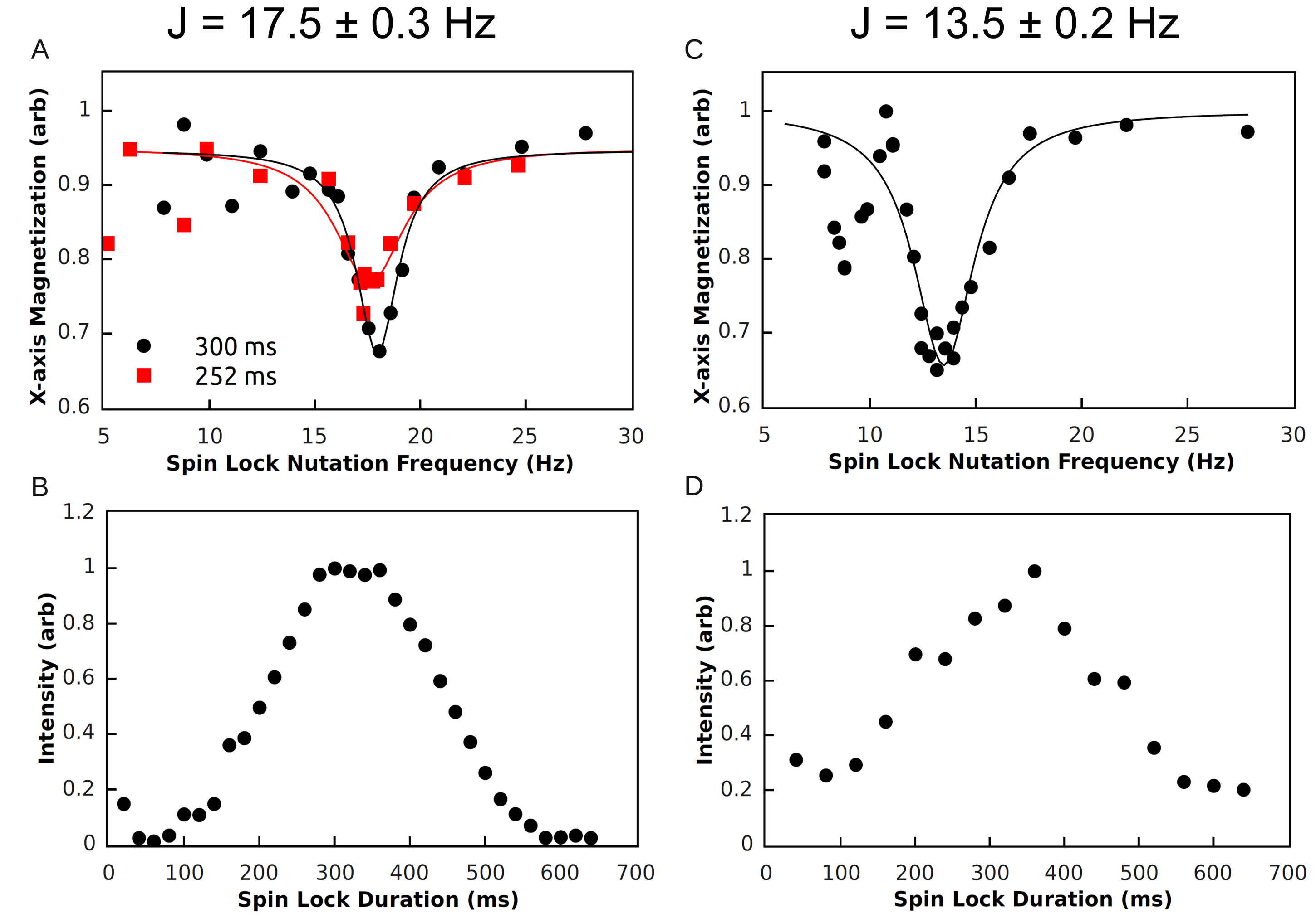
δ = 3.20 ppm: T_1 = 430 ± 5 ms
T_S = 2.15 ± 0.05 s
δ = 3.71 ppm: T_1 = 912 ± 7 ms
T_S = 25 ± 0.8 s
(shown below)



Sequence A is performed with a range of spin lock powers to find the J-coupling strength:

δ = 3.71 ppm
J = 17.5 ± 0.3 Hz

δ = 3.20 ppm
J = 13.5 ± 0.2 Hz



Sequence B is performed with a range of spin lock durations to find the chemical shift difference:

Δv = 2.22 ± 0.3 Hz   Δv = 2.10 ± 0.06 Hz

SLIC was more effective than M2S at transferring magnetization to the singlet state.

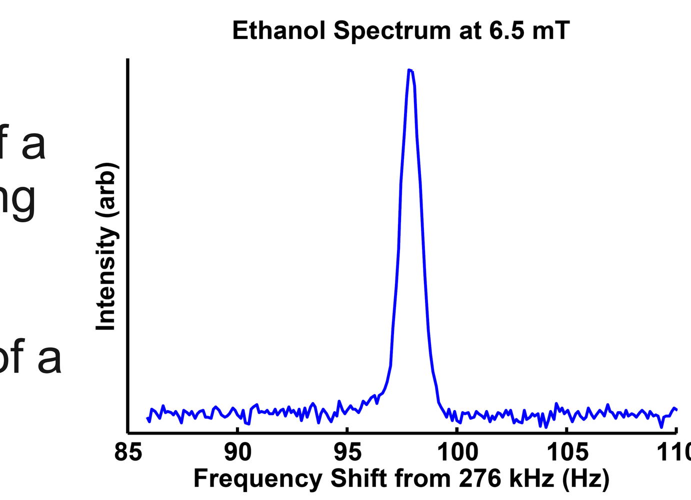
Efficiency of Triplet-Singlet Transfer		
M2S	69%	28%
SLIC	82%	49%

Spectroscopy at 6.5 mT

We obtain proton spectra at 6.5 mT (276 kHz proton frequency) using a home-built MRI system.

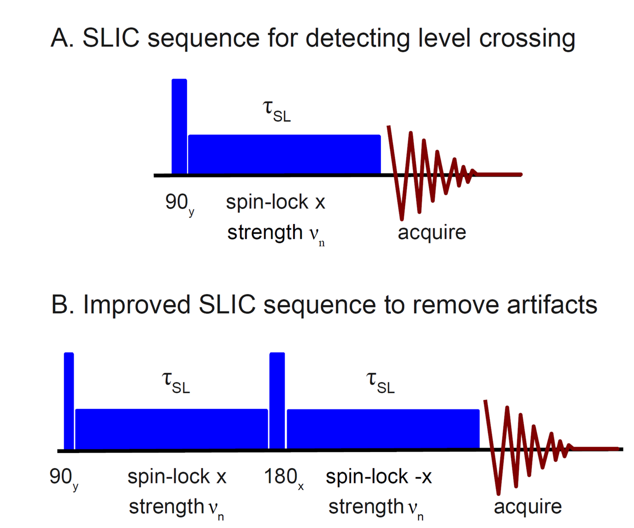
Spectroscopy at very low fields traditionally requires the addition of a heteronucleus to create a J-coupling spectrum.

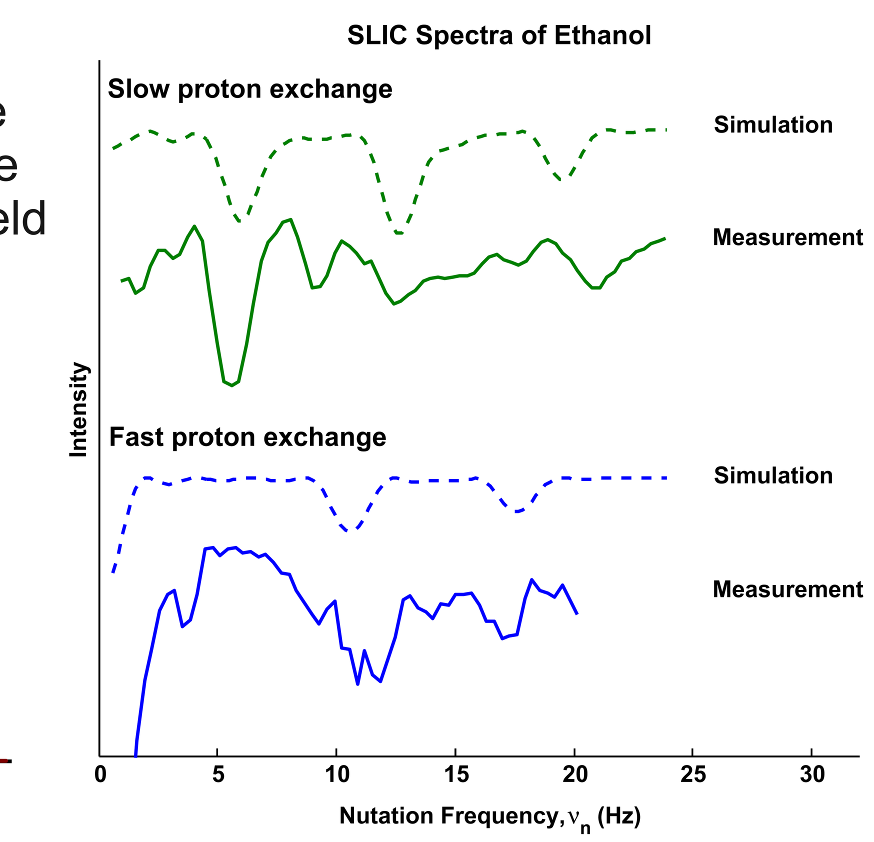
Otherwise, the spectrum consists of a singlet spectral line.

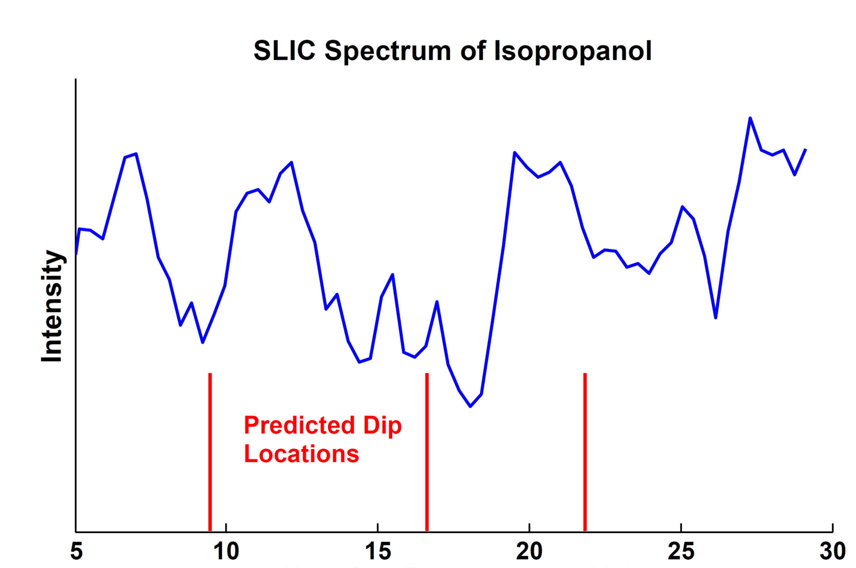


With the SLIC sequence, we can detect the magnetization transfer that occurs when spin locking produces a level crossing between dressed states.

We use a modified sequence containing an echo to remove artifacts caused by slow B-field shifts away from resonance.







For hydrated ethanol, dips occur at 3/2 J and 5/2 J.

Dehydrated ethanol has a more complex spectrum due to coupling with the -OH proton.

For hydrated isopropanol, dips occur near 3/2 J, 5/2 J, and 7/2 J.

Summary

We have shown that the SLIC technique is a versatile tool for the measurement and manipulation of strongly-coupled spin systems.

SLIC is an alternative to the M2S sequence for creating long-lived singlet states, and it can be used in low- and moderate-field instruments as a way to derive more information from poorly resolved spectra.