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UNIVERSITY OF SOUTHAMPTON

Faculty of Engineering and Physical Sciences
School of Chemistry

**Advanced Methodology for ^{103}Rh NMR
Spectroscopy**

by

Harry Harbor-Collins

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*A thesis for the degree of
Doctor of Philosophy*

June 2025

University of Southampton

Abstract

Faculty of Engineering and Physical Sciences
School of Chemistry

Doctor of Philosophy

Advanced Methodology for ^{103}Rh NMR Spectroscopy

by Harry Harbor-Collins

Despite the ubiquitous presence of rhodium complexes in catalysis, and the favourable 100% natural abundance of the spin-1/2 ^{103}Rh nucleus, ^{103}Rh NMR parameters in the literature are notably sparse. This apparent dissonance is in part a consequence of the very low gyromagnetic ratio of ^{103}Rh and hence its dismal NMR sensitivity.

In this thesis, we aim to improve the accessibility of ^{103}Rh NMR by developing advanced methodologies, which build upon existing techniques to improve ^{103}Rh NMR sensitivity whilst simultaneously mitigating experimental hurdles associated with the practice. Furthermore, we will broaden the scope of ^{103}Rh NMR by developing methodology to access and study the nascent singlet state in a ^{103}Rh spin pair.

To mitigate the poor sensitivity of the ^{103}Rh nucleus, we demonstrate ^1H enhanced ^{103}Rh NMR methodology for the rapid acquisition of ^{103}Rh NMR spectra and parameters; including ^{103}Rh relaxation time constants over a range of magnetic fields. Moreover, a scheme is described for suppressing ringing artifacts, a common hurdle in the direct observation of low gyromagnetic ratio nuclei. We employ selective ^{18}O labelling to break the magnetic equivalence of a ^{103}Rh spin pair and facilitate the estimation of the ^{103}Rh - ^{103}Rh J-coupling; as well as provide access to the ^{103}Rh singlet state. We present the first measurement of an ^{18}O induced ^{103}Rh secondary isotope shift and report the first instance of singlet order generated in a ^{103}Rh spin pair. The field dependence of both the relaxation of ^{103}Rh longitudinal and singlet spin order is measured via field cycling experiments. We evaluate the rhodium formate paddlewheel complex as a vehicle for sustaining long lived ^{103}Rh singlet order.

Through the development of polarisation transfer techniques, we stand to greatly improve the accessibility, sensitivity and scope of the NMR technique for ^{103}Rh nuclei in complexes that exhibit prerequisite heteronuclear scalar couplings.

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Declaration of Authorship

I declare that this thesis and the work presented in it is my own and has been generated by me as the result of my own original research.

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;
2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
3. Where I have consulted the published work of others, this is always clearly attributed;
4. Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
5. I have acknowledged all main sources of help;
6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
7. Parts of this work have been published as:
H. Harbor-Collins *et al.*, J. Chem. Phys. **159**, 104307 (2023) [1]
H. Harbor-Collins *et al.*, J. Chem. Phys. **160**, 014305 (2024) [2]
H. Harbor-Collins *et al.*, Magnetic Resonance **5**, 121-129 (2024) [3]

Signed:.....

Date:.....

Acknowledgments

A PhD is not a solo venture; rather it is a collaborative undertaking of which would not be possible without the support of those in not just the academic, but also personal aspects of one's life. Accordingly, I would like to take the time to express my gratitude to those that are ultimately responsible for the success of this PhD project and to whom I am extremely grateful.

Most foremost I thank my supervisor, Prof. Malcolm H. Levitt, for providing me the opportunity to do this PhD. It was Malcolm's lectures during my time as a chemistry undergraduate that had first allured me to NMR, and in the years since Malcolm has helped me attain a deep appreciation and fondness for the field. Malcolm's patience and guidance has proved instrumental in the success of this project especially during the initial stages where its viability looked less than certain. I, along with the rest of the NMR community, revere Prof. Malcolm H. Levitt as a titan of the field, as well as a most venerable academic in general. I cannot speak highly enough of Malcolm's virtues, nor thank him enough for all that he has done for me and my family.

Furthermore, I would like to thank Dr. Mohamed Sabba. Mohamed is one of the most brilliant scientists I've had the good fortune of working with, his expertise in both the theoretical and experimental aspects of NMR is truly remarkable and I am incredibly grateful to have worked alongside him in this project. Much of what I now know can be attributed to Mohamed, to his enthusiasm and to his patience in taking the time to teach me. I am honoured to have worked with Mohamed and even more so to call him a friend.

I wish to also extend my thanks to Dr. Markus Leutzsch who was crucial in not just the inception of this project but also during the work throughout.

Additionally I would like to thank all current and past members of MagRes at the University of Southampton, in particular: Dr. Soumya Singha Roy; Dr. Giuseppe Pileio; Dr. Laurynas Dagys; Dr. James Whipham; Dr. Christain Bengs; Dr. Gamal Moustafa; Dr. George Bacanu; Dr. Murari Soundararajan; Dr. Bonifac Legrady; Dr. Thomas Robertson; Urvashi Heramun; Dr. Oksana Bondar.

To my family, for your resiliency and steadfastness in your support of me and each other, I thank you. Though we are often apart (often not even all on the same continent!), I find contentment in the knowledge we are not alone. Bound by our shared values and experiences, my Mother, Gillian Claire; my Father, Paul Collins; and my siblings: Alice Harbor-Collins, Georgia Harbor-Collins, and Ben Hawke you have my unconditional support and appreciation as I likewise have yours.

To Shannon Austin and Charlie Hughes, I am grateful for your generosity and support, especially during what proved to be a challenging time; and for that I am sincerely thankful.

To my wife and best friend, Skye Harbor-Collins, for reasons I am unable to articulate using words alone, I thank you. Much has happened and changed in the decade I've known you; however you remain an unwavering source of stability and calm in my life, for which I am more grateful than you could ever know. Moreover, in giving us our son, William Harbor-Collins, you have blessed me with a purpose greater than any other I have known, as well as an even deeper appreciation for all that you do for us. I truly could not have done it without you.

And finally, to William, I thank you for giving me perspective and purpose, but most of all, I thank you for teaching me just how much I appreciate getting enough sleep!

Acronyms

AHT Average Hamiltonian Theory.

CPMG Carr-Purcell-Meiboom-Gill.

CSA Chemical Shift Anisotropy.

gM2S Generalised Magnetisation to Singlet.

HMQC Heteronuclear Multiple Quantum Coherence.

HSQC Heteronuclear Single Quantum Coherence.

INEPT Insensitive Nucleus Enhancement by Polarisation Transfer.

JA J-Anisotropy.

LLS Long-Lived State.

M2S Magnetisation to Singlet.

MAS Magic Angle Spinning.

NMR Nuclear Magnetic Resonance.

ppm parts per million.

QSEO Quasi Singlet Eigen-Order.

rf radio frequency.

SLIC Singlet Lock Induced Crossing.

SO Singlet-Order.

SR2K Scalar Relaxation of the Second Kind.

STL Singlet Triplet Leakage.

We choose to go to the moon in this decade and do the other things, not because they are easy, but because they are hard, because that goal will serve to organize and measure the best of our energies and skills, because that challenge is one that we are willing to accept, one we are unwilling to postpone, and one which we intend to win, and the others, too.

John F. Kennedy

Chapter 1

The NMR phenomenon

In the following chapter, we will explore the origin of the Nuclear Magnetic Resonance (NMR) phenomenon as well as present the necessary quantum mechanics required for its description.

1.1 Nuclear spin magnetism

Atomic nuclei are comprised of neutrons and protons, which belong to a class of particles known as fermions. Fermions are characterised by having half integer spin, which is a form of intrinsic angular momentum with an associated magnetic moment [4]. Neutrons and protons combine, adhering to nuclear structure theory, to form an atomic nucleus with a net nuclear spin (represented by the spin quantum number I) and thus, a net magnetic moment. The magnitude of a given nuclei's magnetic moment is given by the product $I\gamma$ where γ is the gyromagnetic ratio (a constant unique to the nucleus under study). In this thesis we are principally concerned with the NMR of spin-1/2 nuclei, which contain a magnetic dipole moment that can be manipulated by resonant rf pulses, of which are central to the NMR technique.

1.2 Basic NMR theory

1.2.1 Spin states

Spin configurations are described using eigenvectors, which, when acted upon by a corresponding eigenoperator, return the original eigenvector scaled by an eigenvalue. An important operator in NMR represents the z-component of the angular momentum, $\hat{I}_z$, which acts on an eigenvector $\vec{\psi}$ to return the eigenvalue m_I .

$$\hat{I}_z \vec{\psi} = m_I \vec{\psi} \quad (1.1)$$

m_I is the azimuthal quantum number and can take any value between $+I$ and $-I$ in integer steps. Therefore, for a nucleus with the spin quantum number I , there exists $2I+1$ eigenvalues for the $\hat{I}_z$ operator, each of which correspond to a unique spin state eigenvector - compactly denoted using the Dirac notation as $|I, m_I\rangle$ [5]. Individual spin states are orthonormal, that is to say:

$$\langle I, m_I' | I, m_I \rangle = \delta_{m_I' m_I} \quad (1.2)$$

For a spin-1/2 nucleus there exist 2 orthonormal spin states denoted $|1/2, +1/2\rangle$ and $|1/2, -1/2\rangle$, which represent a spin being aligned parallel and antiparallel to the z-axis respectively.

We can introduce a shorthand for the spin states of a spin-1/2 nucleus as follows:

$$|1/2, +1/2\rangle = |\alpha\rangle \text{ \& } |1/2, -1/2\rangle = |\beta\rangle \quad (1.3)$$

1.2.2 Superposition states

It is not necessary for a nuclear spin to be confined to a single spin state eigenvector. In general, state vectors are constructed as linear combinations of individual spin states, each with a particular weighting.

$$|\psi\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle = \begin{bmatrix} c_\alpha \\ c_\beta \end{bmatrix} \quad (1.4)$$

For example, where c_α and c_β are finite and non zero, equation 1.4 represents a single spin-1/2 system in a superposition state. The spin is neither aligned purely with or against the z-axis but rather is a mixture of both orientations. Upon measurement (by applying the $\hat{I}_z$ spin operator) the superposition collapses and the spin assumes either the $|\alpha\rangle$ or $|\beta\rangle$ state. The probability of assuming either state is given by the square modulus of the respective state's coefficient.

1.2.3 Composite systems

State vectors corresponding to individual nuclear spins can be formally combined into a single composite system by taking the direct (Kronecker) product between states.

For example, we can combine a spin prepared in the spin up alpha state with another spin prepared in the spin down beta state.

$$|\alpha\rangle \otimes |\beta\rangle = |\alpha\beta\rangle \quad (1.5)$$

Or in vector form:

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \quad (1.6)$$

It is this procedure we use to generate a state vector for a pair of spins-1/2.

1.2.4 Zeeman splitting

In the absence of a magnetic field, spin states are degenerate in energy. However, on exposure to an applied magnetic field, they are split in an interaction referred to as Zeeman splitting.

The classical energy of the interaction between a magnetic dipole and an applied magnetic field is given by the equation:

$$E = -\vec{\mu}^\dagger \cdot \vec{B} = -\begin{bmatrix} \mu_x & \mu_y & \mu_z \end{bmatrix} \cdot \begin{bmatrix} B_x \\ B_y \\ B_z \end{bmatrix} \quad (1.7)$$

Where $\vec{\mu}$ is the magnetic dipole vector and $\vec{B}$ is the magnetic field vector.

Substitution of $\vec{\mu}$ with its quantum mechanical analogue, the spin vector: $\vec{\mu} \rightarrow \gamma\hbar\vec{I}$ gives us the Zeeman interaction Hamiltonian (an interaction Hamiltonian is an operator that returns the energy of a given quantum mechanical interaction):

$$\hat{H}^Z = -\gamma\hbar \vec{I} \cdot \vec{B} \quad (1.8)$$

The external magnetic field is typically defined as being aligned with the z-axis. Therefore, equation 1.8 reduces to:

$$\hat{H}^Z = -\gamma\hbar \hat{I}_z \cdot B_0 = \omega_0\hbar I_z \quad (1.9)$$

where $\omega_0 = -\gamma B_0$ is the Larmor frequency, and $\hbar$ is the reduced Planck constant.

In the case of a single spin-1/2 with a positive gyromagnetic ratio, the Zeeman interaction splits its two accessible spin states such that the $|\alpha\rangle$ state, which is aligned parallel with the field, is lowered in energy; whereas the $|\beta\rangle$ state, which is aligned antiparallel, is raised in energy. The energy difference between states is proportional to the Larmor frequency.

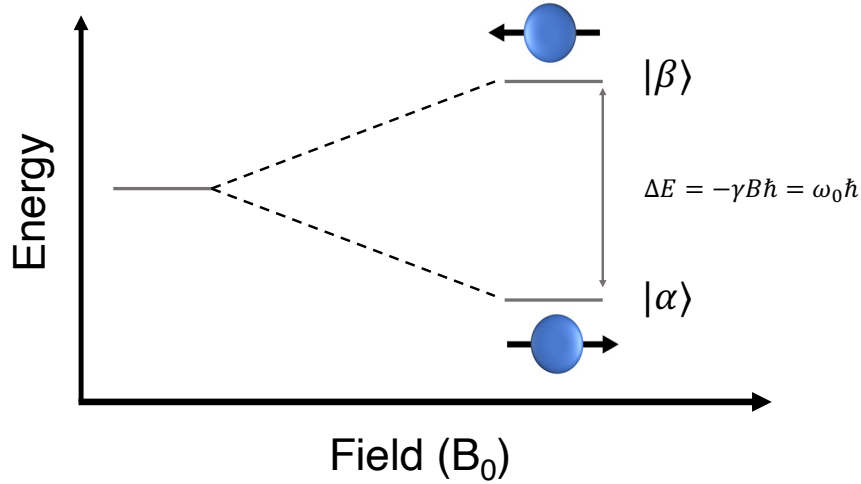


FIGURE 1.1: Splitting of single spin-1/2 spin states upon Zeeman interaction with a static field. In this figure, the field is aligned along the horizontal axis.

1.2.5 State vector evolution in time

A state vector evolves in time according to the time dependent Schrödinger equation, which is given by the equation below:

$$\frac{d}{dt}\vec{\psi}(t) = -i\hbar\hat{H}(t)\vec{\psi}(t) \quad (1.10)$$

Where $\hat{H}(t)$ is the nuclear spin Hamiltonian operator, which corresponds to the total energy of a given nuclear spin system and is constructed from the sum of all spin interactions present. In general, the spin Hamiltonian is time dependent. Equation 1.10 can be solved to yield:

$$\vec{\psi}(t) = \hat{T} \exp \{ -i\hat{H}(t)\tau \} \vec{\psi}(0) = \hat{U}(t,0)\vec{\psi}(0) \quad (1.11)$$

where $\hat{T}$ is the time ordering operator and $\hat{U}(t,0)$ is the *propagator* during τ where τ is the time difference between $\vec{\psi}(0)$ and $\vec{\psi}(t)$.

For the case of an isolated spin-1/2 in a static magnetic field, the only interaction present is the Zeeman interaction, which is time independent; thus, so too is the Hamiltonian, which simply reduces to equation 1.9. In this instance, we can solve equation 1.11 to yield (while setting $\hbar = 1$):

$$\vec{\psi}(t) = c_1 \exp \left\{ -i \frac{\omega_0}{2} \tau \right\} |\alpha\rangle + c_2 \exp \left\{ i \frac{\omega_0}{2} \tau \right\} |\beta\rangle \quad (1.12)$$

We see that in the presence of the static field, the individual spin states acquire a phase that oscillates in time.

We can evaluate how the observable properties of this single spin-1/2 system evolve in time by taking the expectation value of the corresponding observable operators with $\vec{\psi}(t)$. For instance, taking the expectation value of either transverse angular momentum spin operators ($\hat{I}_x/\hat{I}_y$) shows that transverse spin polarisation precesses in the transverse plane at the Larmor frequency. Whereas the expectation value of the $\hat{I}_z$ spin operator is time independent and simply proportional to the relative weightings of the $|\alpha\rangle$ and $|\beta\rangle$ spin states.

$$\begin{aligned} \langle \hat{I}_x \rangle(t) &= \langle \psi(t) | \hat{I}_x | \psi(t) \rangle = \frac{1}{2} c_\alpha^* c_\beta \exp \{ -i \omega_0 \tau \} + \frac{1}{2} c_\beta^* c_\alpha \exp \{ -i \omega_0 \tau \} \\ \langle \hat{I}_y \rangle(t) &= \langle \psi(t) | \hat{I}_y | \psi(t) \rangle = -\frac{1}{2} c_\alpha^* c_\beta i \exp \{ -i \omega_0 \tau \} + \frac{1}{2} c_\beta^* c_\alpha i \exp \{ -i \omega_0 \tau \} \\ \langle \hat{I}_z \rangle &= \langle \psi(t) | \hat{I}_z | \psi(t) \rangle = \frac{1}{2} (c_\alpha^* c_\alpha - c_\beta^* c_\beta) \end{aligned} \quad (1.13)$$

1.2.6 The density operator

In reality, spins do not exist in isolation but instead are surrounded by an abundance of other like nuclei. Therefore, we require a framework for describing entire spin ensembles. For this purpose, we introduce the spin density operator $\hat{\rho}$ [6]:

$$\hat{\rho} = \frac{1}{N} \sum_n^N |\psi_n\rangle \langle \psi_n| = \overline{|\psi\rangle \langle \psi|} \quad (1.14)$$

Where the index n denotes a given spin and N represents the total number of spins in an ensemble.

The density operator is formed as an ensemble average such that the macroscopic expectation value for a given observable is given by:

$$\langle \hat{O} \rangle = \text{Tr}(\hat{\rho} \hat{O}) \quad (1.15)$$

1.2.7 Time evolution of the density operator

The density operator evolves in time, whilst making the usual substitution $\hbar = 1$, according to the Liouville-von Neumann equation:

$$\frac{d}{dt}\hat{\rho}(t) = -i\hat{H}(t)\hat{\rho}(t) \quad (1.16)$$

Where $\hat{H}(t)$ represents the time dependent Hamiltonian commutation super-operator (a super operator is an operator that acts upon another operator). Such that the action of $\hat{H}(t)$ upon an arbitrary density operator, $\hat{\rho}$, yields the commutation of operators $\hat{H}(t)$ and $\hat{\rho}$,

$$\hat{H}(t)\hat{\rho} = \hat{H}(t)\hat{\rho} - \hat{\rho}\hat{H}(t) \quad (1.17)$$

The time evolution of the expectation value is simply:

$$\langle \hat{O}(t) \rangle = \text{Tr}(\hat{\rho}(t)\hat{O}) \quad (1.18)$$

1.2.8 Thermal equilibrium

For an ensemble of spins at thermal equilibrium at temperature T , the populations of individual spin states is dictated by the Boltzmann distribution,

$$P_i = \frac{\exp\{-\hbar E_i/k_b T\}}{\sum_j^N \exp\{-\hbar E_j/k_b T\}} \quad (1.19)$$

where P_i is the probability of a given spin populating the i th spin state, E_i is the energy of the i th spin state, k_b is the Boltzmann constant and the equation quotient is the partition function (a sum over all accessible spin states).

The Boltzmann distribution tells us that low energy spin states are preferentially populated over the high energy spin states.

For an ensemble of spins with positive gyromagnetic ratio interacting only with a static field, the energies of the individual spin states are determined by the Zeeman interaction and equation 1.19 reduces to,

$$P_i = \frac{\exp \{ -\hbar\omega_0 m_z^i / k_b T \}}{\sum_j^N \exp \{ -\hbar\omega_0 m_z^j / k_b T \}} \quad (1.20)$$

Spin states aligned parallel with the field are lowered in energy; therefore the Boltzmann distribution dictates that they'll be preferentially populated relative to the spin states that have their angular momenta aligned antiparallel to the field.

The unequal population of spin states means that, at thermal equilibrium, there exists a net spin-polarisation along the axis of the static field.

1.2.9 Manipulation of spin polarisation

By itself, spin polarisation along the axis of the static field is rather uninteresting. Fortunately through the application of coherent radiofrequency (rf) fields we are able to manipulate polarisation into various forms of detectable spin-order.

An rf pulse takes the form of an oscillating B_1 magnetic field applied at an angle to the applied B_0 field. An on resonance B_1 oscillates at the nuclear Larmor frequency (ω_0) of the spin under study such that, in the rotating frame, the rf field appears static to the precessing spin.

Nuclear spins precess anticlockwise about the rf field such that spin polarisation is brought out of alignment with the B_0 field and rotated towards the transverse plane. The exact flip angle is dependent on the duration of the pulse:

$$\beta = \gamma B_1 \tau = \omega \tau \quad (1.21)$$

Here β is the flip angle of the pulse, B_1 is the magnitude of the rf field, γ is the nuclear gyromagnetic ratio and τ is the pulse duration. The product of B_1 and γ yields the spin nutation frequency of the rf field (ω).

By modulating the phase, ϕ , of a pulse, one can control the orientation of the B_1 field and thus the axis spins are rotated about.

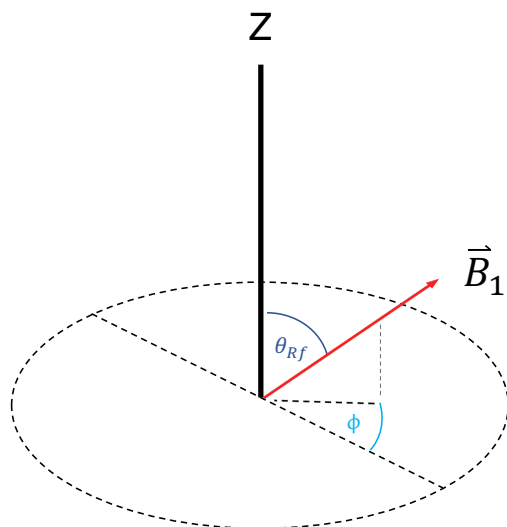


FIGURE 1.2: Resonant rf B_1 field applied at an angle θ_{Rf} to the axis of the external B_0 field (Z) with the phase ϕ . The B_1 field is expressed in the rotating frame, which rotates at the frequency of the B_1 field; hence B_1 is time independent in this frame.

Of particular interest to NMR are rf pulses applied perpendicular to the B_0 field with a flip angle of 90° and 180° respectively. These have the effect of rotating polarisation into the transverse plane and inverting it respectively.

1.2.10 Signal detection

Spin polarisation along the axis of the static field is difficult to detect. Instead, we opt to acquire signals from polarisation orientated in the transverse plane; where detection is far easier.

Equation 1.13 describes how spin polarisation rotated into the transverse plane precesses at the nuclear Larmor frequency. The precessional motion of spin angular momentum induces a current in a nearby receiver coil. These currents are in turn digitised and processed to produce signals in the resulting NMR spectrum.

1.2.11 Anatomy of an NMR experiment

With knowledge of how spin polarisation is manipulated and ultimately detected, we may now provide a general description of how the typical NMR experiment is performed.

The basic anatomy of an NMR experiment can be dissected into three major components.

1. *Preparation*: The preparation component involves allowing the spin system under study to reach its initial state. The initial state must be known and reproducible; hence, almost always corresponds to thermal equilibrium longitudinal polarisation along the axis of the static field.
2. *Excitation*: In the excitation component, spin polarisation is manipulated via a series of applied rf pulses to generate a desired mode of nuclear spin order. We collectively refer to this series of pulses as being the *pulse sequence* of an NMR experiment.
3. *Detection*: During detection, spin polarisation is brought into the transverse plane, wherein its precessional motion is detected by the receiver coil and processed to generate signals in the resulting NMR spectrum.



FIGURE 1.3: The basic anatomy of an NMR experiment.

1.2.12 Signal intensity

The intensity of the acquired NMR signal is proportional to the total spin magnetisation, which for an ensemble of homonuclear single spin-1/2 nuclei is given by [7],

$$M = \frac{\gamma \hbar N P}{2} \quad (1.22)$$

where N is the total number of spins and P is the spin polarisation as given by,

$$P = \frac{N_\alpha - N_\beta}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \quad (1.23)$$

where N_α and N_β represent the number of spins in states α and β , respectively. At thermal equilibrium, the relative populations of states is dictated by the Boltzmann Distribution (section 1.2.8); hence,

$$P = \tanh \left(\frac{\gamma \hbar B_0}{2 K_b T} \right) \quad (1.24)$$

Unfortunately, under typical NMR conditions, the thermal equilibrium spin polarisation is always very small. For example, ^1H spin polarisation at 298 K and in a static field of 10 T is only 0.003%, and for nuclei with smaller gyromagnetic ratios, the polarisation is even worse.

Accordingly, for typical NMR conditions, we can make the approximation $\hbar\omega_0/2k_bT \ll 1$ as well as use equations 1.22 and 1.24 to derive the following relation for the sample magnetisation:

$$M \propto \gamma^2 B_0 \quad (1.25)$$

Because we can only detect the net difference in spin state populations and net nuclear spin polarisation is typically very minimal, net spin magnetisation, and hence NMR signals, are intrinsically very weak.

1.2.13 NMR sensitivity and the gyromagnetic ratio

Although signals are inherently weak, spectroscopic sensitivity may still be high if the noise levels are low.

The general NMR signal to noise ratio ($\frac{S}{N}$) can be approximated, in the absence of relaxation, as depending on the equation [7, 8, 9, 10]:

$$\left(\frac{S}{N}\right) \sim \gamma_{src} \gamma_{obs}^{\frac{3}{2}} B_0^{\frac{3}{2}} \quad (1.26)$$

Where γ_{src} is the gyromagnetic ratio of the nucleus in which polarisation is sourced; while γ_{obs} is the gyromagnetic ratio of the nucleus that ultimately induces a signal in the receiver. B_0 is simply the applied magnetic field. In standard homonuclear experiments, the source and observed nucleus are one and the same; therefore, equation 1.26 reduces to just $\left(\frac{S}{N}\right) \sim \gamma^{\frac{5}{2}} B_0^{\frac{3}{2}}$. However, the distinction between source and observed nucleus becomes relevant in the case of heteronuclear polarisation transfer experiments as discussed later in section 1.6.

Equation 1.26 makes use of the approximation $\hbar\omega_0/2k_bT \ll 1$; as well as the linear dependence of the voltage induced in the receiver on $\gamma_{obs} B_0$. Furthermore, the noise is approximated as having the following dependence: $N = (\gamma_{obs} B_0)^{\frac{1}{2}}$.

We see that sensitivity is worse for experiments involving nuclei with small gyromagnetic ratios; particularly when the observed nucleus has a small gyromagnetic ratio.

1.3 Internal nuclear spin interactions

The interactions between nuclear spin angular momenta and the externally applied magnetic fields discussed thus far, although fundamental to the NMR technique, tell us nothing of the various internal spin interactions originating from the sample itself.

Crucially, it is these internal spin interactions that give NMR its venerable spectroscopic power, for they are responsible for structure of the NMR spectrum; as well as for the phenomenon of spin relaxation.

1.3.1 General form of interaction Hamiltonians

For the description of NMR experiments we need only be concerned with the spin Hamiltonian and not the full molecular Hamiltonian.

The total internal spin Hamiltonian can be written as a sum of individual Hamiltonians, each describing a specific interaction Λ .

$$\hat{H}_{Int}(t) = \sum_{\Lambda}^N \hat{H}^{\Lambda}(t) \quad (1.27)$$

Spin interactions can be categorised into two primary types, coherent and incoherent. Coherent interactions are experienced identically by all members of a spin ensemble, whereas incoherent interactions differ instantaneously for different ensemble members. Thus, we may write the internal spin Hamiltonian as the sum of a coherent and incoherent components denoted $\hat{H}_0^{int}$ and $\hat{H}_1^{int}(t)$ respectively:

$$\hat{H}_{Int}(t) = \sum_{\Lambda}^N \hat{H}^{\Lambda}(t) = \hat{H}_0^{int} + \hat{H}_1^{int}(t) \quad (1.28)$$

It is the coherent component determines the structure of the NMR spectrum; whereas the incoherent component induces spin relaxation.

The Hamiltonian for a given spin interaction can be expressed as follows [11, 12]:

$$\hat{H}^{\Lambda}(t) = c^{\Lambda} \vec{I} \cdot A^{\Lambda}(t) \cdot \vec{X}_{\Lambda} \quad (1.29)$$

Where c^{Λ} is the coefficient unique to Λ , $\vec{I}$ is a spin vector, $A^{\Lambda}(t)$ is a spatial tensor for interaction Λ , which is time dependent in the laboratory frame (see below) and $\vec{X}_{\Lambda}$ is interaction dependent vector, which depending on the interaction may be the same vector as I , another spin vector, a field vector or an angular momentum vector.

The laboratory frame is typically defined as having the z-axis aligned with the static magnetic field, which is static. Whereas molecules in solution are constantly tumbling, which modulates their internal molecular axes relative to the static field; thus giving the spatial part of an interaction its time dependence when expressed in the laboratory frame.

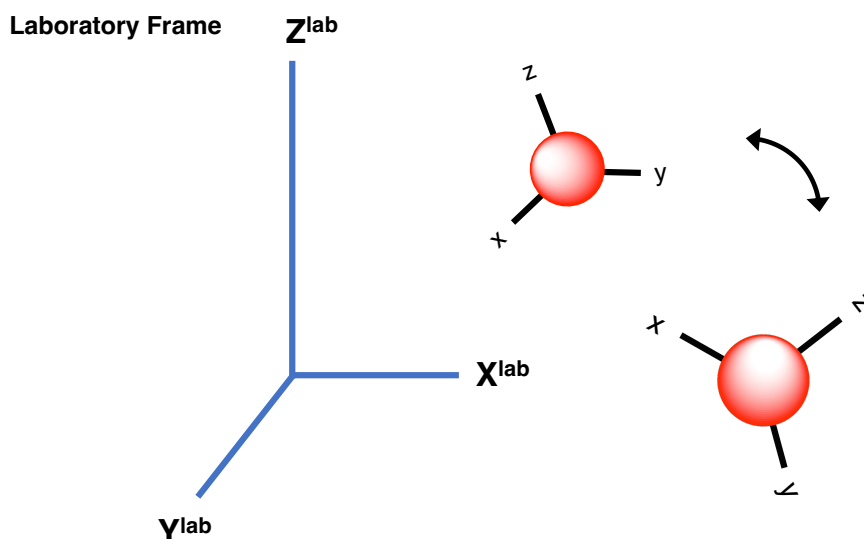


FIGURE 1.4: Internal molecular axes are time dependant relative to the static laboratory frame due to molecular tumbling.

When tensors are expressed as spherical tensors, we can transform between reference frames (e.g principle to laboratory) via Wigner matrices [12].

1.3.2 Chemical shift

The chemical shift is an indirect interaction between the static magnetic field and nuclear spins as mediated by the involvement of electrons.

A brief summary for the mechanism of the chemical shift interaction is given as follows: In the presence of a static field, the motion of the electron cloud surrounding a nuclear site generates a local magnetic field that interacts with the nuclear spin. The local field may either augment or oppose the static field such that the effective field at the site of the nuclear spin is slightly shifted.

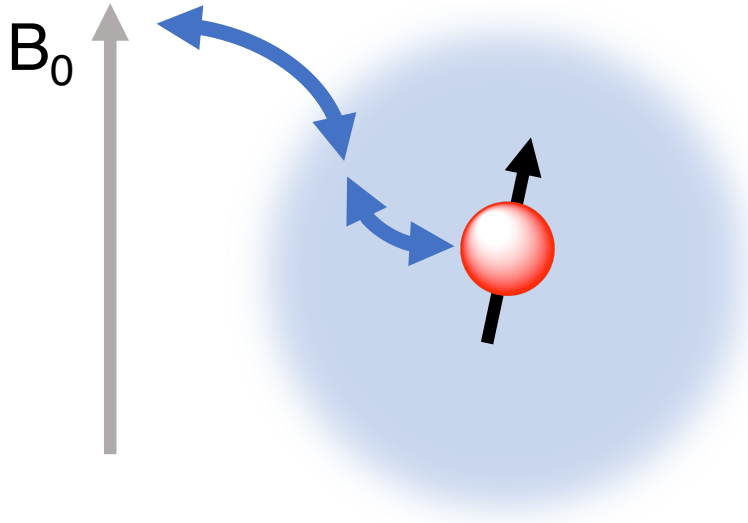


FIGURE 1.5: The chemical shift interaction. Electron density is depicted by blue cloud.

The corresponding interaction Hamiltonian is given by [12]:

$$\hat{H}^{\text{CS}} = \sum_i^N \gamma_i \vec{I}_i \cdot \boldsymbol{\sigma} \cdot \vec{B}_0 \quad (1.30)$$

Where $\vec{B}_0$ is the static field vector and $\boldsymbol{\sigma}$ is the nuclear chemical shift tensor, which reflects the local chemical environment at a given nuclear site.

The chemical shift tensor takes the form of a 3x3 matrix:

$$\boldsymbol{\delta} = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix} \quad (1.31)$$

which can be decomposed into a rank-0 isotropic component, rank-1 traceless antisymmetric component and a rank-2 traceless symmetric component [13, 14]:

$$\boldsymbol{\delta} = \boldsymbol{\delta}^{\text{iso}} + \boldsymbol{\delta}^- + \boldsymbol{\delta}^+ \quad (1.32)$$

The coherent rank-0 isotropic component is time independent and defines the positions of chemically shifted peaks in the NMR spectrum.

Conversely, the incoherent antisymmetric rank-1 and symmetric rank-2 traceless components contribute to relaxation.

1.3.3 Dipolar coupling

Dipolar couplings represent direct magnetic interactions between spins through space.

The mechanism of the dipolar coupling interaction is easy to conceptualise. Consider two spin-1/2s separated in space by the vector: $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. Each spin has an associated magnetic moment, which interacts at the site of the other spin. The interaction is mutual, that is to say the first spin also experiences the field generated by the second spin.

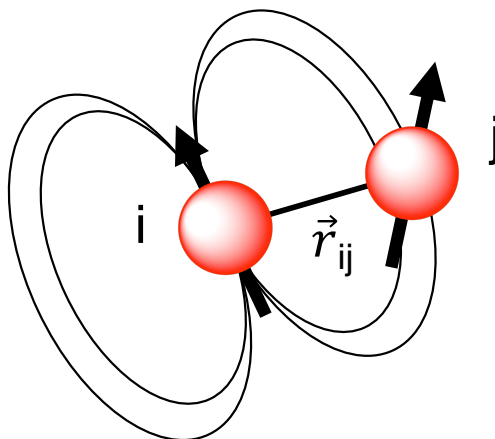


FIGURE 1.6: Magnetic field at spin j as generated by spin i

The corresponding Hamiltonian for the dipolar interaction between two spins is given as follows:

$$\hat{H}^{DD} = b_{ij} \left(\frac{3(\vec{I}_i \cdot \vec{r}_{ij})(\vec{I}_j \cdot \vec{r}_{ij})}{r_{ij}^2} - \vec{I}_i \cdot \vec{I}_j \right) \quad (1.33)$$

where r_{ij} is the distance between spins i and j and b_{ij} is the dipolar coupling constant, which is a measure of the dipolar interaction strength and is given by:

$$b_{ij} = -\frac{\mu_0 \gamma_i \gamma_j}{4\pi r_{ij}^3} \quad (1.34)$$

where μ_0 is the permittivity of free space.

We may also write equation 1.33 in a way that conforms with the general interaction Hamiltonian expression shown in equation 1.29 as follows:

$$\hat{H}^{DD} = b_{ij} \vec{I}_i \cdot \mathbf{D}^{ij} \cdot \vec{I}_j \quad (1.35)$$

where $\mathbf{D}^{ij}$ is the dipolar coupling tensor, wherein its elements are given by [15]:

$$\mathbf{D}_{\mu\nu}^{ij} = \delta_{\mu\nu} - 3e_\mu(i)e_\nu(j) \quad (1.36)$$

where $\delta_{\mu\nu}$ is the Kronecker product and e_μ and e_ν are components along coordinates μ and ν respectively.

Decomposition of $\mathbf{D}^{ij}$ in the same way as done for the chemical shift reveals that the isotropic component is equal to zero [15] i.e the isotropic dipolar coupling interaction between spins is averaged out during molecular tumbling; so is absent from the NMR spectrum. Similarly the rank-1 component is also absent. Only the rank-2 traceless symmetric component remains, and which contributes to relaxation.

1.3.4 Spin-spin coupling

The spin-spin coupling (J-coupling) is an indirect coupling between spins as mediated by bonding electrons.

A brief description of the spin-spin coupling mechanism in the case of two spin-1/2 nuclei connected by a single bonding orbital containing two electrons is given as follows: The hyperfine interaction between the first nuclear and electron spin alters the energy of the second bonding electron, which in turn has an effect on the hyperfine interaction energy between the second electron and nuclear spin.

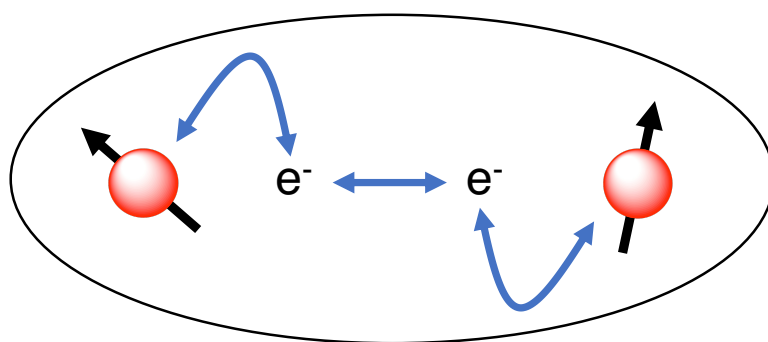


FIGURE 1.7: The spin-spin coupling interaction as mediated by bonding electrons within a bonding orbital.

The interaction Hamiltonian for the spin-spin coupling between two spin-1/2s is given by [12]:

$$\hat{H}^J = 2\pi \vec{I}_i \cdot \mathbf{J} \cdot \vec{I}_j \quad (1.37)$$

Where $\vec{I}_i$ and $\vec{I}_j$ are the individual spin vectors and $\mathbf{J}$ is the J-coupling tensor.

Upon the usual decomposition of the tensor $\mathbf{J}$, we unveil a coherent isotropic rank-0 component, which provides spin-spin couplings in the NMR spectrum; as well as the incoherent antisymmetric rank-1 and symmetric rank-2 traceless components, which can conceivably contribute to relaxation.

1.3.5 Spin-rotation

The spin-rotation interaction occurs between the nuclear spin and magnetic fields generated by the rotational motion of molecules.

The mechanism of the interaction is outlined as follows: molecules consist of positively charged nuclei and negatively charged electrons. Upon molecular rotation i.e during molecular tumbling, the charges circulate, which forms electric currents. These currents have associated magnetic fields that can interact with nuclear spins.

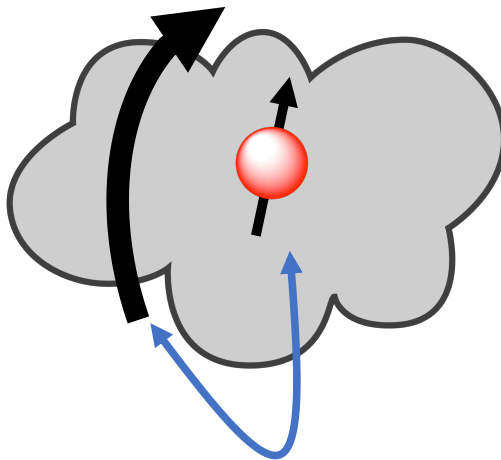


FIGURE 1.8: The spin-rotation interaction. Direction of molecular rotation indicated by curved black arrow.

The interaction Hamiltonian for the spin-rotation interaction is given by:

$$\hat{H}^{SR} = \sum_i^N \vec{I}_i \cdot \mathbf{C}^i \cdot \vec{L} \quad (1.38)$$

where $\mathbf{C}^i$ is the spin-rotation tensor for spin i and $\vec{L}$ is the molecular angular momentum vector.

The spin-rotation interaction is incoherent and contributes to spin relaxation, especially in small molecules and gasses [14].

1.3.6 Random field interaction

The random field interaction accounts for any additional randomly fluctuating fields experienced at the site of a nuclear spin.

The corresponding interaction Hamiltonian between a spin and random fluctuating field is given by:

$$\hat{H}^{RDM}(t) = \sum_i^N \gamma_i \vec{I}_i \cdot \vec{B}_i^{RDM}(t) \quad (1.39)$$

Predictably, the random field interaction is incoherent and contributes to spin relaxation.

1.4 Total spin Hamiltonian

We may now write the total spin Hamiltonian as a sum of all external and internal spin interactions:

$$\hat{H}_{total}(t) = \hat{H}^Z + \hat{H}^{CS} + \hat{H}^J + \hat{H}^{CSA}(t) + \hat{H}^{JA}(t) + \hat{H}^{DD}(t) + \hat{H}^{SR}(t) + \hat{H}^{RDM}(t) \quad (1.40)$$

where $\hat{H}^{CSA}(t)$ represents the Chemical Shift Anisotropy (CSA) interaction arising from the rank-1 antisymmetric and rank-2 symmetric incoherent components of the chemical shift tensor, $\hat{H}^{CSA}(t) = \hat{H}^{CSA(-)}(t) + \hat{H}^{CSA(+)}(t)$. Likewise, $\hat{H}^{JA}(t)$ represents the J-Anisotropy (JA) interaction arising from the rank-1 antisymmetric and rank-2 symmetric incoherent components of the spin-spin coupling tensor, $\hat{H}^{JA}(t) = \hat{H}^{JA(-)}(t) + \hat{H}^{JA(+)}(t)$.

Collecting together the coherent interactions yields (whilst setting $\hbar = 1$):

$$\begin{aligned} \hat{H}_0 &= \hat{H}^Z + \hat{H}^{CS} + \hat{H}^J \\ &= \sum_i^N \omega_{0i} (1 - \delta^{iso}) \hat{I}_{zi} + 2\pi \sum_i^N \sum_{j>i}^N J_{ij} \vec{I}_i \cdot \vec{I}_j \end{aligned} \quad (1.41)$$

where J_{ij} is the isotropic J-coupling constant between spins i and j .

The remaining interactions constitute the total incoherent Hamiltonian:

$$\hat{H}_1(t) = \hat{H}^{CSA}(t) + \hat{H}^{JA}(t) + \hat{H}^{DD}(t) + \hat{H}^{SR}(t) + \hat{H}^{RDM}(t) \quad (1.42)$$

1.5 Spin relaxation

For spin-1/2 nuclei, NMR relaxation is induced by local fluctuating magnetic fields at the nuclear sites, which is caused by the thermal motion of molecules [16, 17].

Relaxation is an incoherent process, hence is caused by the incoherent spin interactions outlined in equation 1.42.

Relaxation is driven in the direction of the equilibrium state, which, for a given spin ensemble, is dictated by the Boltzmann distribution and usually corresponds to net spin polarisation along the axis of the static field.

1.5.1 Phenomenological relaxation

The phenomenological decay of longitudinal and transverse components of spin polarisation can be modelled by the solutions to the Bloch equations, which, in the rotating frame, are as follows:

$$\begin{aligned}\langle \hat{I}_x \rangle(t) &= I_x(0) \exp \{-t/T_2\} \\ \langle \hat{I}_y \rangle(t) &= I_y(0) \exp \{-t/T_2\} \\ \langle \hat{I}_z \rangle(t) &= I_z^{eq} + (I_z(0) - I_z^{eq}) \exp \{-t/T_1\}\end{aligned}\tag{1.43}$$

Where $\langle \hat{I}_x(t) \rangle$, $\langle \hat{I}_y(t) \rangle$ and $\langle \hat{I}_z(t) \rangle$ are the respective time dependent expectation values of the Cartesian spin density operators representing spin polarisation along each axis and I_z^{eq} is the equilibrium longitudinal polarisation.

Transverse components of spin polarisation decay exponentially and with the time constant T_2 . Usually, at equilibrium there is no transverse magnetisation; thus, in the limit $t \rightarrow \infty$, $\langle I_x \rangle(t)$ and $\langle I_y \rangle(t)$ decay to 0.

Conversely, at equilibrium, spins are polarised along the static B_0 field such that, in the limit $t \rightarrow \infty$, there exists net longitudinal magnetisation proportional to I_z^{eq} . The difference in longitudinal polarisation at $t = 0$ and at equilibrium decays with the time constant T_1 .

1.5.2 Relaxation superoperator and relaxation rates

How does one take the different incoherent spin interactions and from them derive the different relaxation rate expressions for given modes of spin order? Such a question is non trivial to answer and indeed the intricate field of NMR relaxation theory is beyond the scope of this work. That said, I wish to in this section briefly cover the core concepts of Redfield relaxation theory [18], for it is this theory that is used ultimately in the derivation of the relaxation rate expressions provided later on in this thesis.

Redfield theory proceeds in Liouville space from and is concerned with the equation of motion master equation:

$$\frac{d}{dt}\hat{\rho}(t) = \mathcal{L}(t)\hat{\rho}(t) \quad (1.44)$$

where $\mathcal{L}(t)$ is the Liouvillian and which is given by:

$$\mathcal{L}(t) = -i\hat{H}_0 + \hat{\Gamma} \quad (1.45)$$

where $\hat{H}_0$ contains the coherent spin interactions whereas Γ contains all the incoherent interactions i.e. the ones that drive relaxation.

The relaxation rates of Liouvillian eigenstates are hence obtained through diagonalisation of $\mathcal{L}(t)$. The primary goal of Redfield theory is therefore to derive the Liouvillian, or more specifically the relaxation superoperator, $\hat{\Gamma}$.

Starting with the spin Hamiltonian $\hat{H}(t) = \hat{H}_0 + \hat{H}_1(t)$, Redfield theory estimates $\hat{\Gamma}$ through the application second order perturbation theory to $\hat{H}_1(t)$ as expressed in the interaction frame of $\hat{H}_0$ and under the following assumptions:

1. Stochastic fluctuations: spin-system-lattice interactions are stochastic so have no memory and a zero time average.
2. Stationary processes: absolute time values are irrelevant, only durations (τ) are considered.
3. Smooth dependence of the density matrix $\hat{\rho}$ on time: $\hat{\rho}$ evolves slowly such that $\hat{\rho}(0) \simeq \hat{\rho}(t)$.
4. Integration can use limits up to infinity.

Following this procedure, one attains the following form for $\hat{\Gamma}$:

$$\hat{\Gamma} = \int_0^\infty \overline{\mathcal{L}(t)\mathcal{L}(t+\tau)\tilde{\rho}(t)}d\tau \quad (1.46)$$

where the $\tilde{\rho}(t)$ is the density operator as expressed in the interaction frame of $\hat{H}_0$.

For a more rigorous derivation of $\hat{\Gamma}$ the reader is directed to either Redfield's original article [18] or Pileio's article on singlet relaxation theory [11], which is more relevant for the derivation of the singlet relaxation expressions presented later in this thesis.

1.5.3 T_1 and T_2 relaxometry

In NMR it is often advantageous to measure the T_1 and T_2 relaxation time constants, for they can convey valuable information regarding the different interactions that may be occurring in a given spin system.

To measure a relaxation time constant, one must employ an experimental procedure that both excites and tracks the decay of the relevant form of spin order.

Let us now consider briefly some of the different experimental procedures commonly employed for the measurement of the T_1 and T_2 relaxation time constants.

1.5.3.1 T_1

The inversion-recovery pulse sequence shown in figure 1.9(a) is often used to measure the T_1 relaxation time constant.

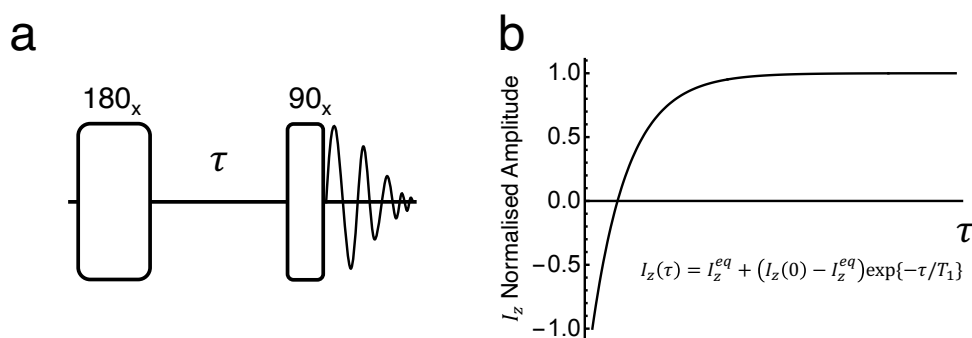


FIGURE 1.9: (a) Standard inversion-recovery pulse sequence for the measurement of T_1 . (b) Trajectory of longitudinal polarisation as a function of delay interval τ . Trajectory follows the solution to the Bloch equation for longitudinal polarisation.

Longitudinal spin polarisation is inverted and then allowed to recover to its equilibrium value during the subsequent delay interval, τ . Recovered longitudinal polarisation is then converted into transverse polarisation for detection by a 90° pulse. The sequence is repeated with variation of the delay τ to follow the recovery of longitudinal polarisation.

The trajectory of longitudinal polarisation as a function of τ (shown in figure 1.9(b)) is then fitted to the solution of the Bloch equation for the trajectory of longitudinal polarisation to extract the T_1 relaxation time constant.

For inversion-recovery experiments, it is good practice to wait $5 \times T_1$ before repeating the sequence; to allow longitudinal polarisation to fully recover (this represents the *preparation* component of the pulse sequence). This can be problematic in instances

where the spin under study has a large T_1 ; because the experiment can become inordinately time consuming.

The saturation-recovery experiment outlined in figure 1.10(a) does not require *any* waiting interval between sequence repetitions; hence, is more practical for longitudinal relaxation measurements in spin systems with large T_1 values.

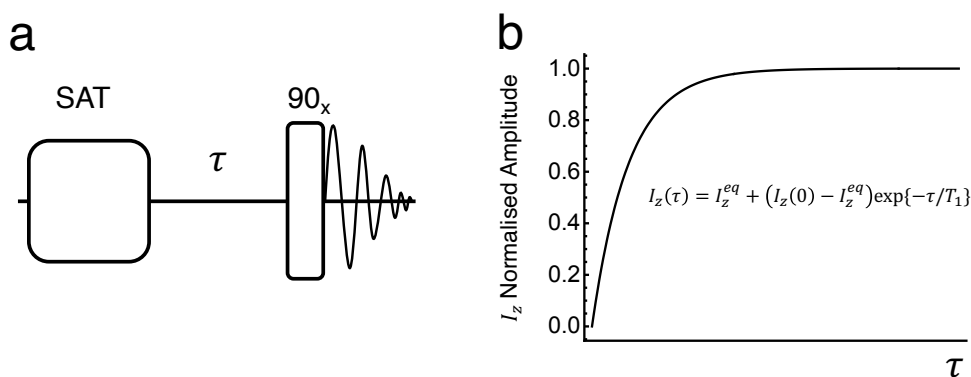


FIGURE 1.10: (a) Standard saturation-recovery pulse sequence for the measurement of T_1 . (b) Trajectory of longitudinal polarisation as a function of delay interval τ . Trajectory follows the solution to the Bloch equation for longitudinal polarisation.

The saturation-recovery experiment works as follows: An initial saturation block (usually in the form of continuous rf irradiation) equalises spin state populations - effectively destroying the net longitudinal polarisation. Longitudinal polarisation is then allowed to recover during the delay interval, τ . Recovered longitudinal polarisation is then converted into transverse polarisation for detection by a 90° pulse. The sequence is repeated with variation of the delay τ to follow the recovery of longitudinal polarisation.

The trajectory of longitudinal polarisation as a function of τ (shown in figure 1.10(b)) is again fitted to the solution of the Bloch equation for the trajectory of longitudinal polarisation to extract the T_1 relaxation time constant.

Because the saturation-recovery experiment begins with the destruction of net longitudinal polarisation, the user is not required to wait for the complete recovery of longitudinal polarisation between sequence repetitions; hence, this experimental procedure is potentially much faster than the inversion-recovery experiment.

1.5.3.2 T_2

Given that we detect transverse polarisation, one may assume that we could measure the T_2 relaxation rate constant by simply rotating spin polarisation into the transverse

plane and measuring the signal amplitude as a function of time. Unfortunately, under real world conditions, there exists a degree of magnetic inhomogeneity across the sample; hence a given spin's exact Larmor frequency differs depending on its position within the sample. Spins with different Larmor frequencies precess at different rates. Therefore, transverse spin polarisation becomes dephased as the differentially precessing individual spin vectors spread out over time, and which results in the loss of net transverse polarisation. Accordingly, to measure the T_2 time constant, we require an experimental procedure capable of reversing or preventing the dephasing of transverse polarisation.

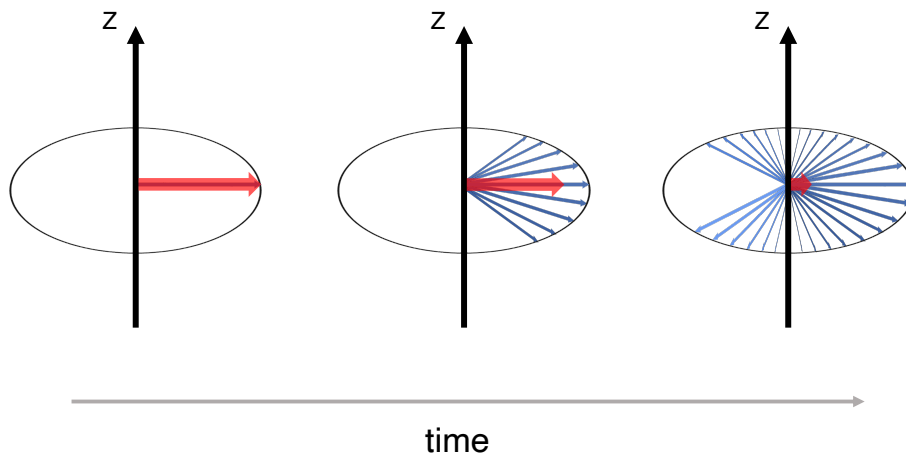


FIGURE 1.11: Dephasing of transverse polarisation with time caused by differentially precessing spins. Dephasing results in loss of net transverse polarisation. Individual spin vectors denoted by blue arrows. Net spin polarisation denoted by transparent red block arrow.

The CPMG (Carr-Purcell-Meiboom-Gill) echo experiment [19], shown in figure 1.12(a), is routinely used for the measurement of the T_2 relaxation time constant.

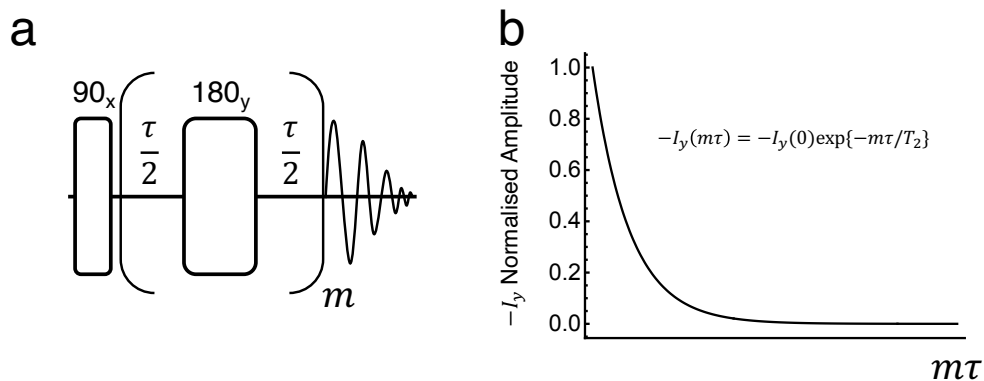


FIGURE 1.12: (a) CPMG pulse sequence for the measurement of T_2 . (b) Trajectory of transverse polarisation as a function of number of Hahn spin-echo loops with the total duration, $m\tau$. Trajectory follows the solution to the Bloch equation for transverse polarisation.

In this experiment, longitudinal polarisation is converted into transverse polarisation by a 90° pulse. Transverse polarisation is then allowed to decay during the CPMG block [19, 20], which consists of m Hahn spin-echoes of the form, $\tau/2 - 180^\circ - \tau/2$ and fixed duration, τ [21]. Remaining transverse polarisation is then detected. The sequence is repeated with variation of m to follow the decay of transverse polarisation.

The Hahn spin-echo refocusses the dephasing of transverse polarisation; whereas the CPMG modification of chaining multiple echoes together in a train suppresses additional dephasing as caused by random translational spin diffusion in an inhomogeneous field [19, 20] (provided the Hahn spin-echo duration, τ , is sufficiently small). The CPMG chain of spin echoes also compensates against confounding effects of mixing with antiphase spin operators; as caused by scalar couplings to additional nuclei [22].

Consequently, the CPMG experimental procedure outlined in figure 1.12(a), under ideal conditions, allows one to follow the decay of transverse polarisation as caused *solely* by T_2 relaxation processes.

The trajectory of transverse polarisation as a function of $m\tau$ (shown in figure 1.12(b)) is then fitted to the solution of the Bloch equation for the trajectory of transverse polarisation to extract the T_2 relaxation time constant. Note that, for the experiment outlined in figure 1.12(a), it is specifically the trajectory of transverse $-I_y$ polarisation that is being observed.

1.6 Heteronuclear polarisation transfer

As aforementioned in section 1.2.13, nuclei with small values of γ suffer from poor NMR sensitivity.

Sensitivity can be improved by increasing the net spin polarisation, for example by increasing the applied field strength and/or by reducing the temperature. Alternatively, we can exploit scalar couplings to transfer polarisation between a relative insensitive and sensitive nucleus in a heteronuclear spin system.

1.6.1 Heteronuclear spin systems

A heteronuclear spin system is formed from two or more types of interacting NMR active nuclei.

For instance, let us consider the case of an interacting heteronuclear spin-1/2 pair in a liquid. The coherent spin Hamiltonian for this spin system may be written as:

$$\hat{H}_0 = \omega_{0I}(1 - \delta_I^{iso})I_z + \omega_{0S}(1 - \delta_S^{iso})S_z + 2\pi J_{IS} \vec{I} \cdot \vec{S} \quad (1.47)$$

where I denotes the more sensitive nuclear spin and S denotes the less sensitive spin.

We see that the Hamiltonian in equation 1.48 is formed from the I -spin chemically shifted Larmor frequency, the S -spin chemically shifted Larmor frequency and the $I \leftrightarrow S$ spin-spin coupling.

The I and S spins are said to be weakly coupled when the condition: $|\omega_{0I} - \omega_{0S}| \gg \pi J_{IS}$, is satisfied [16]. And where this condition is satisfied, the coherent heteronuclear Hamiltonian can be *secularised* to yield:

$$\hat{H}_0 = \omega_{0I}(1 - \delta_I^{iso})I_z + \omega_{0S}(1 - \delta_S^{iso})S_z + 2\pi J_{IS} I_z \cdot S_z \quad (1.48)$$

The secularisation here is based on the following principle: The I and S spins precess at significantly different frequencies; and so the differences in the transverse polarisation interactions between spins average out to zero. Hence, only the longitudinal polarisation components of the $I \leftrightarrow S$ spin-spin interaction remains [16].

1.6.1.1 Alphabet notation

For the work presented in this thesis, it will become necessary to use the *alphabet notation* [16] to describe certain spin systems. In this notation, spins with significantly different chemically shifted Larmor frequencies are denoted by letters with a large separation in the alphabet, i.e AX . In these systems, if the different nuclei are scalar coupled, the coupling will be weak; hence we may use the secularised form of the spin-spin coupling interaction. Conversely, spins with similar chemically shifted Larmor frequencies are denoted by letters with a small separation in the alphabet, i.e AB . Moreover, any couplings between similar nuclei will be strong; so are best described using the *non*-secularised form of the spin-spin coupling interaction.

The subscript of a given letter represents the number of magnetically equivalent spins there are of a given type. For instance, the spin system A_3X contains three identical A spins and one X spin, of which has a significantly different chemically shifted Larmor frequency relative to the A spins.

1.6.2 Polarisation transfer methodologies

For the following discussion on the different polarisation transfer methodologies, relative sensitivities are given in the context of a weakly coupled heteronuclear spin pair i.e a spin system with a Hamiltonian of the form shown in equation 1.48.

Moreover, we assume that polarisation transfer is idealised, i.e achieves maximum conversion and occurs in the absence of relaxation.

1.6.2.1 Direct detection

The signal to noise ratio ($\frac{S}{N}$) for the unaided direct detection of an insensitive nucleus at thermal equilibrium is given by (whilst setting $B_0 = 1$): $(\frac{S}{N}) = \gamma_S^{5/2}$, where γ_S is the gyromagnetic ratio of the insensitive nucleus. In this example, the insensitive nucleus is both the polarisation source and observed nucleus.

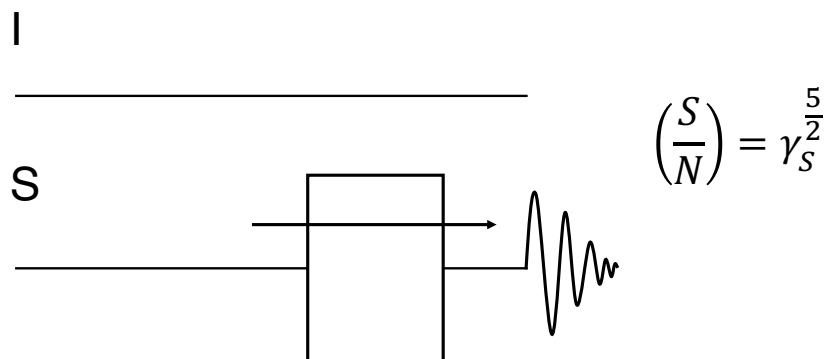


FIGURE 1.13: Unaided 1D direct detection of thermal S -spin polarisation.

Upon transferring polarisation from a more sensitive nucleus via the use of pulse sequences such as *Insensitive Nuclear Enhancement by Polarisation Transfer* (INEPT) [23], we see that the signal to noise ratio is now given by: $(\frac{S}{N}) = \gamma_I \gamma_S^{3/2}$, where γ_I is the gyromagnetic ratio of the more sensitive nucleus. In this example, I acts as the polarisation source nucleus and S is the nucleus being observed and which corresponds to a sensitivity enhancement factor of γ_I/γ_S over thermal polarisation.

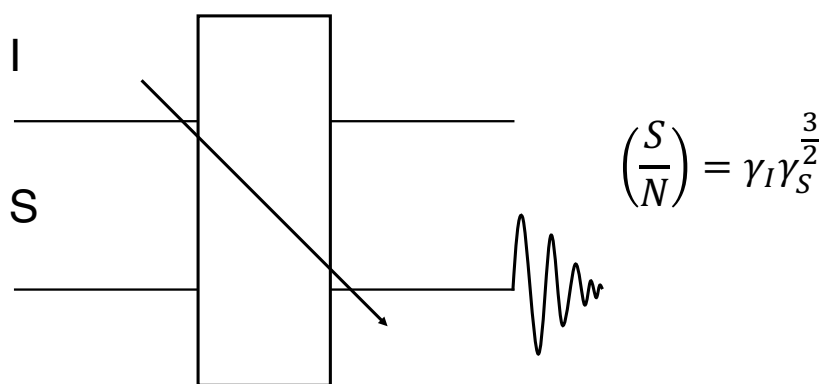


FIGURE 1.14: 1D direct detection of S -spin polarisation as enhanced by polarisation transfer from the I -spin.

1.6.2.2 Indirect detection

To improve sensitivity even further, one may opt to observe resonances indirectly; on the more sensitive heteronucleus.

This is achieved simply by transferring polarisation in reverse i.e from the S spin to I spin. In doing so, the signal to noise ratio of the detected signal becomes: $\left(\frac{S}{N}\right) = \gamma_I^{3/2} \gamma_S$. In this example, S acts as the source nucleus; whereas I is the nucleus being observed (this is the reverse of the previous example). Such a transfer corresponds to a sensitivity enhancement factor of $\gamma_I^{3/2} / \gamma_S$ over thermal polarisation.

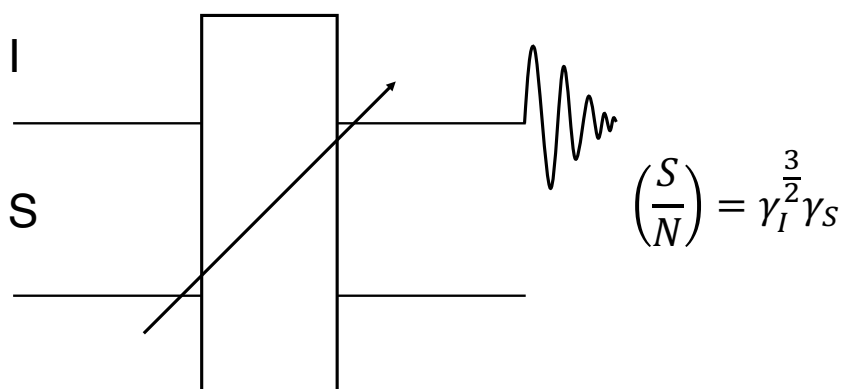


FIGURE 1.15: 1D indirect detection of S -spin polarisation detected on I spin as enhanced by polarisation transfer from the S -spin.

Ultimately, to achieve the maximum sensitivity enhancement, one can perform a *double* transfer, i.e a $I \rightarrow S$ polarisation transfer followed by the reverse $S \rightarrow I$ transfer. For this scheme, both the nucleus in which polarisation is sourced and the nucleus being observed is the more sensitive nucleus I ; ergo, the signal to noise ratio of the detected signal is solely dependent on γ_I , and is given by: $\left(\frac{S}{N}\right) = \gamma_I^{5/2}$, which corresponds to a sensitivity enhancement factor of $\gamma_I^{5/2} / \gamma_S$ over thermal polarisation.

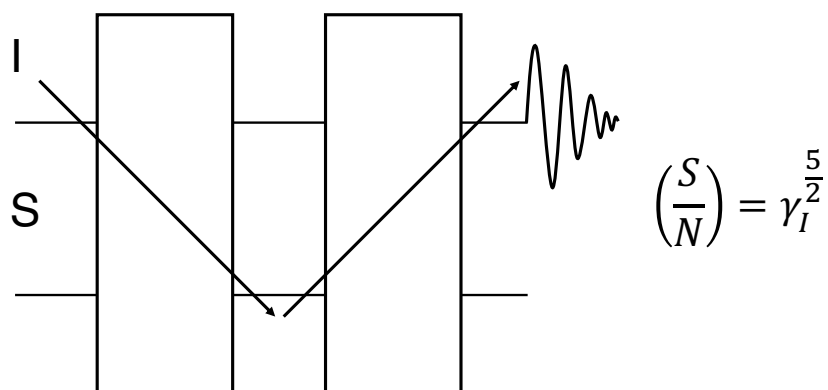


FIGURE 1.16: 1D indirect detection of S -spin polarisation detected on I spin as enhanced by double polarisation transfer.

Furthermore, through the introduction of an incremented delay in between polarisation transfers as shown in figure 1.17, we can obtain a 2D spectrum where the indirect dimension corresponds to the S nucleus.

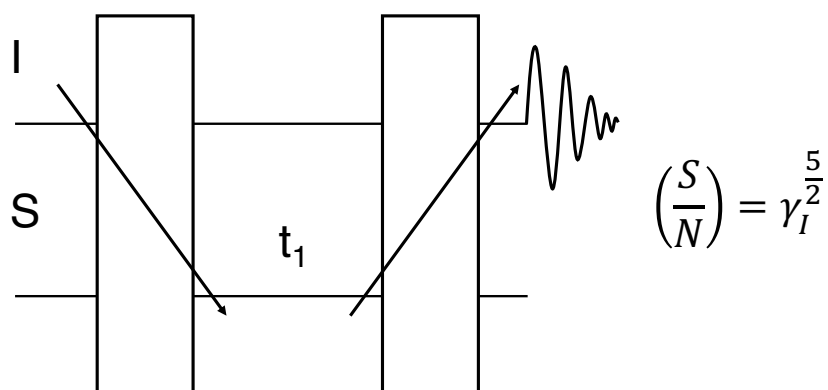


FIGURE 1.17: 2D indirect detection of S -spin spectrum detected on I spin as enhanced by double polarisation transfer where t_1 denotes the incremented delay.

Chapter 2

Singlet NMR

2.1 Singlet states in spin-1/2 pairs

In solution, nuclear spin-1/2 pairs can couple together to form a composite system with total spin of either 0 or 1. The exact nature of this system is dependent on the properties of the spin Hamiltonian in effect.

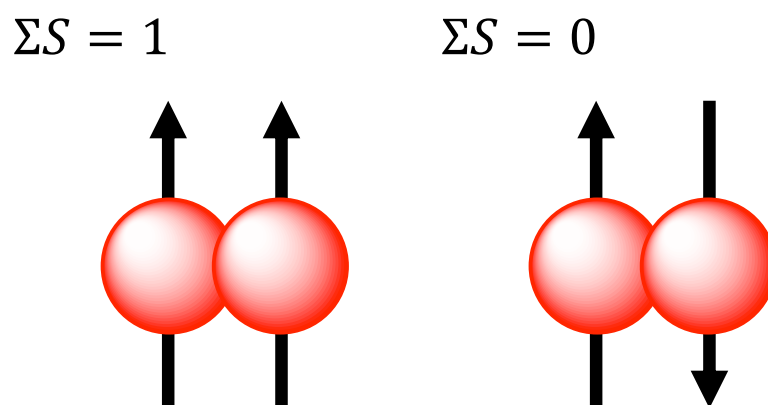


FIGURE 2.1: Examples of composite systems between spin-1/2 pairs. Total spin, ΣS , can take the value 1 or 0.

In this section, we will explore the different spin pair Hamiltonians and their respective eigenbases - with a particular emphasis on the conditions necessary for accessing and sustaining singlet order.

2.1.1 Universal eigenbasis for spin-1/2 pairs

The rotating frame nuclear spin Hamiltonian for a spin-1/2 pair can be written as:

$$\hat{H} = \frac{\Delta}{2}(I_{1z} - I_{2z}) + \Sigma(I_{1z} + I_{2z}) + 2\pi J (\vec{I}_1 \cdot \vec{I}_2) \quad (2.1)$$

where Δ is the isotropic chemical shift difference between spins, Σ is the sum of spin isotropic chemical shifts and J is the intrapair isotropic J-coupling constant.

The Hamiltonian in equation 2.1 may be expressed in the Zeeman basis as follows:

$$\hat{H} = \begin{matrix} |\alpha\alpha\rangle \\ |\beta\alpha\rangle \\ |\alpha\beta\rangle \\ |\beta\beta\rangle \end{matrix} \begin{pmatrix} \frac{J\pi}{2} + \Sigma & 0 & 0 & 0 \\ 0 & -\frac{J\pi}{2} - \frac{\Delta}{2} & J\pi & 0 \\ 0 & J\pi & -\frac{J\pi}{2} + \frac{\Delta}{2} & 0 \\ 0 & 0 & 0 & \frac{J\pi}{2} - \Sigma \end{pmatrix} \quad (2.2)$$

We can introduce the singlet-triplet mixing angle:

$$\theta_{ST} = \arctan\left(\frac{\Delta}{2\pi J}\right) \quad (2.3)$$

and the singlet-triplet energy difference:

$$\Omega = \sqrt{\Delta^2 + 2\pi J^2} \quad (2.4)$$

Such that we may diagonalise this matrix to obtain the following eigenvectors and eigenvalues [24, 25, 26]:

$$\begin{aligned} |S'_0\rangle &= \sin\left(\frac{\theta_{ST} + \frac{\pi}{2}}{2}\right)|\alpha\beta\rangle - \cos\left(\frac{\theta_{ST} + \frac{\pi}{2}}{2}\right)|\beta\alpha\rangle \Rightarrow E_1 = -\frac{J\pi}{2} - \frac{\Omega}{2} \\ |T_+\rangle &= |\alpha\alpha\rangle \Rightarrow E_2 = \frac{J\pi}{2} + \Sigma \\ |T'_0\rangle &= \cos\left(\frac{\theta_{ST} + \frac{\pi}{2}}{2}\right)|\alpha\beta\rangle + \sin\left(\frac{\theta_{ST} + \frac{\pi}{2}}{2}\right)|\beta\alpha\rangle \Rightarrow E_3 = -\frac{J\pi}{2} + \frac{\Omega}{2} \\ |T_-\rangle &= |\beta\beta\rangle \Rightarrow E_4 = \frac{J\pi}{2} - \Sigma \end{aligned} \quad (2.5)$$

These eigenvectors span the universal eigenbasis for a spin-1/2 pair and scale in accordance with the singlet-triplet mixing angle.

2.1.2 Magnetically inequivalent spin-1/2 pairs

In the limit of magnetic inequivalence, θ_{ST} approaches $\frac{\pi}{2}$ and the eigenvectors reduce to:

$$\begin{aligned} &|\alpha\beta\rangle \\ &|\alpha\alpha\rangle \\ &|\beta\alpha\rangle \\ &|\beta\beta\rangle \end{aligned} \tag{2.6}$$

One may recognise this basis as just the pure Zeeman basis for two spin-1/2s.

2.1.3 Magnetically equivalent spin-1/2 pairs

In the limit of magnetic equivalence, θ_{ST} approaches 0 and the (normalised) eigenvectors reduce to:

$$\begin{aligned} &\frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle) \\ &|\alpha\alpha\rangle \\ &\frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle) \\ &|\beta\beta\rangle \end{aligned} \tag{2.7}$$

These eigenvectors form the Singlet-Triplet basis, which consists of three spin-1 triplet states and the spin-0 singlet state.

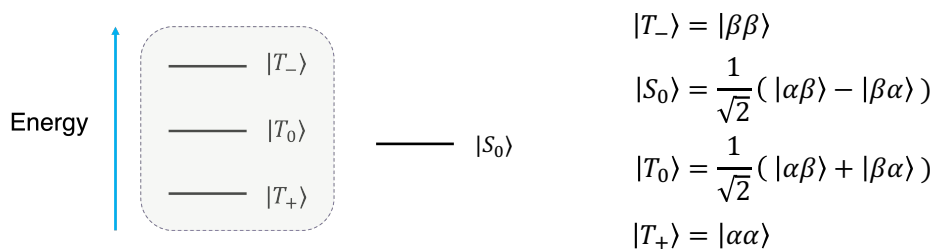


FIGURE 2.2: Spin-0 singlet state and spin-1 triplet manifold. The triplet manifold is spin-1; thus has $2(1) + 1 = 3$ individual spin states. Whereas singlets are spin-0, so there is only $2(0) + 1 = 1$ state available. Singlet and triplet states expanded in the Zeeman basis are shown on the right.

The singlet state is exchange *antisymmetric*, meaning that the action of swapping the spin indices returns the same state multiplied by -1. Conversely, the triplet states are exchange *symmetric*, so swapping the spins leaves the triplet states unaltered. This contrast in exchange symmetry signifies that the singlet and triplet states cannot be interchanged by interactions that act symmetrically across the spin pair. The singlet state is effectively segregated from the triplet manifold and therefore is commonly referred to as being a *disconnected eigenstate* [27], which gives singlet spin-order its resistance to dissipation.

2.1.4 Singlet Order

Singlet spin-order (SO) is defined as the population imbalance between the singlet state and the triplet states [28, 25, 29]:

$$Q_{SO} = |S_0\rangle\langle S_0| - \frac{|T_+\rangle\langle T_+| + |T_0\rangle\langle T_0| + |T_-\rangle\langle T_-|}{3} = -\frac{4}{3}\vec{I}_1 \cdot \vec{I}_2 \quad (2.8)$$

Given the isolation of the singlet state, singlet order corresponds to a protected spin configuration and decays with the time constant T_S , which can be many times longer than T_1 . Therefore, singlet states often constitute a so called Long-Lived State (LLS) [25, 27, 28].

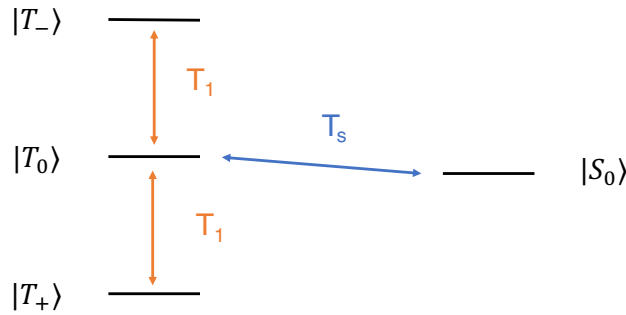


FIGURE 2.3: Within the triplet manifold, the nuclear spin relaxation rate is governed by the T_1 time constant; whereas relaxation between the singlet state and triplet manifold is dictated by the T_s time constant.

2.1.5 Quasi-Singlet Eigenorder

Analogous to singlet order, *quasi*-singlet eigenorder (QSEO) is defined as the population imbalance between the $|S'_0\rangle$ universal eigenstate and triplet manifold wherein the $|T'_0\rangle$ universal eigenstate has taken the place of the pure $|T_0\rangle$ triplet state [26].

$$\begin{aligned}
Q_{QSEO} &= |S'_0\rangle\langle S'_0| - \frac{|T_+\rangle\langle T_+| + |T'_0\rangle\langle T'_0| + |T_-\rangle\langle T_-|}{3} \\
&= -\frac{4}{3} \left((\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y}) \cos \theta_{ST} + \left(\frac{\hat{I}_{1z} - \hat{I}_{2z}}{2} \right) \sin \theta_{ST} + \hat{I}_{1z}\hat{I}_{2z} \right)
\end{aligned} \tag{2.9}$$

2.1.6 Field cycling of QSEO to SO

In the low field, spins are rendered equivalent as $\Delta \rightarrow 0$; thus SO is exact eigenorder of the Hamiltonian. Therefore, on adiabatic field cycling from high to low field, QSEO is transformed into SO. Likewise, SO is transformed back into QSEO on adiabatic field cycling from low to high field.

2.1.7 Adiabaticity

Here, adiabatic field cycling refers to a gradually changing magnetic field such that spins may adapt their configuration in tandem with the slowly changing Hamiltonian.

If field cycling is not adiabatic (i.e. is diabatic), the sudden approximation holds and spins are prevented from adapting their configuration; thus remain in their initial state regardless of the final Hamiltonian.

2.1.8 Generation of singlet order

Singlet order generation necessitates the coherent transfer of polarisation between the triplet manifold and singlet state. However, such transitions are forbidden in magnetically equivalent spin pairs.

The key is to switch the symmetry across the spin pair during the course of the experiment [30, 25]. When symmetry is broken, spins are rendered magnetically inequivalent i.e. $\Delta > 0$ and the coherent transfer of polarisation from the triplet manifold into the singlet state is permitted - allowing for the generation of singlet order. Afterwards, symmetry can be reinstated across the spin pair to quench any further transitions - maximising singlet lifetimes.

Symmetry can be broken and reinstated through a variety of different mechanisms. For instance, one may break and subsequently reintroduce symmetry via chemical reactions [31], or by field cycling an inequivalent system between high field where $\Delta > 0$ and low field where the chemical shift difference diminishes ($\Delta \rightarrow 0$) [32]. Alternatively, one may sustain singlet order in high field by applying resonant spin locking; thus suppressing the spin pair chemical shift difference [25].

This principle of symmetry switching is central to singlet NMR methodology and has been exploited to generate long-lived singlet order in a plethora of spin-1/2 pairs [33, 34, 32].

Below I discuss some of the major pulse sequences involved in the generation of singlet order; as well as the respective spin regimes they are used in. Please note, this list is by no means exhaustive and there exists a multitude of schemes for generating singlet order across a range of different conditions.

2.1.8.1 Weak coupling regime

Nuclear singlet order was first generated in 2004 by Carravetta et al. In this seminal example, singlet order was generated in a weakly coupled ^{13}C spin pair within 2,3-dibromothiophene [32]. In the weakly coupled regime, spins are magnetically inequivalent i.e $\Delta \gg J$ and $\theta_{ST} \rightarrow \frac{\pi}{2}$. In this experiment, singlet-precursor order, defined here as a population excess of the $|\alpha\beta\rangle$ state, is generated in high field before being subsequently converted into pure singlet order as the chemical shift difference, Δ , diminishes and the $|\alpha\beta\rangle$ state transforms into the $|S_0\rangle$ state during adiabatic sample transport to low field [25, 32].

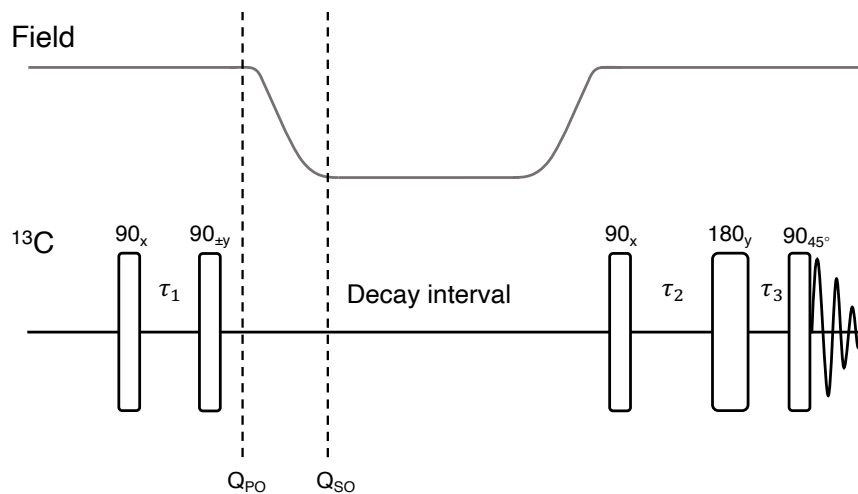


FIGURE 2.4: The pulse sequence used for the generation of ^{13}C singlet order in 2,3-dibromothiophene. $\tau_1 = |\frac{\pi}{\Delta}|$, $\tau_2 = |\frac{\pi}{2\Delta}| + |\frac{1}{4J}|$ and $\tau_3 = |\frac{1}{4J}|$ where Δ is the high field chemical shift difference between ^{13}C spins. Q_{PO} represents precursor-singlet-order, corresponding to a population excess of the $|\alpha\beta\rangle$ state; whereas Q_{SO} represents singlet-order - corresponding to a population excess of the $|S_0\rangle$ state. Singlet-order is converted to observable magnetisation on return to high field and after subsequent ^{13}C pulses.

2.1.8.2 Strong coupling regime

The Magnetisation to Singlet (M2S) and Spin Lock Induced Crossing (SLIC) pulse sequences were designed to generate singlet order for spin pairs in the strongly coupled regime [35, 36]. In this regime, spins are near magnetic equivalence, i.e $\Delta \ll J$ and $\theta_{ST} \rightarrow 0$.

The M2S pulse sequence is based on J-synchronised echos of the general form:

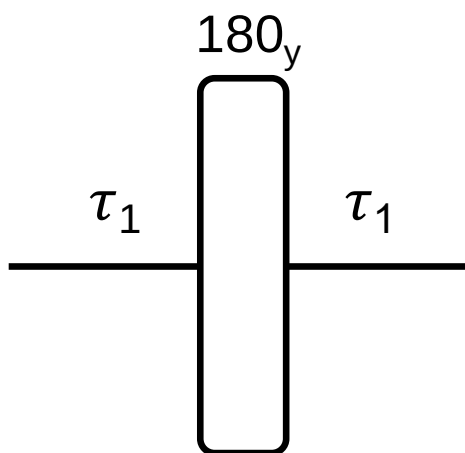


FIGURE 2.5: The J-synchronised echo where $\tau_1 = \frac{1}{4J}$.

J-synchronised echos are hence a modified form of the standard spin echo block but where the delays are synchronised to the spin pair scalar coupling, $\tau_1 = \frac{1}{4J}$. The effect of this pulse sequence element is a rotation of $2\theta_{ST}$ degrees about the x axis of the $|S_0\rangle, |T_0\rangle$ singlet-triplet subspace [37].

The M2S sequence in full is shown in figure 2.6 and which proceeds as follows: the initial 90° pulse generates coherences in the triplet manifold and is followed by an echo train of $2n$ iterations, where $n = \frac{\pi}{4\theta_{ST}}$ (to the nearest integer) and which converts $|T_0\rangle$ into $|S_0\rangle$; hence creates coherences between $|S_0\rangle$ and the outer triplet states. A successive 90° pulse and τ_1 J-synchronised delay then converts the outer triplet states into the central $|T_0\rangle$ state thus generating a coherence between $|T_0\rangle$ and $|S_0\rangle$, which is subsequently converted into singlet order by a second echo train of n iterations.

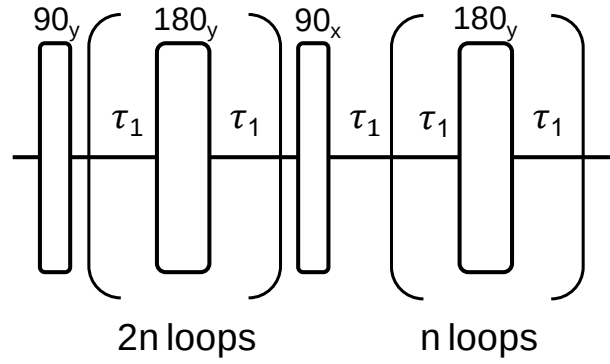


FIGURE 2.6: The M2S pulse sequence for the generation of singlet order for spin pairs in the strong coupling regime. The echo delay τ_1 is equal to $\frac{1}{4J}$. The delay τ_2 controls the phase of the zero-quantum coherence between $|S_0\rangle$ and $|T_0\rangle$.

For the return transfer (i.e from singlet order back to magnetisation) the M2S sequence is repeated but in reverse chronological order [35].

To populate the singlet state, the SLIC sequence utilises a continuous, resonant, spin locking field applied along the same axis as spin magnetisation and at the same frequency as the intrapair J-coupling to equalise the energies of the singlet and triplet states in the rotating frame. Singlet order is maximally generated after spin locking for the duration $\frac{1}{\Delta\sqrt{2}}$ [36, 38].

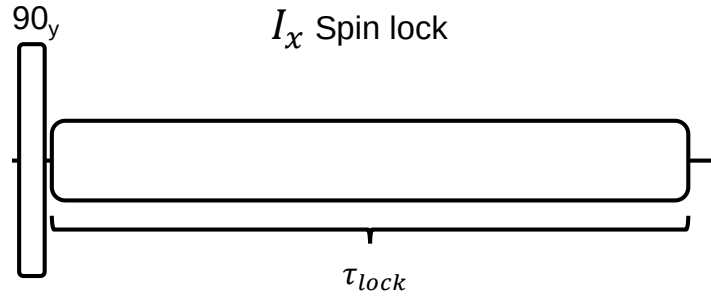


FIGURE 2.7: The SLIC pulse sequence for the generation of singlet order for spin pairs in the strong coupling regime. The spin locking field frequency is equal to the spin pair J-coupling.

2.1.8.3 Intermediate coupling regime

The pulse sequences above, although efficient in their respective regimes, are ineffective in generating singlet order for systems in the so called intermediate coupling regime i.e where Δ is on the same order as J and $\theta_{ST} \rightarrow \frac{\pi}{4}$.

Generalised Magnetisation to Singlet (gM2S) is a modified variant of M2S for use in both the strong coupling and intermediate coupling spin regime [29]. Whereas the standard M2S sequence induces rotations about the x axis of the $|S_0\rangle, |T_0\rangle$ zero quantum subspace, the gM2S sequence instead induces rotations in the same subspace but about a axis tilted by 45° with respect to the x and z axes [29, 26]. This modification, coupled with the appropriate choice of J-synchronised echo delays, enables gM2S to excite singlet order across a wider range of singlet-triplet mixing angles: $0 \geq \theta_{ST} \leq 67.5^\circ$, compared to the M2S excitation range of: $0 \geq \theta_{ST} \leq 45^\circ$.

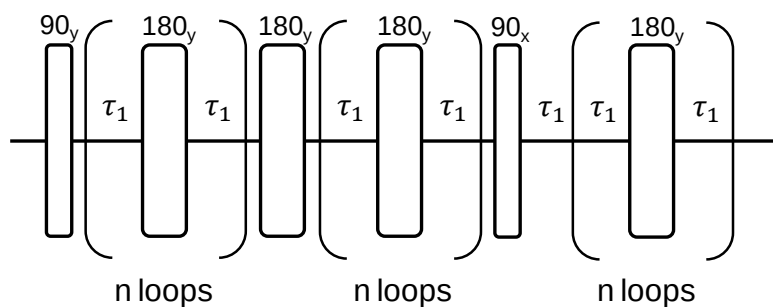


FIGURE 2.8: The gM2S pulse sequence for the generation of singlet order for spin pairs in both the strong coupling and intermediate regime.

PulsePol is a sequence originally developed for the spectroscopy of nitrogen vacancy centers in diamond [39] that has since been applied to the context of singlet-triplet inter-conversion in liquids [40]. The PulsePol sequence is formed from six repeating pulses and 4 inter pulse delays and can be expressed using the RN_n^ν symmetry notation taken from symmetry-based recoupling concepts [41]. Much like gM2S, PulsePol is capable of generating singlet order in both the strong coupling and intermediate coupling spin regime. However, where the PulsePol sequence really excels is in its robustness against rf amplitude and offset errors, which is especially apparent when the sequence is 'rifled' i.e when the phase of every other 180° pulse has been shifted by 180 degrees.

$$RN_n^\nu$$

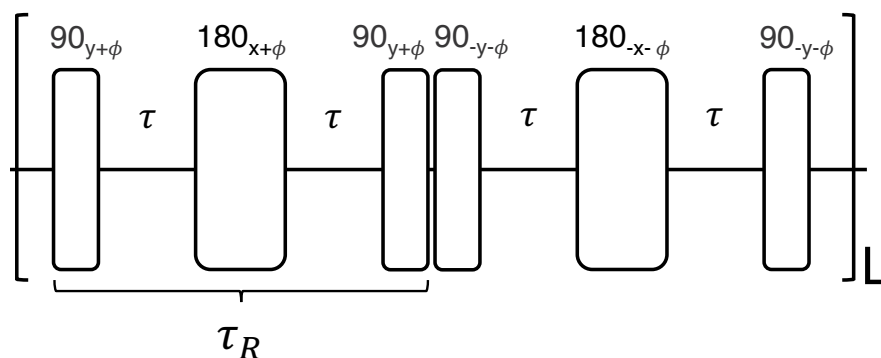


FIGURE 2.9: PulsePol sequence with the symmetry RN_n^ν . Pulse phases and τ delay intervals are dependent on the given symmetry numbers of the sequence.

A more thorough description of PulsePol; as well as R-sequences in general is presented in chapter 3.

2.1.9 Generation of QSEO from SO

QSEO in a spin-1/2 pair can be generated from SO using a sequence with an effective propagator, under ideal conditions, of the following form:

$$\hat{U}_{S_2S'} = \exp \{i \theta_{ST} \hat{I}_y^{ZQ}\} \quad (2.10)$$

where $\hat{I}_y^{ZQ}$ represents the single transition operator [42] along the y-axis in the $|T_0\rangle, |S_0\rangle$ zero quantum subspace.

Under $\hat{U}_{S_2S'}$, the population of the $|S_0\rangle$ singlet state is exchanged with the $|S'_0\rangle$ universal eigenstate; thus converting SO into QSEO.

Although there exists numerous sequences which generate propagators of the form $\hat{U}_{S_2S'}$ [26, 43, 44], their description is beyond the scope of this work. For a thorough description of QSEO and methods for its generation, the reader is instead directed to the Ph.D thesis of Sabba [26].

2.2 Singlet relaxation

Singlet spin order, although resistant, is not immune from dissipation. Mechanisms that act symmetrically across the spin pair cannot interconvert the singlet and triplet states; however singlet order is still vulnerable to a range of incoherent interactions capable of inducing relaxation as well as singlet-triplet leakage (a coherent mechanism involving off diagonal coherences between the singlet state and triplet manifold).

The total singlet order relaxation rate constant is given as the sum of all mechanisms:

$$R_s^\Lambda = \frac{1}{T_s} = \sum_{\Lambda}^N \frac{1}{T_s^\Lambda} \quad (2.11)$$

Where the index Λ denotes a given singlet relaxation mechanism.

Note, the following relaxation rate expressions apply to spin systems in the extreme narrowing limit, i.e where molecular tumbling is much faster than the Larmor frequency ($\omega_0\tau_c \ll 1$).

2.2.1 Intrapair dipolar coupling

The intrapair dipolar coupling relaxation mechanism arises from the fluctuation of the dipolar coupling between spins *within* the spin pair during molecular tumbling.

The contribution to the spin pair longitudinal relaxation rate by the intrapair dipolar coupling mechanism is as follows [26, 11]:

$$R_1^{intraDD} = \frac{3}{2} b_{ij}^2 \tau_c \quad (2.12)$$

Where τ_c is the rank-2 rotational correlation time in seconds.

The intrapair dipolar coupling relaxation mechanism is typically dominant for the case of longitudinal (T_1) relaxation; however, because the intra-pair dipolar coupling mechanism acts symmetrically across the spin pair, it is unable to induce relaxation of singlet order [11].

$$R_s^{intraDD} = 0 \quad (2.13)$$

2.2.2 Out of pair dipolar coupling

In general, singlet order is not immune to relaxation caused by fluctuating dipolar couplings to nuclei outside of the spin pair - unless the respective coupling constants are symmetrical across the spin pair, in which case, the singlet relaxation rate is zero. Thus the magnitude of the out of pair dipolar singlet relaxation rate is strongly correlated to the subtended angle made between the intra-pair vector and external nuclear spin.

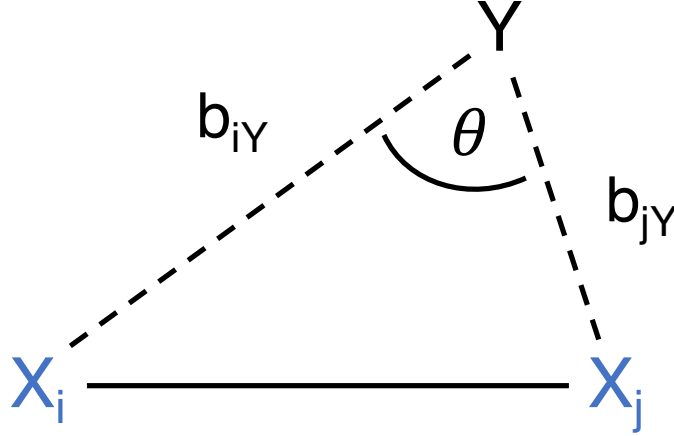


FIGURE 2.10: Out of pair dipolar coupling between homonuclear spin pair (X_i and X_j) and external nuclei Y . Subtended angle θ is between intra-pair vector (solid black line) and Y . b_{iY} and b_{jY} are the respective out of pair dipolar couplings.

The longitudinal relaxation rate for this mechanism (R_1^{outDD}) is given by [26],

$$R_1^{outDD} = \frac{2}{3} \tau_c \sum_Y I_Y(I_Y + 1)(b_{iY}^2 + b_{jY}^2) \quad (2.14)$$

Where I_Y is the spin quantum number of the Y^{th} spin.

Whereas the singlet relaxation rate for this mechanism (R_s^{outDD}) is given by [45, 26, 46],

$$R_s^{outDD} = \frac{4}{3} \tau_c \sum_Y I_Y(I_Y + 1)(b_{iY}^2 + b_{jY}^2 - b_{iY}b_{jY}(3 \cos^2 \theta - 1)) \quad (2.15)$$

Where θ is the subtended angle as shown in figure 2.10.

2.2.3 Chemical Shift Anisotropy

As shown by equation 1.42, both the rank-1 antisymmetric and rank-2 symmetric CSA components of the chemical shift interaction are capable of inducing spin relaxation.

The symmetric CSA longitudinal CSA relaxation rate for a spin pair is as follows [13, 37, 33]:

$$R_1^{CSA^{(+)}} = \frac{1}{10} \gamma_i \gamma_j B_0^2 \tau_c \left(\|\sigma_i^+\|^2 + \|\sigma_j^+\|^2 \right) \quad (2.16)$$

where $\|A\|$ represents the Frobenius norm of tensor A (the square root of the sum of all squared elements of A).

The antisymmetric CSA longitudinal CSA relaxation rate for a spin pair is as follows [26, 13, 37, 33]:

$$R_1^{\text{CSA}^{(-)}} = \frac{1}{6} \gamma_i \gamma_j B_0^2 \tau_1 \left(\|\sigma_i^-\|^2 + \|\sigma_j^-\|^2 \right) \quad (2.17)$$

where τ_1 is the rank-1 correlation time, which corresponds to the correlation time for components that rotate as rank-1 spherical harmonics and, in the case of isotropic rotational diffusion, is related to τ_c through $\tau_1 = 3\tau_c$ [14].

The singlet CSA relaxation mechanism arises from the rotational modulation of the *difference* in nuclear shielding tensors across the spin pair, where the relevant relaxation rate expressions are given by [45, 26, 37, 33]:

$$R_s^{\text{CSA}^{(+)}} = \frac{2}{9} \gamma_i \gamma_j B_0^2 \tau_c \|\Delta\sigma^+\|^2 \quad (2.18)$$

and

$$R_s^{\text{CSA}^{(-)}} = \frac{2}{3} \gamma_i \gamma_j B_0^2 \tau_c \|\Delta\sigma^-\|^2 \quad (2.19)$$

Where $\Delta\sigma^+ = \sigma_i^+ - \sigma_j^+$ and $\Delta\sigma^- = \sigma_i^- - \sigma_j^-$.

Note that the large coefficient of the antisymmetric CSA rate - even minor antisymmetric components are capable of inducing significant singlet relaxation.

The singlet CSA relaxation mechanism is inactive for spins with identical shielding tensors.

Ironically, the symmetry switching methods required for the generation of singlet order expose the singlet state to the CSA mechanisms - compromising singlet lifetimes. This emphasises the need for rapid reinstatement of molecular symmetry across the spin pair once singlet order has been established to prevent the untimely decoherence of spin order.

2.2.4 Spin-rotation

Assuming the spin-rotation tensor is uniaxial and that the molecule is a spherical top, the spin-rotation longitudinal relaxation rate for each nucleus in the spin pair is given by [14, 11]:

$$R_1^{SR} = \frac{I^2}{9\hbar^2\tau_c} (2C_\perp^2 + C_\parallel^2) \quad (2.20)$$

where I is the isotropic moment of inertial in units of kg m^2 , $C_\perp$ is the perpendicular (transverse) and $C_\parallel$ are the parallel (largest) components of the spin-rotation tensor when expressed in its principal axes frame.

The singlet spin-rotation relaxation rate is proportional to the difference in nuclear spin-rotation tensors. And assuming $C_{\parallel,i} = C_{\parallel,j}$ (in addition to the same assumptions for R_1^{SR}) the singlet spin-rotation relaxation rate is given by [11]:

$$R_s^{SR} = \frac{I^2}{9\hbar^2\tau_c} (2(C_{\perp,i} - C_{\perp,j})^2 + (C_{\parallel,i} - C_{\parallel,j})^2) \quad (2.21)$$

2.2.5 Singlet-Triplet Leakage

In non-equivalent spin pairs, singlet order is not an exact eigenorder of the spin Hamiltonian; so is not preserved under free evolution. In these instances, the singlet operator Q_{SO} displays a complex spin dynamical behaviour leading to a relaxation mechanism referred to as Singlet-Triplet Leakage (STL), in which the isotropic chemical shift difference within the spin pair induces coherent oscillations between the singlet state and the rapidly relaxing triplet manifold [45].

Assuming spins have uniaxial shielding tensors with the same value of $\sigma_{\text{CSA}} = \frac{3}{2}(\delta_{zz} - \sigma^{iso})$, the STL singlet relaxation rate is given by the following expression [33, 37]:

$$R_s^{\text{STL}} = \frac{\Delta^2 \gamma_i \gamma_j B_0^2 \left(5b_{ij}^2 + \frac{4}{3} \gamma_i \gamma_j B_0^2 \sigma_{\text{CSA}}^2 \right) \tau_c}{60\pi^2 J_{ij}^2} \quad (2.22)$$

We see that this mechanism is strongest when the isotropic chemical shift difference between spins (Δ) is greatest, which is seen for intermediate and weakly coupled spin regimes. This mechanism may be mitigated via sample transport to low magnetic fields, where $\Delta \rightarrow 0$ and the singlet state becomes an exact eigenstate of the Hamiltonian. Whereas, in the high field, the spin pair chemical shift difference can be suppressed via the application of coherent rf fields. Alternatively, high field singlet order may be converted into QSEO, which is preserved under free evolution and hence immune to STL.

2.2.6 Additional singlet relaxation mechanisms

Besides those already mentioned, any additional incoherent interaction that acts asymmetrically across the spin pair can induce singlet relaxation.

For example, the Scalar Relaxation of the Second Kind (SR2K) singlet relaxation mechanism occurs when spins are differentially coupled to an additional, rapidly relaxing, nucleus. This mechanism is most potent when the additional nucleus is relaxing on the same timescale as either the Larmor frequency of the spin pair, or the intrapair J-coupling [47, 48].

2.3 QSEO relaxation rate expressions

Expressions for the relaxation of QSEO in the extreme narrowing limit ($\tau_c \omega_0 \ll 1$) are given as follows [26]:

Under the intra-pair dipolar coupling mechanism:

$$R_{S'}^{intraDD}(\theta_{ST}) = \frac{2}{15} b_{12}^2 \tau_c \left(\sin^2(\theta_{ST}) + 6 \sin^2\left(\frac{\theta_{ST}}{2}\right) \right) \quad (2.23)$$

Under the out of pair dipolar coupling mechanism:

$$R_{S'}^{outDD}(\theta_{ST}) = \frac{8}{9} \tau_c \sum_Y I_Y(I_Y + 1) \left(\frac{1}{2} \left(b_{iY}^2 + b_{jY}^2 - 2b_{iY}b_{jY}(3 \cos \theta - 1) \right) \cos^2 \theta_{ST} \right. \\ \left. - 2b_{iY}b_{jY}(3 \cos \theta - 1) \cos \theta_{ST} + b_{iY}^2 + b_{jY}^2 \right) \quad (2.24)$$

Under the symmetric CSA relaxation mechanism:

$$R_{S'}^{CSA+}(\theta_{ST}) = \frac{2}{15} \gamma_i \gamma_j B_0^2 \tau_c \left(\left(\cos^2\left(\frac{\theta_{ST}}{2}\right) + \frac{2}{3} \cos \theta_{ST} \right) \right. \\ \left. \|\Delta\sigma^+\|^2 + \sin^2\left(\frac{\theta_{ST}}{2}\right) \|\sigma_i^+ + \sigma_j^+\|^2 \right) \quad (2.25)$$

Under the antisymmetric CSA relaxation mechanism:

$$R_{S'}^{CSA^-}(\theta_{ST}) = \frac{2}{9}\gamma_i\gamma_j B_0^2\tau_1 \left(\cos^2\left(\frac{\theta_{ST}}{2}\right) \|\Delta\sigma^-\|^2 + \sin^2\left(\frac{\theta_{ST}}{2}\right) \|\sigma_i^- + \sigma_j^-\|^2 \right) \quad (2.26)$$

One observes that the relaxation of QSEO is dependant on the singlet-triplet mixing angle θ_{ST} ; and that in the limit of magnetic equivalence, i.e where $\Delta \rightarrow 0$ and $\theta_{ST} = 0$, the expressions above reduce to those for shown for the relaxation of SO.

Chapter 3

R-sequences and PulsePol

Many spin order manipulations in this work are carried out using different implementations of the ‘PulsePol’ sequence [39, 49, 40]. In this chapter, I will introduce the symmetry based framework borrowed from solid state NMR to describe the PulsePol sequence; as well as apply average Hamiltonian theory [50] for the analysis of spin transformations under the relevant implementations.

The analysis in this section is done under the assumption of being in the limit of strong rf pulses, i.e pulses are assumed to have zero duration.

3.1 R-sequences

R-sequences are cyclic pulse sequences comprised of alternating R-elements. An R-element is a pulse sequence component that rotates spins by an odd multiple of 180° about the $\pm x$ -axis [51, 41]. Under ideal conditions, and in the absence of any other interactions, propagation under an R-element is given by,

$$\hat{U}_R = \exp \{ -i\pi I_x \} = \hat{R}_x(180^\circ) \quad (3.1)$$

where $\hat{R}_x(180^\circ)$ denotes a rotation operator of 180° about the x-axis.

R-sequences were originally developed for broadband heteronuclear decoupling [51] and later applied in the context of symmetry based recoupling in MAS solid state NMR experiments [41, 52, 53].

Symmetry based R-sequences are constructed adhering to a set of three integer symmetry numbers denoted N , n and ν ; such that a given R-sequence may be denoted using the syntax RN_n^ν . Ultimately, it is these symmetry numbers which define the selection rules of a given R-sequence and hence its average Hamiltonian.

The procedure for constructing an R-sequence of the arbitrary symmetry RN_n^ν is stated below,

- Define the base R-element (for example a standard 180° x-pulse or composite pulse).
- The duration of an individual R-element is given by $\tau_R = n\tau_r/N$ where τ_r denotes the rotational period of the sample (equal to the period of the MAS in the context of solid state recoupling).
- Invert the signs of the pulse phases in the base R-element to produce the conjugate R' element.
- Apply a phase shift (ϕ) of $+\pi\nu/N$ to the pulses of the basic element R and a phase shift of $-\pi\nu/N$ to the pulses of the conjugate element R'.
- The R-sequence of symmetry RN_n^ν hence takes the form,

$$RN_n^\nu = (R)_\phi (R')_{-\phi} \dots (R')_{-\phi} \quad (3.2)$$

A complete R-sequence contains N R-elements or $N/2$ $(R)_\phi (R')_{-\phi}$ pairs and has a total duration of $T = N\tau_r$.

3.2 Average Hamiltonian Theory

Spin evolution under the action of an R-sequence may be succinctly evaluated using Average Hamiltonian Theory (AHT) [50]. A brief overview of the theory is given here to establish the relevant notation and highlight some key points.

In many instances, a nuclear spin Hamiltonian can be dissected into a large component $\hat{H}_a(t)$ and a minor perturbation $\hat{H}_b(t)$:

$$\hat{H}_{total}(t) = \hat{H}_a(t) + \hat{H}_b(t) \quad (3.3)$$

Generally, $\hat{H}_a(t)$ contains interactions with external fields; whereas $\hat{H}_b(t)$ consists of smaller internal inter-spin interactions and, in general, $\hat{H}_a(t)$ and $\hat{H}_b(t)$ do not commute.

Formally, the propagator of a spin system under $\hat{H}_{total}(t)$ from time point t_0 to t_1 is given by,

$$\frac{d}{dt}\hat{U}(t_1, t_0) = -i\hat{H}_{total}(t)\hat{U}(t_1, t_0) \quad (3.4)$$

However, an exact solution for $\hat{U}(t_1, t_0)$ is non trivial to obtain in general.

One may instead express $\hat{H}_b(t)$ in the interaction frame of $\hat{H}_a(t)$ as follows,

$$\tilde{H}_b(t) = \hat{U}_a(t_0, t_1)\hat{H}_b(t)\hat{U}_a(t_1, t_0) \quad (3.5)$$

Such that the interaction frame propagator between time point t_0 and t_1 $\tilde{U}(t_1, t_0)$ solves,

$$\frac{d}{dt}\tilde{U}(t_1, t_0) = -i\tilde{H}_b(t)\tilde{U}(t_1, t_0) \quad (3.6)$$

Note that the large $\hat{H}_a(t)$ component has been removed from the expression - greatly simplifying the problem.

The interaction frame propagator may hence be approximated as,

$$\tilde{U}_b(t_1, t_0) = \exp \{-i\overline{H}_b(t_1, t_0)\tau\} \quad (3.7)$$

where $\overline{H}_b(t_1, t_0)$ represents the effective Hamiltonian over the time period $\tau = t_1 - t_0$.

The effective Hamiltonian $\overline{H}_b(t_1, t_0)$ is evaluated in AHT using the Magnus expansion and thus written as a series expansion as follows [50],

$$\overline{H}_b(t_1, t_0) = \overline{H}_b^{(1)}(t_1, t_0) + \overline{H}_b^{(2)}(t_1, t_0) + \dots \quad (3.8)$$

Effective Hamiltonian terms with superscripts ≥ 2 are here considered as correction terms to $\overline{H}_b^{(1)}(t_1, t_0)$ and are ignored in this work.

Thus, the effective Hamiltonian is simply expressed as,

$$\overline{H}_b(t_1, t_0) \simeq \overline{H}_b^{(1)}(t_1, t_0) \quad (3.9)$$

where $\overline{H}_b^{(1)}(t_1, t_0)$ is the effective Hamiltonian over the interval $\tau = t_1 - t_0$,

$$\overline{H}_b^{(1)}(t_1, t_0) = \frac{1}{\tau} \int_{t_0}^{t_1} \tilde{H}_b(t) dt \quad (3.10)$$

3.3 PulsePol

PulsePol is an R-sequence where the base R-element is a *windowed* $90_y 180_x 90_y$ composite 180° pulse [54]. Here, windowed refers to the presence of delays between pulses. PulsePol was originally conceived for polarization transfer between electron and nuclear spins in the context of nitrogen-vacancy diamond magnetometry [39]; however, there exists great variability in the application of the PulsePol sequence depending on the choice of pulse phases and R-element duration. And in this work we are principally concerned with the application of the PulsePol sequence for singlet order generation and cross polarisation in liquids.

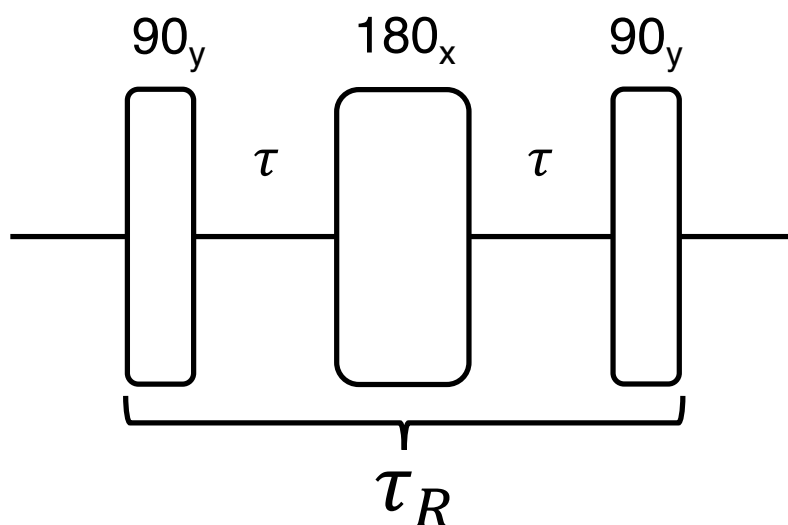


FIGURE 3.1: PulsePol base R-element where τ denotes inter-pulse delay.

3.3.1 Singlet-Triplet interconversion

The PulsePol sequence was applied to the context of singlet-triplet interconversion in 2022 by Sabba et al [40]. Wherein the RN_n^v symmetry notation was adopted in the interpretation of the sequence's spin dynamics. In analogy to MAS solid state recoupling experiments, the J-coupling plays the role of the mechanical rotation, such that the relevant rotational period $\tau_r = 1/J$ and thus $\tau_R = n/NJ$ and the complete R-sequence duration $T = n/J$.

For sequences constructed with symmetry numbers that satisfy singlet-triplet interconversion selection rules [40], transitions are induced between the outer triplet states and the singlet state.

One such symmetry that satisfies the relevant selection rules is $R4_1^1$, which is constructed following the procedure set out in section 3.1 and using the base R-element shown in figure 3.1. Once constructed, If one then applies a global $+45^\circ$ phase shift to all pulses of the $R4_1^1$ sequence we attain the sequence shown in figure 3.2:

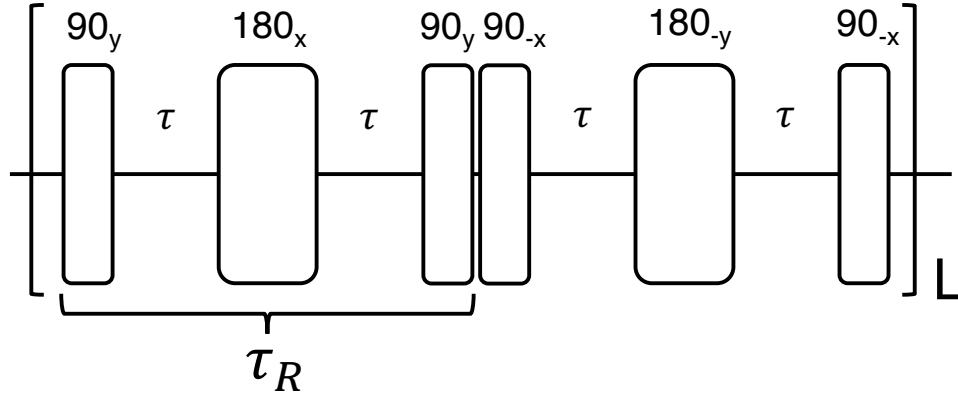


FIGURE 3.2: Repeating RR' PulsePol pair with symmetry $R4_1^1$ and a $+45^\circ$ phase shift to all pulses and where $\tau_R = 1/4J$. The index L represents the number of loops.

The $+45^\circ$ phase shift has no effect on the generation of singlet order, but rather ensures that all pulse phases are either zero or a multiple of $\pi/2$, which simplifies the programming of the sequence.

AHT can be used to analyse the evolution of a coupled homonuclear spin pair under the PulsePol sequence.

Beginning with the homonuclear coupled spin pair Hamiltonian in the Cartesian product operator basis,

$$\hat{H} = \frac{\Delta}{2} (\hat{I}_{1z} - \hat{I}_{2z}) + 2\pi J (\hat{I}_1 \cdot \hat{I}_2) \quad (3.11)$$

and assuming the case of near equivalence i.e when $\Delta \ll J$, the chemical shift difference term can be expressed in the interaction frame of the J-coupling. An ensuing AHT treatment of the PulsePol sequence yields a first order average Hamiltonian of,

$$\overline{H}^{(1)} = -\omega_{nut}^{ST} (\hat{I}_x^{ST} \cos \phi_{ST} + \hat{I}_y^{ST} \sin \phi_{ST}) \quad (3.12)$$

where $\hat{I}_x^{ST}$ and $\hat{I}_y^{ST}$ represent single transition operators [42] between an outer triplet state and singlet state, ω_{nut}^{ST} is the singlet-triplet nutation frequency given by: $\omega_{nut}^{ST} = \Delta |\kappa_{1\pm 11\pm 1}|$, where Δ is the spin pair chemical shift difference and $\kappa_{1\pm 11\pm 1}$ is the sequence scaling factor, which is dependent on the R-element and a specific sequence's

symmetry numbers [40]. ϕ_{ST} is the phase of the effective field given by: $\phi_{ST} = \arg(\kappa_{1-11-1})$. For the symmetry $R4_1^1$, $\phi_{ST} = 0$ and equation 3.12 reduces to: $\bar{H}^{(1)} = -\omega_{nut}^{ST} \hat{I}_x^{ST(-)}$.

To return to longitudinal magnetisation from singlet order, the same PulsePol sequence can be applied again to induce further evolution in the singlet-triplet subspace and back towards longitudinal spin order.

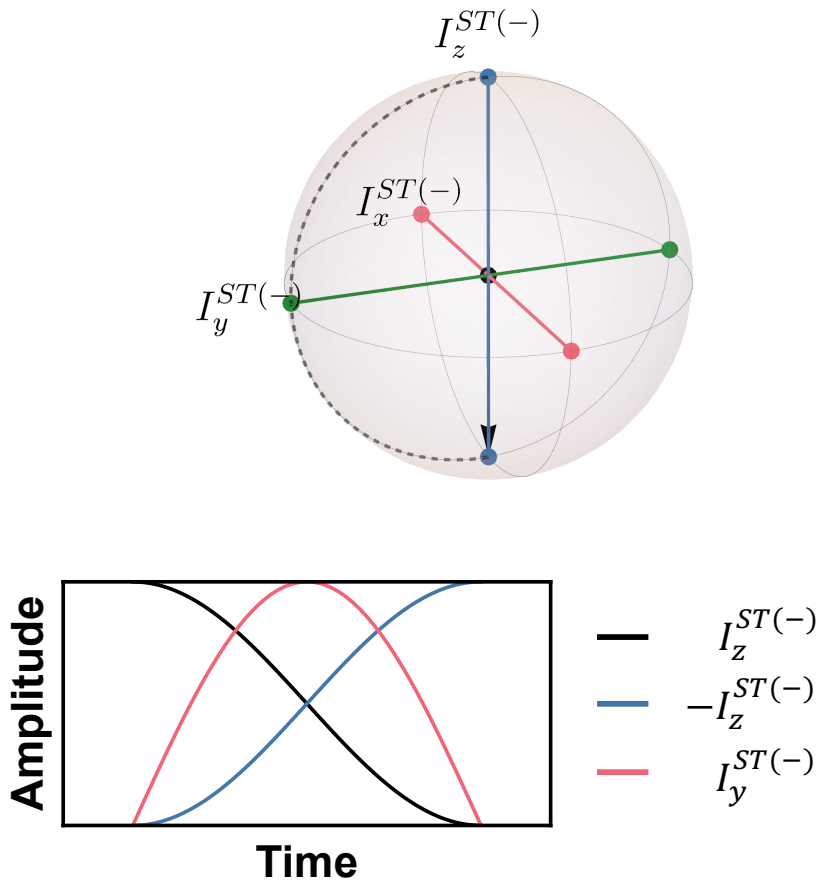


FIGURE 3.3: Trajectory of spin order in the $|T_{-}\rangle, |S_0\rangle$ zero quantum subspace under the $R4_1^1$ average Hamiltonian starting from longitudinal magnetisation. A population excess of the outer triplet state $|T_{-}\rangle$ corresponding to $I_z^{ST(-)}$ is converted into a population excess of the $|S_0\rangle$ singlet state corresponding to $-I_z^{ST(-)}$. During the evolution, Spin order passes through $|T_{-}\rangle$ and $|S_0\rangle$ coherences corresponding to $I_y^{ST(-)}$. Indeed, if the sequence is stopped halfway through, one may observe NMR coherences between the singlet state and triplet manifold.

3.3.2 Riffled implementation

Improved robustness against rf amplitude mismatch and resonance offset can be attained through *riffling* [40]. Riffling involves shifting the phase of the conjugate R-element's 180° pulse by 180° . Assuming ideal and infinitely short pulses, this modification has no effect on the sequence's spin dynamics but suppresses errors on subsequent R-sequences.

The riffled implementation of the $R4_1^1$ sequence shown in figure 3.2 is shown in figure 3.4.

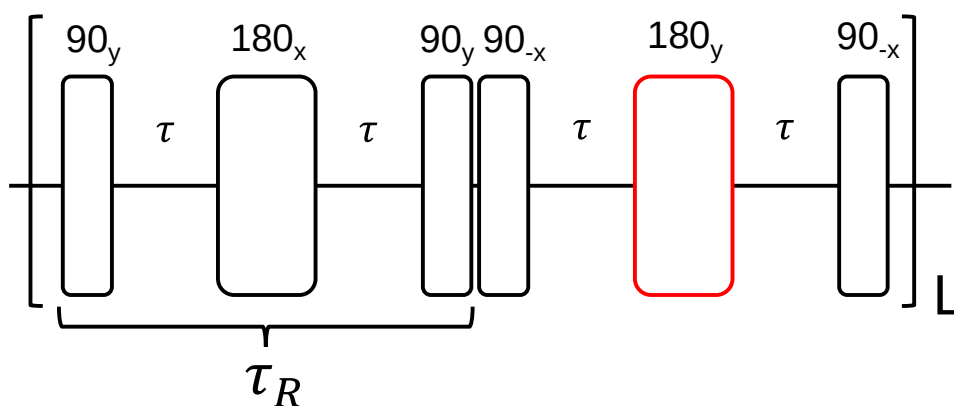


FIGURE 3.4: Riffled variant of repeating RR' PulsePol pair with symmetry $R4_1^1$ and a $+45^\circ$ phase shift to all pulses and where $\tau_R = 1/4J$. Riffled pulse shown in red. The index L represents the number of loops.

3.4 DualPol cross polarisation

The PulsePol sequence can also be used to induce heteronuclear cross-polarisation. In this implementation, the PulsePol sequence is applied simultaneously to the rf channels of both scalar coupled nuclei. We hence refer to this application as 'Dual channel PulsePol' or 'DualPol' for short.

In this implementation, the pulse phases remain unchanged from those in defined in the singlet-triplet case; however, the R-element duration is now no longer constrained by the sequence's symmetry numbers. In DualPol the only constraint for the R-sequence duration is that it must be much shorter than the period of any relevant J-couplings.

DualPol is capable of efficient and robust polarisation transfer between spins even in the strong coupling regime; where the standard refocused INEPT sequence ordinarily breaks down [55, 56, 57, 58, 59].

The DualPol sequence used for heteronuclear polarisation transfer in this thesis is constructed from the 45° phase shifted $R4_1^1$ PulsePol sequence defined in subsection 3.3.1 and is given by,

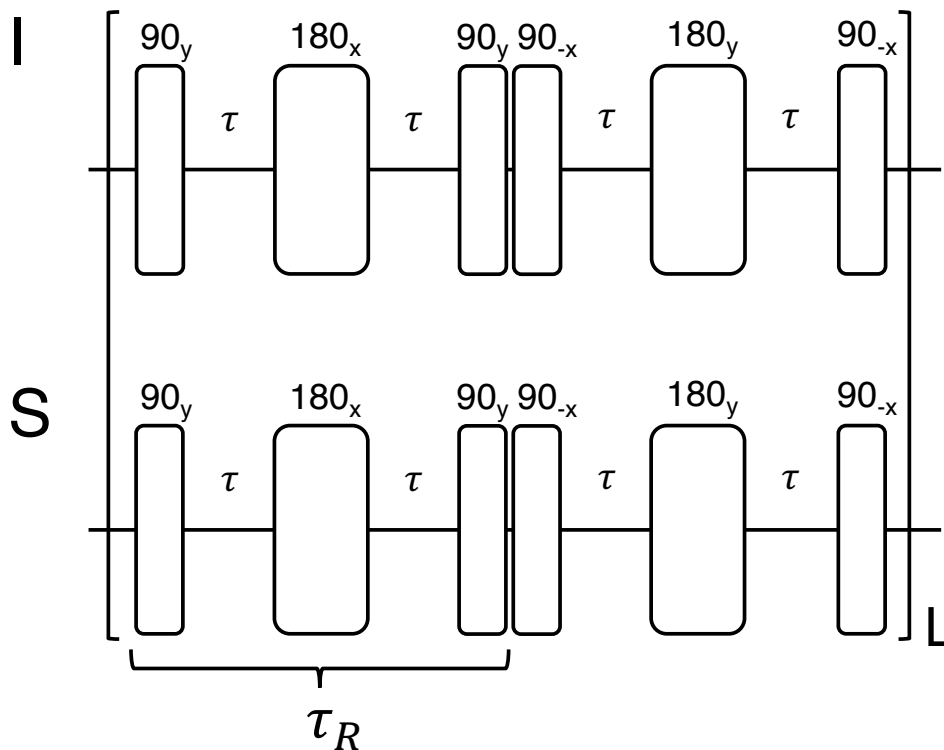


FIGURE 3.5: DualPol variant of the $+45^\circ$ phase shifted $R4_1^1$ PulsePol sequence for heteronuclear cross-polarisation between spins I and S. R-element duration is no longer constrained by symmetry numbers. Note the riffled implementation.

We may again employ AHT in the analysis of the DualPol sequence.

For the simplest case of polarisation transfer between just two spin-1/2's, we begin with the coupled *heteronuclear* two-spin Hamiltonian written in the cartesian product operator basis,

$$\hat{H} = \frac{\Delta}{2}(\hat{I}_{1z} - \hat{S}_z) + 2\pi J_{IS} (\hat{I}_z \cdot \hat{S}_z) \quad (3.13)$$

In this regime, the Larmor frequencies are well separated i.e $\Delta \gg J_{IS}$; therefore, we use the secularised form of the J-coupling. Moreover, we can express the J-coupling in the interaction frame of the chemical shift difference. An ensuing AHT treatment of the DualPol sequence yields a first order average Hamiltonian of,

$$\overline{H}^{(1)} = \kappa_{DP} \times 2\pi J_{IS} (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y) \quad (3.14)$$

In the limit of strong rf pulses, the DualPol scaling factor is given by: $\kappa_{DP} = \frac{1}{2}$. One may recognise equation 3.14 as corresponding to an anisotropic Hartmann-Hahn Hamiltonian [60]. Hence, between two coupled spin-1/2s, the DualPol sequence interchanges z-magnetisation at a nutation frequency of: $\omega_{nut} = 2\pi J_{IS}$.

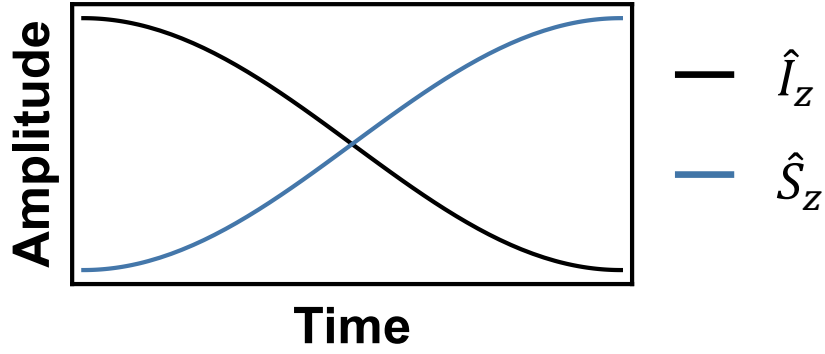


FIGURE 3.6: Transfer of $\hat{I}_z \rightarrow \hat{S}_z$ under the action of a theoretical anisotropic HH Hamiltonian of the form in equation 3.14 for a spin-1/2 pair and with a scaling factor of $\frac{1}{2}$. The period is given by $1/J$.

3.4.1 DualPol simulated robustness

The simulated robustness of the DualPol sequence against S -spin rf amplitude mismatch and S -spin rf resonance offset for I to S spin polarisation transfer in a two spin-1/2 spin system is explored with a comparison to the refocused-INEPT [61] sequence and standard Hartmann-Hahn sequence [62].

In the following simulations, the following time independent background Hamiltonian is employed:

$$\hat{H} = 2\pi J(\hat{I}_z \cdot \hat{S}_z) + 2\pi k 1000 \hat{S}_z \quad (3.15)$$

where $J = 10$ Hz such that the optimal duration, T , for $I \rightarrow S$ spin polarisation transfer for all sequences simulated here is given by: $T = \frac{1}{J} = \frac{1}{10}$ seconds.

The k parameter controls the rf resonance offset of the S spin in the rotating frame.

rf pulses of finite duration are simulated using the following rf Hamiltonian:

$$\hat{H}_{rf}(A, \hat{I}_\phi, \hat{S}_\phi) = 2\pi \omega_{nut}(\hat{I}_\phi + A \hat{S}_\phi) \quad (3.16)$$

where terms containing ϕ control the phases of the pulse on the respective spins, A is a parameter that controls the rf amplitude mismatch on the S spin and ω_{nut} is the nutation frequency of the pulse, which was kept at a constant value of: $\omega_{nut} = 1$ kHz.

The duration of a pulse is given by:

$$\text{Pulse duration}(\beta) = \frac{\beta}{2\pi |\omega_{nut}|} \quad (3.17)$$

where β is desired the flip angle of the pulse.

3.4.1.1 DualPol sequence

The simulated DualPol sequence is shown in figure 3.7.

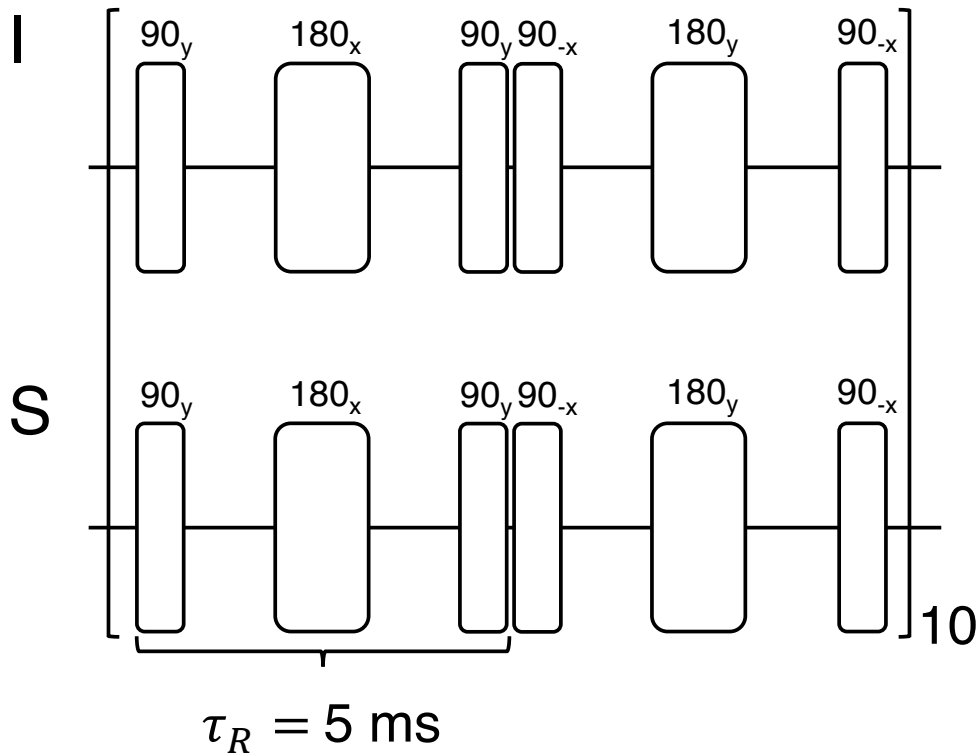


FIGURE 3.7: Simulated DualPol sequence for $\hat{I}_z \rightarrow \hat{S}_z$ polarisation transfer. R-sequence duration given by: $\tau_R = 5$ ms. Loop counter $L = 10$ for a total of 20 R-elements with a total duration $T = 100$ ms.

3.4.1.2 Refocused-INEPT sequence

The simulated refocused-INEPT sequence is shown in figure 3.8.

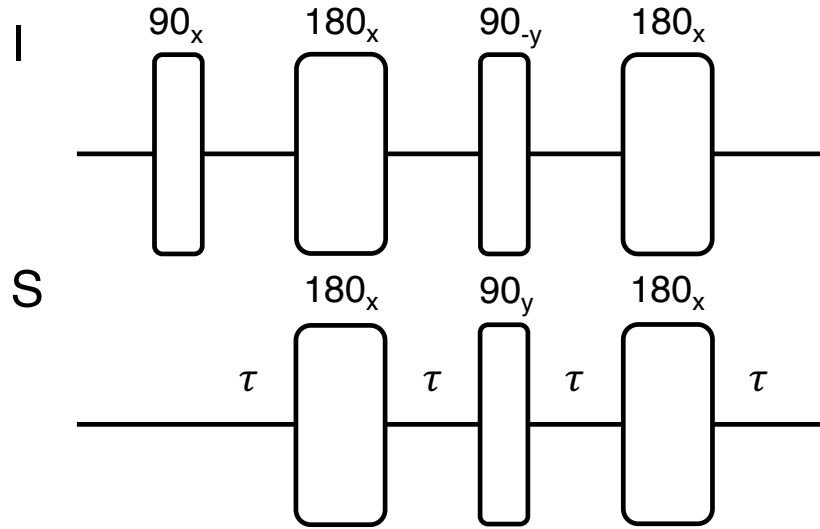


FIGURE 3.8: Simulated refocused-INEPT sequence for $\hat{I}_z \rightarrow \hat{S}_x$ polarisation transfer.
 $\tau = \frac{1}{4J} = \frac{1}{40}$ seconds.

3.4.1.3 Hartmann-Hahn sequence

The simulated Hartmann-Hahn sequence is shown in figure 3.9. The spin locking fields were simulated using the rf Hamiltonian in equation 3.16 and where the phase was parameter $\phi = x$ for both I and S and the pulse duration was set to $\frac{1}{J}$. The nutation frequency of the spin locking fields was 1 kHz.

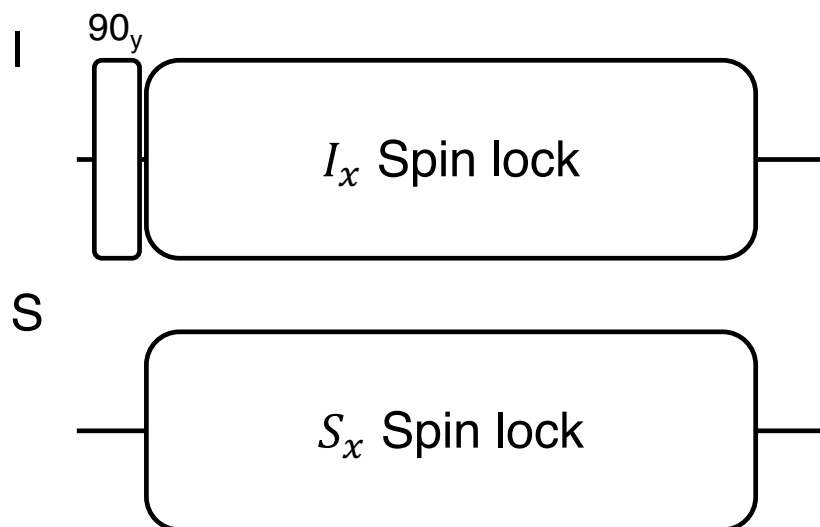


FIGURE 3.9: Simulated Hartmann-Hahn sequence for $\hat{I}_z \rightarrow \hat{S}_x$ polarisation transfer. Spin lock duration is equal to $\frac{1}{J}$.

3.4.1.4 Robustness against S spin rf resonance offset

The simulated robustness of a given pulse sequence against S spin rf resonance offsets is attained by plotting the $\hat{I}_z \rightarrow \hat{S}_z$ polarisation transfer efficiency as a function of the k parameter in the background Hamiltonian (equation 3.15). For these simulations, the A parameter in the simulated pulses (equation 3.16) was set to 1.

The simulated robustness against S spin rf Resonance offset for the DualPol, refocused-INEPT and Hartmann Hahn polarisation transfer pulse sequences is shown in figure 3.10. The DualPol sequence performs similarly to the refocused-INEPT sequence with respect to S spin resonance offset errors and both sequences perform significantly better than standard Hartmann Hahn sequence.

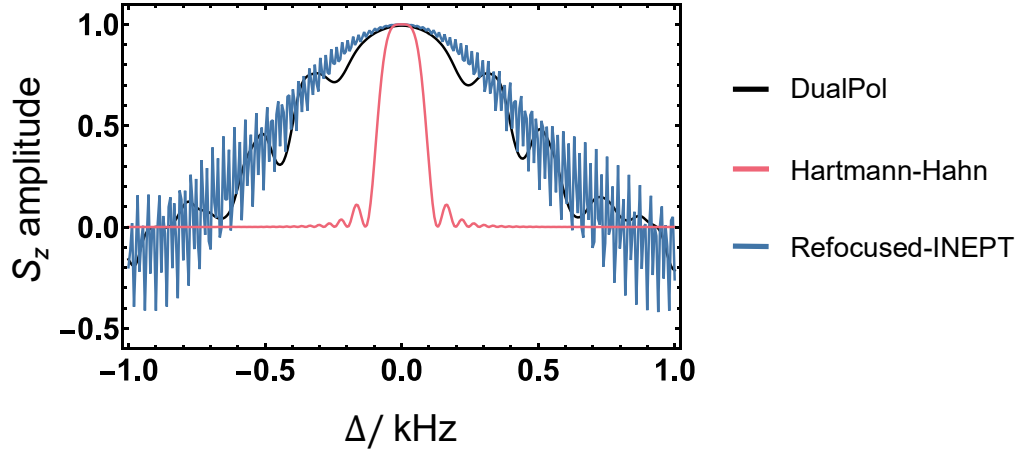


FIGURE 3.10: Robustness of DualPol, refocused-INEPT and Hartmann Hahn pulse sequences against S spin resonance offset for $\hat{I}_z \rightarrow \hat{S}_z$ polarisation transfer in a two spin-1/2 spin system.

3.4.1.5 Robustness against S spin rf amplitude mismatch

The simulated robustness of a given pulse sequence against S spin rf amplitude mismatch is attained by plotting the $\hat{I}_z \rightarrow \hat{S}_z$ polarisation transfer efficiency as a function of the A parameter in the rf Hamiltonian (equation 3.16). For these simulations, the k parameter for the background Hamiltonian (equation 3.15) was set to 0.

The simulated robustness against S spin rf amplitude mismatch for the DualPol, refocused-INEPT and Hartmann Hahn polarisation transfer pulse sequences is shown in figure 3.11. The DualPol sequence exhibits superior robustness against rf amplitude mismatch compared to both the refocused-INEPT and Hartmann Hahn pulse sequence.

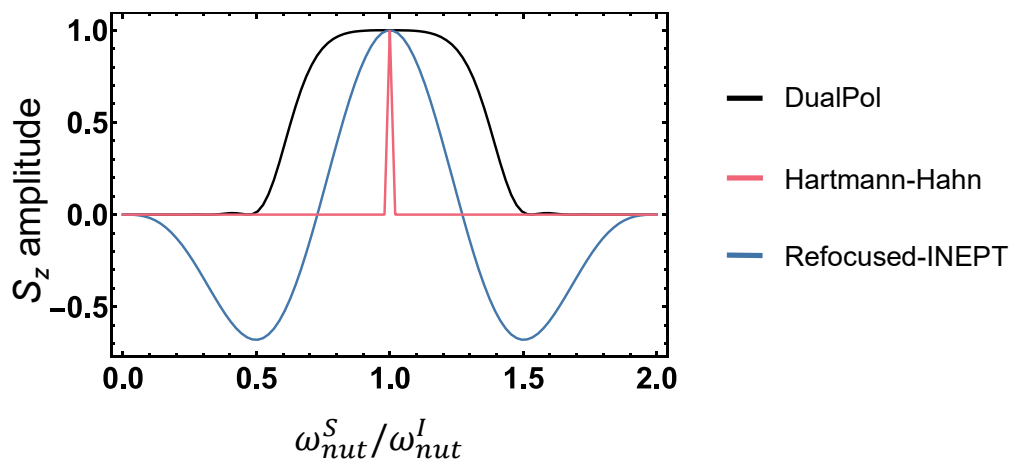


FIGURE 3.11: Robustness of DualPol, refocused-INEPT and Hartmann Hahn pulse sequences against S spin amplitude mismatch for $\hat{I}_z \rightarrow \hat{S}_z$ polarisation transfer in a two spin-1/2 spin system.

3.4.1.6 DualPol robustness contour plot

The robustness of the DualPol sequence for polarisation transfer in a two spin-1/2 spin system simultaneously against both S spin rf resonance offset and rf amplitude mismatch is shown in figure 3.12. The error resistant composite pulse [54] base R-element, coupled with the riffled modification gives the PulsePol (and hence DualPol) sequence significant resistance against both S spin rf amplitude mismatch and resonance offset errors [40]. Similarly, other Hartmann-Hahn type cross polarisation sequences, such as DIPSI [63], MLEV [64], WALTZ [65] and MGS [60, 66] sequences, have been noted as performing well in the presence of errors [64, 67, 68].

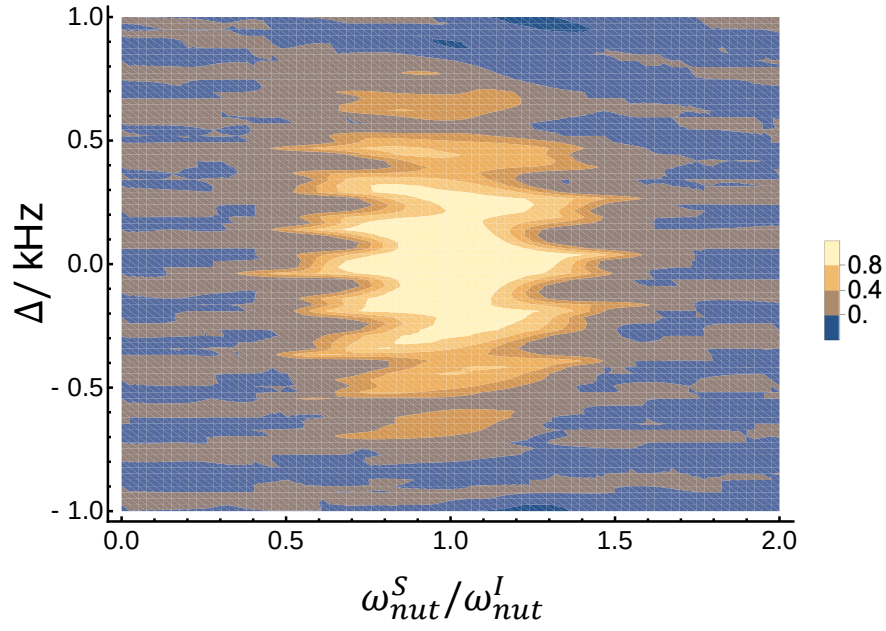


FIGURE 3.12: Contour plot of the robustness of the DualPol sequence for cross polarisation across two spin-1/2's. Robustness against rf amplitude mismatch shown on the horizontal axis and robustness against S spin resonance offset shown along the vertical. DualPol was simulated using 20 R-elements with a total duration of $1/J$ where $J = 10$ Hz. The contours represent the different I to S spin transformation amplitudes.

Conversely, The robustness of the standard Hartmann-Hahn cross polarisation sequence in a two spin-1/2 spin system simultaneously against both S spin rf resonance offset and rf amplitude mismatch is shown in figure 3.13.

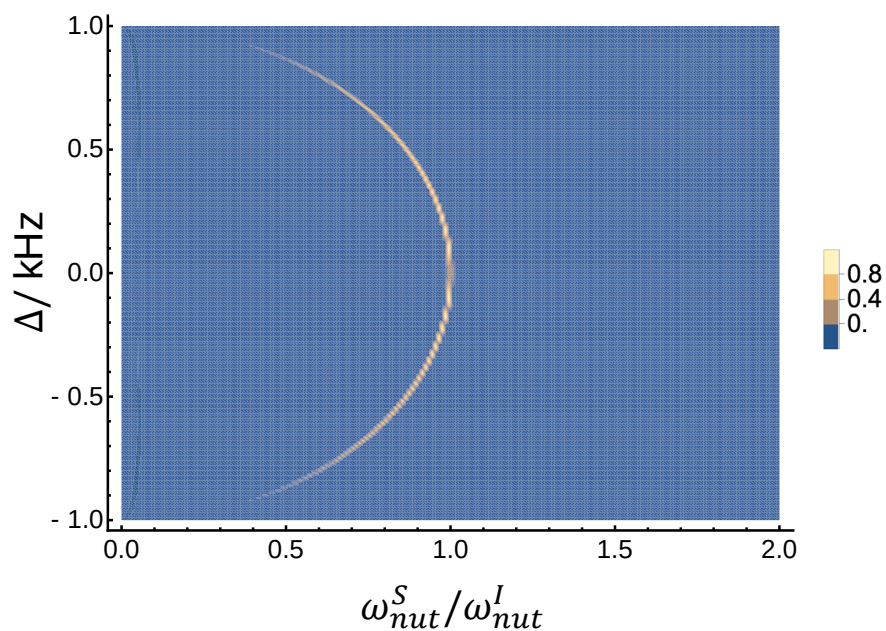


FIGURE 3.13: Contour plot of the robustness of the standard Hartmann-Hahn sequence for cross polarisation across two spin-1/2's. Robustness against rf amplitude mismatch shown on the horizontal axis and robustness against S spin resonance offset shown along the vertical. Sequence was simulated with a total duration of $1/J$ where $J = 10$ Hz. The contours represent the different I to S spin transformation amplitudes.

The standard Hartmann-Hahn sequence is highly sensitive to both rf mismatch and S spin resonance offset errors; hence, is a less versatile sequence for performing polarisation transfers.

Chapter 4

^{103}Rh NMR

In this chapter, we introduce the ^{103}Rh nucleus and discuss its NMR properties. We see how the ^{103}Rh NMR technique is plagued by various experimental difficulties that have prevented it from becoming a mainstream practice - in spite of the ubiquitous presence of rhodium containing catalysts in industry and research alike [69, 70, 71, 72, 73, 74, 75, 76]. Yet, we will also see that, through the development of NMR methodology, the accessibility of the technique can be greatly improved. Finally, we evaluate the potential of ^{103}Rh spin pairs for sustaining long-lived singlet spin order.

4.1 The ^{103}Rh nucleus

The ^{103}Rh nucleus carries the distinction of being one of only four spin-1/2 nuclei with a natural abundance of 100%, with the others being ^{19}F , ^{31}P and ^{89}Y . Yet, it has largely been neglected by spectroscopists. So much so, ^{103}Rh belongs to a collection of nuclei Brian Mann dubbed *Cinderella nuclei* [77], i.e spin-1/2 transition metal nuclei with very small gyromagnetic ratios.

TABLE 4.1: Gyromagnetic ratio (γ) of ^{103}Rh relative to ^1H and ^{13}C . Note the negative gyromagnetic ratio of ^{103}Rh .

Nucleus	$\gamma / 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$	γ relative to ^1H
^1H	26.752	1
^{13}C	6.728	0.251
^{103}Rh	-0.847	-0.0317

4.2 Sensitivity

As discussed in section 1.2.13, standard NMR sensitivity is proportional to $\gamma^{\frac{5}{2}}$; therefore, ^{103}Rh NMR signals are often obscured by a dense fog of background noise. Compounding the misery further, many ^{103}Rh complexes exhibit poor solubility in most NMR solvents, so the number of precessing ^{103}Rh spins per sample is limited. Consequently, since the seminal example from 1979 [78], directly detected ^{103}Rh spectra have been seldom reported in the literature [79, 80, 81, 82].

4.3 Acoustic ringing

An unfortunate feature of many ^{103}Rh spectra is an oscillating baseline caused by so called acoustic ringing, which is a phenomenon associated with the very small gyromagnetic ratio of ^{103}Rh . ^{103}Rh rf pulses induce mechanical oscillations in the metal components of the magnet and probe that in turn generate rf signals that are picked up by the receiver [83, 84].

Acoustic ringing may be alleviated by introducing a 'dead time' before signal acquisition to allow the ringing to dissipate. The time taken for acoustic ringing to dissipate after the final ^{103}Rh pulse is on the order of a few milliseconds. The introduction of a dead time may in theory introduce undesired phasing effects - but these may be compensated against using various echo techniques [85]. Moreover, ringing may be mitigated by *overcoupling* the probe (i.e purposely adjusting the probe such that it is slightly mismatched), which helps to attenuate the extent of ringing picked up by the receiver - albeit at a cost to signal sensitivity [86, 87, 83, 85, 84].

4.4 Chemical shielding

The NMR spectra of ^{103}Rh complexes are characterised by a wide chemical shift range spanning $\sim 12,000$ ppm [77, 88, 89], which is attributed to the large variability in shielding tensors inherent to ^{103}Rh nuclei - as well as transition metals in general [90]. Furthermore, ^{103}Rh shielding tensors are often highly anisotropic; thus shielding is significantly modulated during molecular tumbling. This culminates in ^{103}Rh spin relaxation in liquids typically being dominated by the CSA mechanisms - especially in complexes with low molecular symmetry [91].

The total ^{103}Rh shielding (σ) can be dissected into a diamagnetic component (σ_D), which originates from the core electrons and a paramagnetic component (σ_P), which arises from the mixing of excited and ground electronic states within the frontier d-orbitals [88, 77, 92, 89].

$$\sigma = \sigma_D + \sigma_P \quad (4.1)$$

The diamagnetic contribution opposes the external magnetic field and hence increases shielding at the ^{103}Rh nuclear site. This contribution is relatively insensitive to the ^{103}Rh environment and has been estimated for ^{103}Rh to be on the order of -4500 to -5000 ppm [93, 94]. Conversely, the paramagnetic contribution augments the external magnetic field and hence results in *deshielding* at the ^{103}Rh site. The degree of paramagnetic shielding varies dramatically depending on a given complex's coordination sphere and ligand field strength. Indeed, it is the paramagnetic contribution that is responsible for the wide chemical shift range seen for ^{103}Rh .

The paramagnetic shielding is determined principally by the energy difference between ground and excited electronic states (ΔE); as well as the ^{103}Rh atomic radius (r). For a given rhodium complex, ΔE depends on the ligand field strength and hence varies in accordance with the spectrochemical series. Whereas, r depends on the degree of d-orbital contraction brought about by ligation and hence varies in accordance with the so called nephelauxetic (Greek: cloud expanding) series [95, 96, 97]. Ergo, coordination to a weak field (small ΔE) 'hard' (small r) ligand corresponds to large ^{103}Rh chemical shifts and coordination to a strong field (large ΔE) 'soft' (large r) corresponds to small ^{103}Rh chemical shifts.

Additional contributions to shielding can arise from solvent effects and dynamic processes such as chemical exchange [95, 98]. Moreover, the substitution of an element near the ^{103}Rh centre by a different isotope of the same element (i.e. ^{18}O for ^{16}O or ^{35}Cl for ^{37}Cl etc) can effect the ^{103}Rh chemical shift by altering the relevant bond(s) vibrational energies in a process known as the secondary isotope effect [99].

^{103}Rh shielding tensors are sensitive to temperature fluctuations, with the isotropic ^{103}Rh chemical shift deviating by as much as 0.5-1.5 ppm/K [88, 92]. The origin of this dependence is due to the effect of temperature on the vibrational motion of metal-ligand bonds [98]. Failure to control sample temperature during lengthy experiments will contribute to ^{103}Rh signal broadening.

4.5 Relaxation

In general, owing to the low gyromagnetic ratio, ^{103}Rh spin relaxation is often inefficient. Not least relaxation induced by the dipolar mechanisms, which are curtailed by small dipolar couplings inherent to ^{103}Rh nuclei - even over short distances. Conversely, in suitably anisotropic environments the ^{103}Rh CSA may prove large enough to induce significant spin relaxation. Furthermore, again under suitable conditions, spin rotation may likewise provide an important route to relaxation.

Long ^{103}Rh T_1 lifetimes can complicate the acquisition of ^{103}Rh NMR spectra and parameters, for, in experiments requiring multiple scans, one finds themselves waiting an inordinately long time for the re-equilibration of ^{103}Rh longitudinal polarisation in between transients.

4.6 ^{103}Rh NMR methodology

Clearly, the unaided direct detection of ^{103}Rh resonances is impractical and almost always necessitates the, often time consuming, averaging of *many* transients - even at higher fields where net ^{103}Rh spin polarisation is greater.

Consequently, in the years since its inception, polarisation transfer techniques have become central to the methodology of ^{103}Rh NMR, wherein scalar couplings to more sensitive nuclei are exploited to improve sensitivity.

Polarisation transfer methods have been employed in the acquisition of numerous ^{103}Rh spectra in instances where unaided detection would otherwise be impractical [100, 101, 102, 103, 104, 105, 88, 92, 106].

As discussed in section 1.6.2 the largest sensitivity enhancements are achieved when one opts to observe resonances indirectly - on the more sensitive heteronucleus, which fully takes advantage of the far superior signal to noise afforded by a larger gyromagnetic ratio.

The relative sensitivity enhancements afforded by different pulse sequence methodologies relative to unaided direct ^{103}Rh detection are shown in figure 4.1 [89].

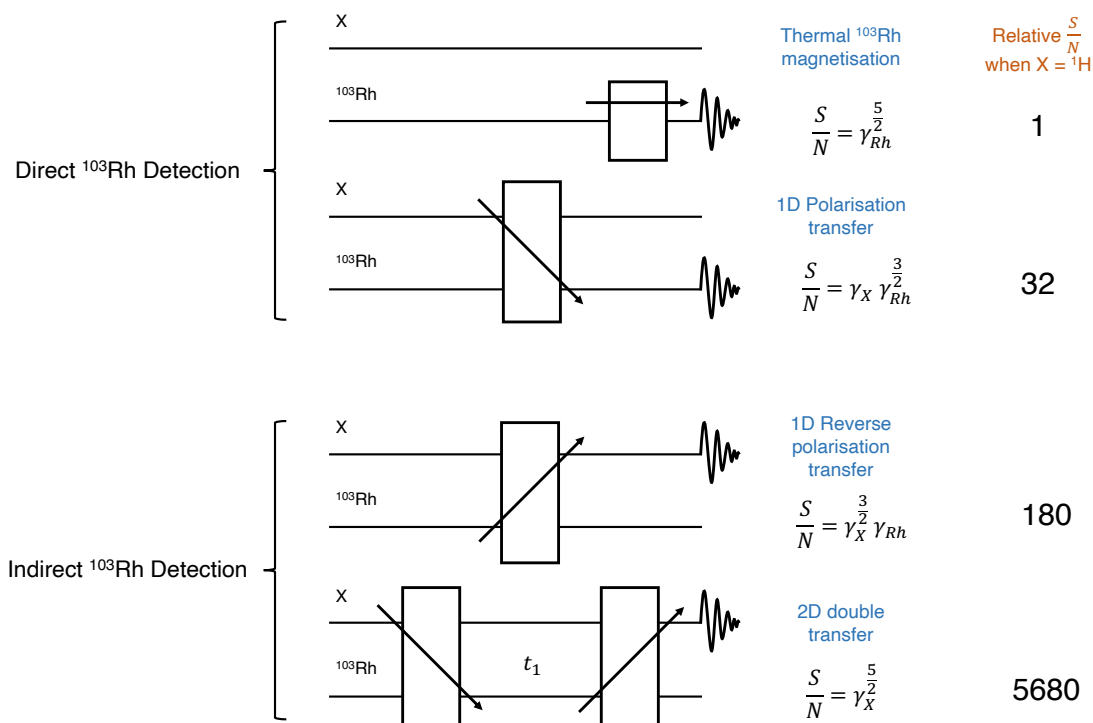


FIGURE 4.1: Sensitivity of different pulse sequences where 'X' denotes a given heteronucleus.

In 2021, Caló et al. combined INEPT and HMQC polarisation transfer methods in the design of a triple resonance 2D experiment for the rapid detection of ^{103}Rh chemical shifts belonging to a range of different ^{103}Rh paddlewheel complexes [92]. The experiment they devised was able to exploit the sensitivity of protons - even in complexes that lacked a direct ^1H - ^{103}Rh scalar coupling. Where required, ^1H and ^{103}Rh nuclei were instead linked via a mutually coupled ^{13}C nucleus.

The triple resonance pulse sequence begins by transferring ^1H polarisation to a ^{13}C via an INEPT block. Then, HMQC is performed between the ^{13}C and ^{103}Rh ; after which, polarisation is returned back to the ^1H for signal readout by a reverse-INEPT block.

With this sequence, Caló et al. produced 2D spectra consisting of rhodium resonances in as little as just 4 minutes; whereas unaided direct observation of the same resonances would have taken many hours.

The advent of triple resonance pulse sequences has significantly broadened the scope of complexes accessible to the ^{103}Rh NMR technique. In suitable cases, ^{103}Rh spectral data can now be acquired rapidly and without the need for time consuming experiments with many acquired transients.

Unfortunately, the heteronuclear spin operators generated by HMQC techniques are unsuitable for the estimation of ^{103}Rh longitudinal and transverse relaxation time constants, which is a limitation we aim to address in this thesis.

4.7 Potential of ^{103}Rh for harbouring long-lived spin order

Given that singlet relaxation rates are proportional to the square of the gyromagnetic ratio, singlet order generated in ^{103}Rh spin pairs is anticipated to exhibit substantially longer lifetimes than those already seen in ^{13}C spin pairs, which currently set the benchmark for the longest singlet lifetimes with T_s time constants exceeding an hour in certain molecules [33, 34].

Auspiciously, the ^{103}Rh paddlewheel complexes studied by Caló et al. contain a ^{103}Rh spin pair at the centre and hence present the ideal basis for generating ^{103}Rh singlet order. Indeed, in this work, we will investigate the potential of ^{103}Rh singlet order in the rhodium formate paddlewheel complex; wherein a single formate ligand has been selectively ^{18}O labelled to break the symmetry across the dirhodium bond via the secondary isotope effect [107, 99] - generating a strongly coupled ^{103}Rh - ^{103}Rh spin pair and allowing access to the ^{103}Rh singlet state.

Moreover, rhodium formate exhibits heteronuclear scalar couplings between ^{103}Rh and ^1H nuclei, which facilitates the use of polarisation transfer techniques for the improvement of ^{103}Rh NMR sensitivity.

In solution, solvent molecules reversibly ligate the axial positions of the rhodium formate paddlewheel complex as shown in figure 7.1.

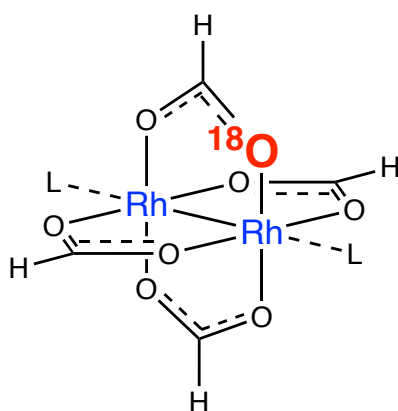


FIGURE 4.2: Molecular structure of rhodium formate paddlewheel complex with a formate ligand singly ^{18}O labelled. The symmetry across the dirhodium bond has been broken, allowing access to the rhodium singlet state. ^{103}Rh spin pair shown in blue and reversible axial ligation by solvent molecules (L) denoted by dashed lines.

4.8 Summary

^{103}Rh is a nucleus that presents significant challenges in its NMR spectroscopy principally due to its inherent insensitivity, which itself is a consequence of its small gyromagnetic ratio. And yet, it is this inherent insensitivity that makes ^{103}Rh an attractive nucleus for sustaining long-lived singlet order, where the ^{103}Rh paddlewheel complexes present the ideal basis for its generation.

Through the development of sensitivity enhancing methodology, we stand to improve the accessibility of the ^{103}Rh NMR technique; as well as to broaden the scope of the practice to encompass singlet NMR.

Chapter 5

Experimental

5.1 Probe tuning

^1H and ^{103}Rh Spectra were acquired at a magnetic field strength of 9.4 T using a standard commercial Bruker 5 mm NMR BBO probe ($^1\text{H}/^2\text{H}/^{109}\text{Ag}-^{31}\text{P}$) equipped with a z-gradient with a maximum strength of 50 G cm^{-1} . ^{13}C spectra were acquired at a magnetic field strength of 14.1 T using a standard commercial Bruker 5 mm TBI probe ($^{13}\text{C}/^1\text{H}/^2\text{H}/^{109}\text{Ag}-^{31}\text{P}$) equipped with a z-gradient with a maximum strength of 50 G cm^{-1} .

Proton resonances are referenced to the absolute frequency 400.14300 MHz and ^{13}C resonances are referenced to the absolute frequency 150.90300 MHz; whereas ^{103}Rh resonances are referenced to an absolute frequency that is proportional to the protons ($\Xi(^{103}\text{Rh}) = 3.16\%$) per the most common convention [88, 89], and which at 9.4 T corresponds to an absolute frequency of 12.64452 MHz.

Probes were tuned manually by hand beyond manufacturer specifications to reach ^{103}Rh ; however were left slightly overcoupled to reduce ringdown times.

The radiofrequency amplitudes on the ^1H and ^{103}Rh channels were both adjusted to give an intentionally matched nutation frequency of $\omega_{\text{nut}}/(2\pi) \simeq 4\text{ kHz}$, corresponding to a 90° pulse duration of $62.5\text{ }\mu\text{s}$.

5.2 Radio frequency channel isolation

To prevent noise from the ^{103}Rh channel interfering in spectra, rf channels were isolated using standard low and bandpass filters. At the preamplifier output: a 30 MHz lowpass filter (Chemagnetics) on the ^{103}Rh channel, a 400 MHz bandpass filter (K&L

Microwave) on the ^1H channel, and a 61 MHz bandpass filter (FSY Microwave) on the ^2H lock channel was installed.

5.3 Motorised sample shuttle

Field cycling of NMR samples was performed using a motorised fast shuttling system [108] installed above our Oxford 9.4 T NMR magnet as described below.

The sample is held by a spinor, which is attached to a track that extends up and out of the magnet and into the stray field. This track is connected to a motor, which receives commands inputted to the spectrometer by the user to transport the sample out of and back into the magnet. The height of the sample relative to the centre of the magnet determines the field strength it experiences as shown by figure 5.1.

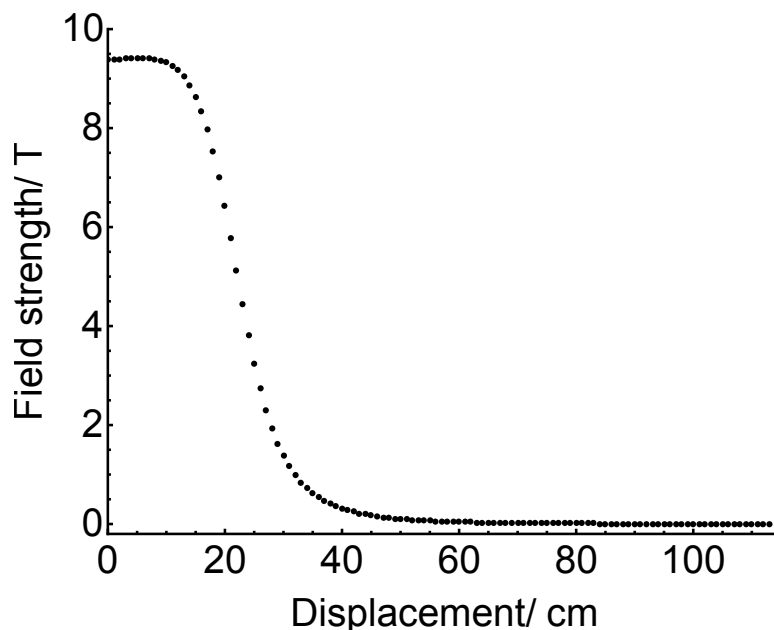


FIGURE 5.1: Measured field profile of the Oxford 9.4 T magnet. Total magnetic field strength in Tesla is plotted against displacement from the centre of the NMR probe in cm.

A magnetic shield, which is placed above the magnet, provides the user a controllable and homogeneous low field environment.

The user has control over the shuttling parameters including the transport duration and shuttling profile. In the experiments described here, the transport duration was kept constant at 1 second. Maximum sample height was 113.8 cm, which corresponds to the centre of the magnetic shield; where the magnetic field was set to 1 mT.

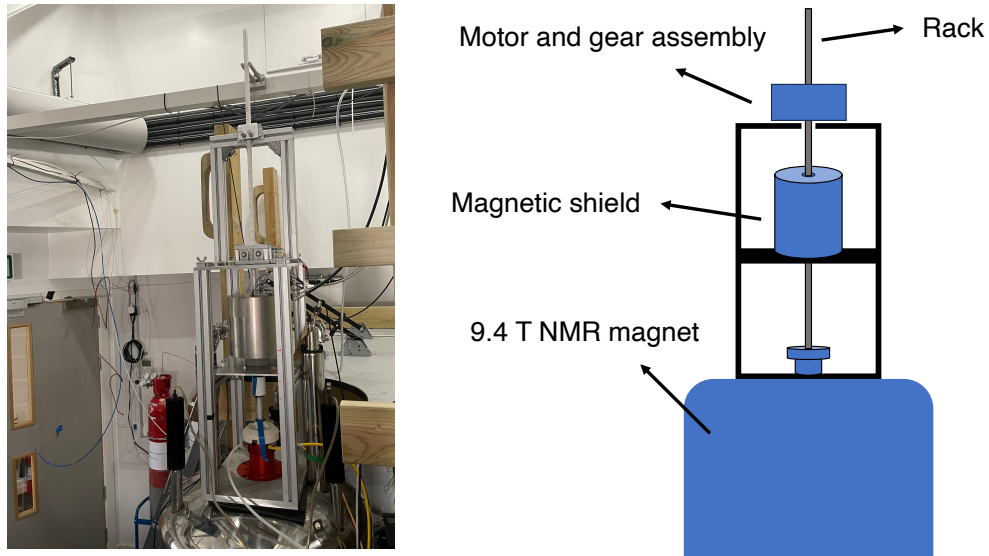


FIGURE 5.2: (Left) photograph of motorised shuttle installed above a 9.4 T magnet. (Right) simplified schematic of shuttling system. In both the photograph and schematic, the shuttle is shown in the down position; thus the sample is located in the centre of the magnet high field region.

Samples undergoing shuttling follow a sigmoidal trajectory of the following form:

$$\text{Displacement}(t) = \frac{L(-1 + \exp \{k + k(-1 + 2t)\})}{(-1 + \exp \{k\})(1 + \exp \{k + k(-1 + 2t)\})} \quad (5.1)$$

where L is the maximum displacement of the sample relative to the centre of the NMR probe and k is the steepness of the curve.

The sigmoidal shuttling ensures that the sample follows a smooth trajectory - minimizing jerk forces which can otherwise lead to the sample tube slipping; as well as sample sloshing. Moreover, under a sigmoidal trajectory, the sample moves more gradually through the rapidly changing magnetic field at the centre of the magnet such that adiabaticity of the field cycling is ensured.

In this work, the steepness parameter k was set to 6, which, when setting the maximum displacement to $L = 1$ m and using a total shuttling time of 1 second, corresponds to the shuttling profile shown in figure 5.3.

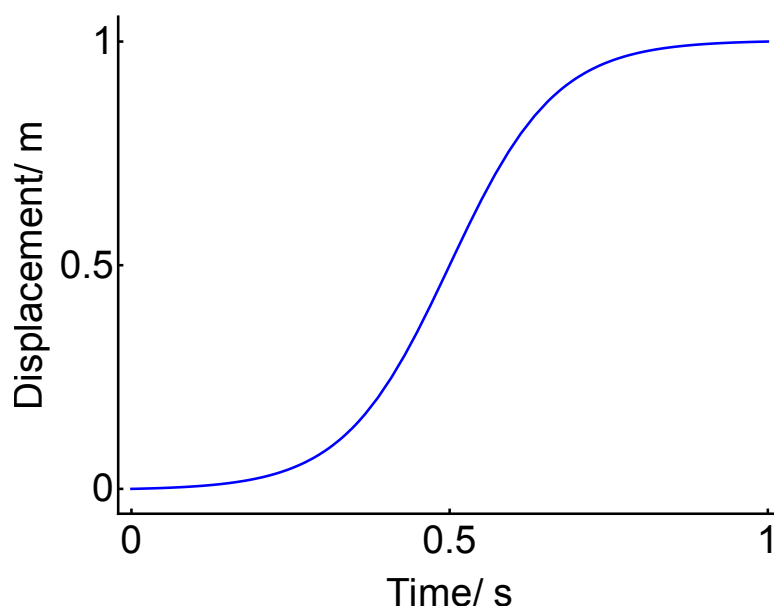


FIGURE 5.3: Plot of sample displacement from the centre of the magnet vs time for shuttling of sample 1 m out of the magnet centre over 1 second.

During shuttling experiments, the lock was turned off to suppress spectral artefacts.

5.4 Computational

Quantum chemical geometry optimisation and shielding tensor calculations for the rhodium formate complex axially ligated by solvent THF molecules were performed using the ORCA program package version 5.0.3 [109]. ^{103}Rh shielding tensors were computed at the TPSSh/SARC-ZORA-TZVPP level of theory.

Rhodium formate spin-rotation tensors were provided by Alexej Jerschow (see Appendix G).

Relaxation rate calculations and spin dynamics simulations and computations were performed using the SpinDynamica Mathematica package [110]. When calculating maximum theoretical enhancement factors afforded by different polarisation transfer pulse sequences, a numerical simulation is performed in which the enhancement factor is plotted against the relevant time parameter. The enhancement factor theoretical maximum is then taken as the value of the *first* maximum of the plot.

5.5 Pulse sequence design

The pulse sequences presented in this work have a modular design and are formed from smaller pulse sequence elements.

5.6 Composite pulses

Composite pulses were used to minimize the effects of rf field inhomogeneity and are denoted by shaded black rectangles in the pulse sequence diagrams. All composite pulses are implemented using the symmetrized BB1 composite pulse scheme [111, 112] in which a simple pulse β_ϕ (where β is the flip angle and ϕ is the phase) is replaced by:

$$(\beta/2)_\phi 180_{\phi+\theta_W} 360_{\phi+3\theta_W} 180_{\phi+\theta_W} (\beta/2)_\phi \quad (5.2)$$

Where $\theta_W = \arccos(-\beta/(4\pi))$. For the $\pi/2$ and π flip angles used throughout this work, of which corresponds to the following sequences:

$$90_\phi \rightarrow 45_\phi 180_{\phi+97.18} 360_{\phi+291.54} 180_{\phi+97.18} 45_\phi \quad (5.3)$$

$$180_\phi \rightarrow 90_\phi 180_{\phi+104.48} 360_{\phi+313.43} 180_{\phi+104.48} 90_\phi \quad (5.4)$$

Chapter 6

^{103}Rh NMR spectroscopy and relaxometry of $\text{Rh}(\text{acac})_3$

In this chapter, we utilise the DualPol cross polarisation sequence in the proton enhanced ^{103}Rh NMR spectroscopy of $\text{Rh}(\text{acac})_3$. Pulse sequence methodology for the acquisition of directly detected ^{103}Rh spectra with effective acoustic ringing filtration; as well as for the rapid measurement of ^{103}Rh T_1 and T_2 relaxation time constants over a range of magnetic field strengths and temperatures is presented.

In this implementation, the DualPol sequence (figure 3.5) uses an R-element duration of $\tau_R = 70$ ms and a repetition number of $L = 11$. The total DualPol sequence duration is $T = 2\tau_R L = 1.54$ s.

Experimental optimisation of the the DualPol sequence for $^1\text{H} \leftrightarrow ^{103}\text{Rh}$ polarisation transfer in $\text{Rh}(\text{acac})_3$ is shown in Appendix A.

In this chapter, experiments were performed on a saturated (~ 140 mM) solution of rhodium acetylacetonate ($\text{Rh}(\text{acac})_3$) dissolved in $350\ \mu\text{L}$ deuterated trichloromethane (CDCl_3) and contained in a standard NMR sample tube. The $\text{Rh}(\text{acac})_3$ powder was originally purchased from Sigma-Aldrich and is a yellow powder, which dissolves in CDCl_3 to form a deep yellow solution. The structure of $\text{Rh}(\text{acac})_3$ is given in figure 6.1.

The ^{103}Rh is weakly coupled to the methine protons on each acac ligand; hence, neglecting the presence of any ^{13}C nuclei, $\text{Rh}(\text{acac})_3$ represents an AX_3 spin system.

For shuttling experiments described here the total shuttling duration was kept constant at 2 seconds, in both directions.

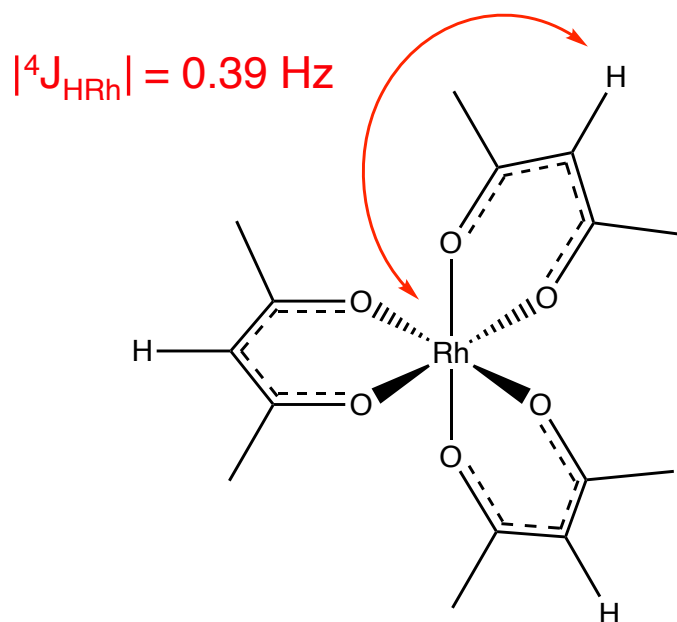


FIGURE 6.1: $\text{Rh}(\text{acac})_3$ structure. This work exploits the $^4J_{\text{HRh}}$ scalar couplings for polarisation transfer between the ^{103}Rh and methine ^1H nuclei.

6.1 NMR spectra

6.1.1 ^1H spectrum

The $\text{Rh}(\text{acac})_3$ ^1H spectrum shown in figure 6.2(a) features two resonances: a singlet at 2.170 ppm corresponding to the six methyl protons on each acac ligand and a weak doublet centred at 5.511 ppm corresponding to the acac methine protons. A zoomed in spectrum showing just the methine resonance is shown in figure 6.2(b).

Early studies on $\text{Rh}(\text{acac})_3$ did not observe couplings between the ^{103}Rh and any other nuclei [82]; however, in 2021 a $|^3J_{\text{CRh}}| = 1.1 \text{ Hz}$ coupling was observed [92] and furthermore, in this work we estimate a long range four bond ^{103}Rh - ^1H spin-spin coupling of $|^4J_{\text{HRh}}| = 0.39 \pm 0.01 \text{ Hz}$.

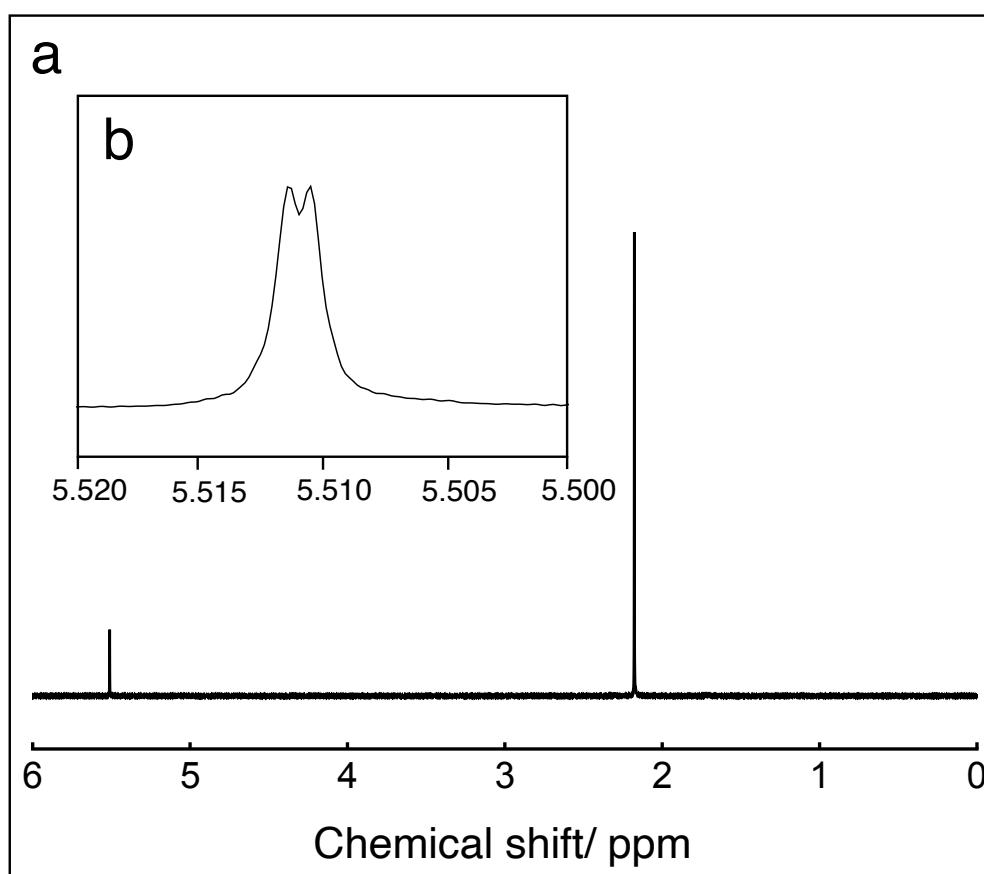


FIGURE 6.2: (a) ^1H spectrum of a ~ 140 mM solution of $\text{Rh}(\text{acac})_3$ in CDCl_3 , acquired at 9.4 T and at 298K in a single scan. Lorentzian line broadening (1 Hz) was applied (b) Expanded view of the methine resonance. Exponential line broadening (-0.2 Hz) was applied.

6.1.2 Proton enhanced ^{103}Rh spectra

The sequence shown in figure 6.3 was used for the acquisition of directly-detected ^{103}Rh spectra, enhanced by polarisation transfer from ^1H nuclei via the DualPol sequence.

After an initial pair of 90° pulses, used for the suppression of ringing artefacts (see below), a DualPol sequence transfers z-magnetization from the ^1H to the ^{103}Rh nuclei. ^{103}Rh z magnetisation is then promptly converted into observable transverse magnetization by a final 90° pulse.

Ringing artifacts are strongly suppressed by a phase-cycled pair of 90° pulses on the proton channel, before the polarisation transfer takes place. The signs of the ^1H magnetization and the ^{103}Rh receiver are simultaneously inverted in successive scans. Since the phases of the ringing are correlated with the phases of the pulses on the ^{103}Rh channel, the ringing is strongly suppressed in the ^{103}Rh spectrum. Further suppression of

ringing is achieved by additional phase cycling of the PulsePol blocks. The sign of the ^{103}Rh magnetization is invariant under global phase shifts of the DualPol sequence, while the ringing contribution is phase-correlated and largely cancels out. Similar logic has been used to design excitation schemes for ringing suppression in homonuclear NMR experiments [113, 114].

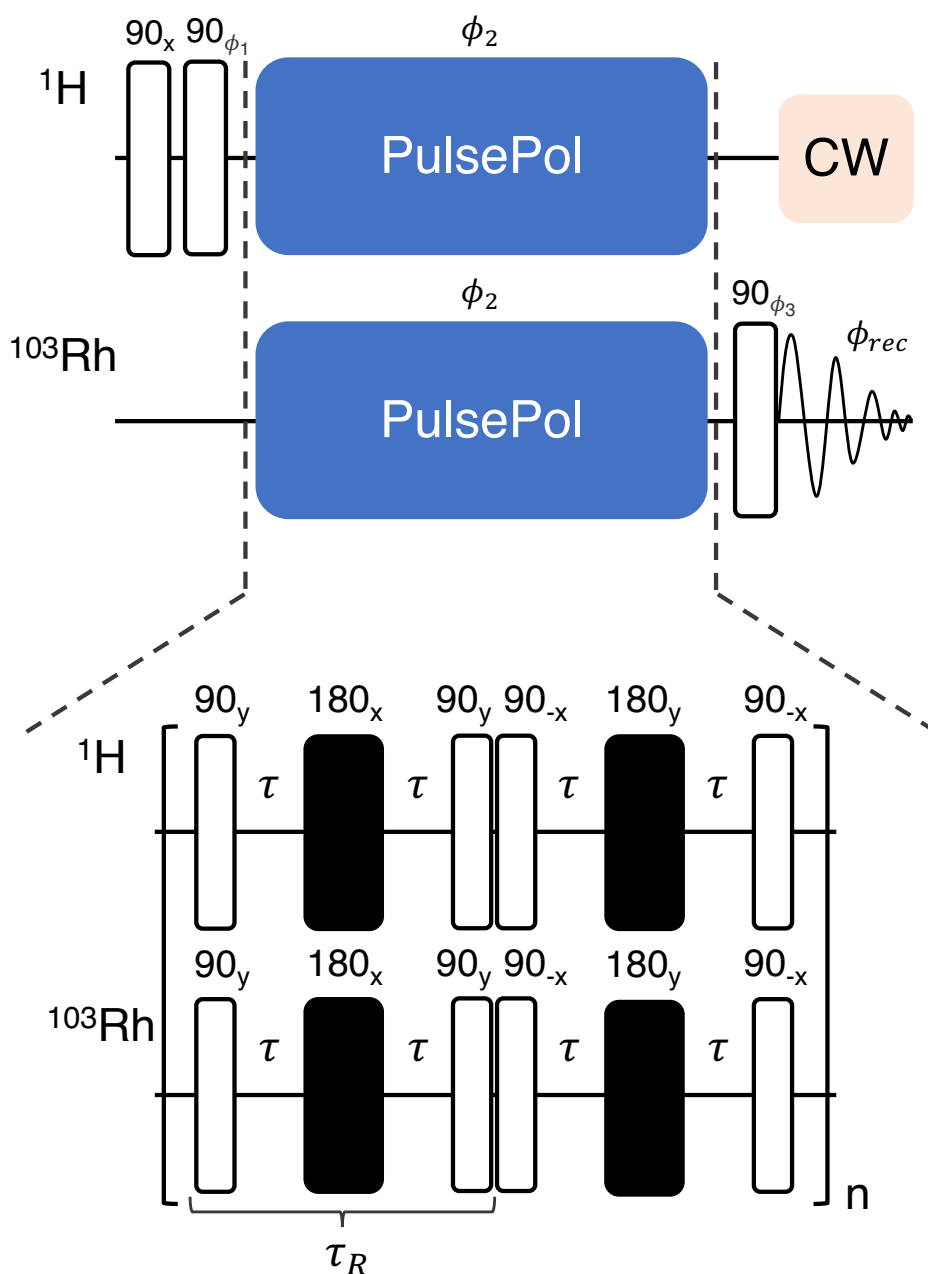


FIGURE 6.3: Pulse sequence for the acquisition of ^1H enhanced ^{103}Rh spectra where an expanded view of the DualPol pulse sequence module is shown at the bottom. The black rectangles indicate symmetrized BB1 composite 180° -pulses (equation 5.4) and τ indicates an interpulse delay. Phase cycles are given by: $\phi_1 = [-x, x, -x, x]$, $\phi_2 = [x, x, -x, -x]$, $\phi_3 = [x, x, x, x, y, y, y, y, -x, -x, -x, -x, -y, -y, -y, -y]$ and the receiver $\phi_{rec} = [x, -x, x, -x, y, -y, y, -y, -x, x, -x, x, -y, y, -y, y]$.

The sequence shown in figure 6.4 was used for the acquisition of a directly detected ^{103}Rh spectrum, enhanced by polarisation transfer from ^1H nuclei via the refocused-INEPT pulse sequence.

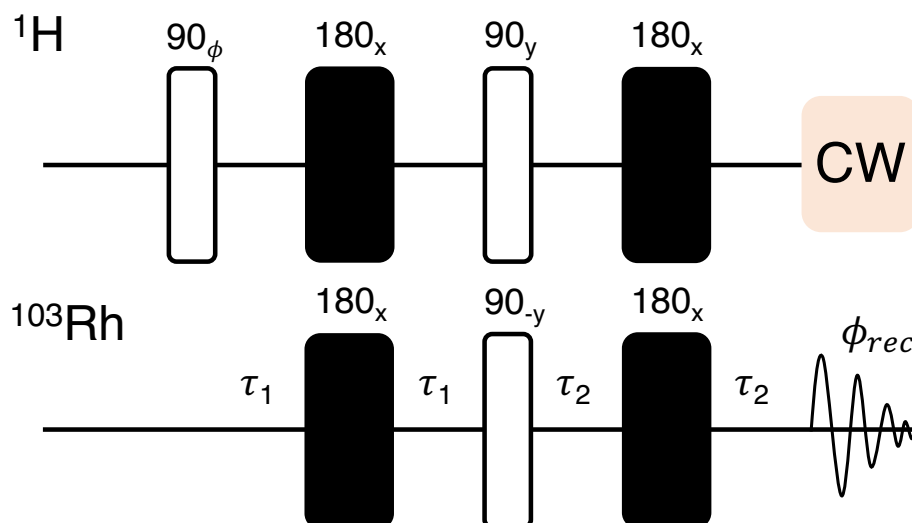


FIGURE 6.4: Pulse sequence for the acquisition of ^1H enhanced ^{103}Rh refocused-INEPT spectra. Phase cycles are given by $\phi = [x, x, -x, -x]$ and the receiver $\phi_{\text{rec}} = [x, x, -x, -x]$. The black rectangles indicate BB1 composite 180° pulses (equation 5.4).

The optimal refocused-INEPT delays for $A \rightarrow X$ polarisation transfer in an AX_3 spin system are given analytically by $\tau_1 = (1/4J)$ and $\tau_2 \simeq (1/10.2J)$ [61]. Assuming a ^1H - ^{103}Rh spin-spin coupling of $J_{\text{HRh}} = 0.39$ Hz, the theoretical optimum echo delay intervals are hence given by: $\tau_1 = 640$ ms and $\tau_2 = 252$ ms. In practice, these delays were optimised experimentally to yield: $\tau_1 = 460$ ms and $\tau_2 = 250$ ms. The τ_1 delay, which is sensitive to proton relaxation, deviates from the theoretical value whereas τ_2 is in good agreement.

Figure 6.5 shows directly detected $^{103}\text{Rh}\{^1\text{H}\}$ spectra as acquired using a single 90° ^{103}Rh pulse applied to ^{103}Rh polarisation at thermal equilibrium, DualPol and refocused-INEPT.

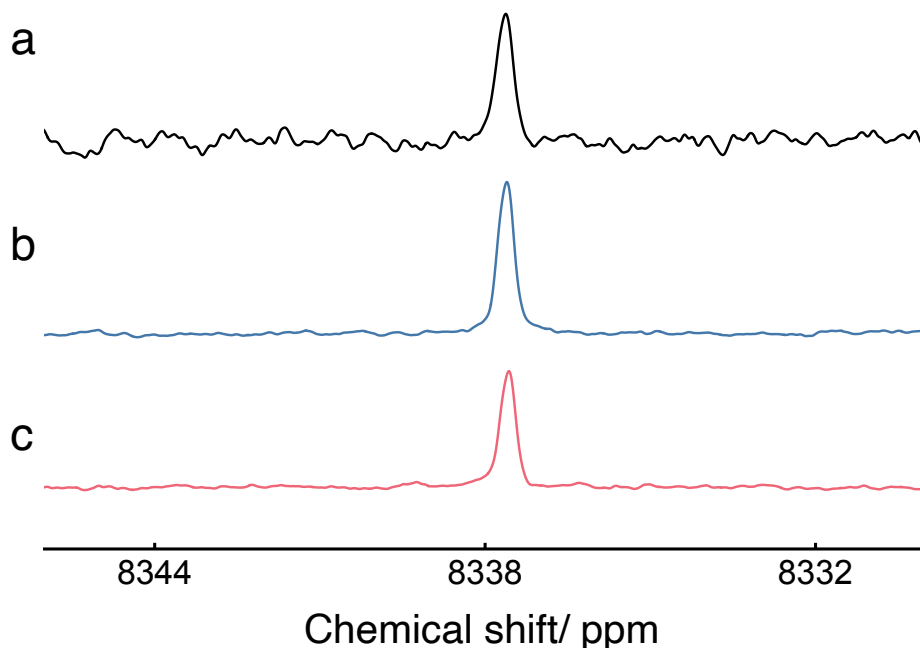


FIGURE 6.5: ^1H -decoupled ^{103}Rh NMR spectra of a ~ 140 mM solution of $\text{Rh}(\text{acac})_3$ in CDCl_3 , in a field of 9.4 T and a temperature of 295 K. Lorentzian line broadening (1 Hz) was applied to all spectra. ^{103}Rh chemical shifts are referenced to the absolute frequency ($\Xi(^{103}\text{Rh}) = 3.16\%$). (a) $^{103}\text{Rh}\{^1\text{H}\}$ spectrum, acquired using 300 transients, each using a single ^{103}Rh 90° pulse. The total experimental duration was ~ 12 hours. (b) $^{103}\text{Rh}\{^1\text{H}\}$ spectrum, acquired using 16 scans and the pulse sequence shown in figure 6.3, with $n = 11$ repetitions of the DualPol sequence. The total experimental duration was 5 minutes. (c) $^{103}\text{Rh}\{^1\text{H}\}$ spectrum, acquired using 16 scans and refocused-INEPT. The total experimental duration was 5 minutes.

All spectra exhibit a single peak centred at 8337.6 ppm. The DualPol sequence enhanced the ^{103}Rh signal strength by a factor of ~ 23 over thermal ^{103}Rh magnetisation; whereas the refocused-INEPT sequence yielded an enhancement factor of ~ 17 .

6.2 ^{103}Rh chemical shift temperature dependence

The ^{103}Rh chemical shift is temperature-dependent (see Figure 6.6). The temperature-dependence of the ^{103}Rh chemical shift is approximately linear over the relevant temperature range, with a gradient of ~ 1.90 ppm K^{-1} . This is in general agreement with the observation of ~ 1.60 ppm K^{-1} previously reported for the same complex [82, 92].

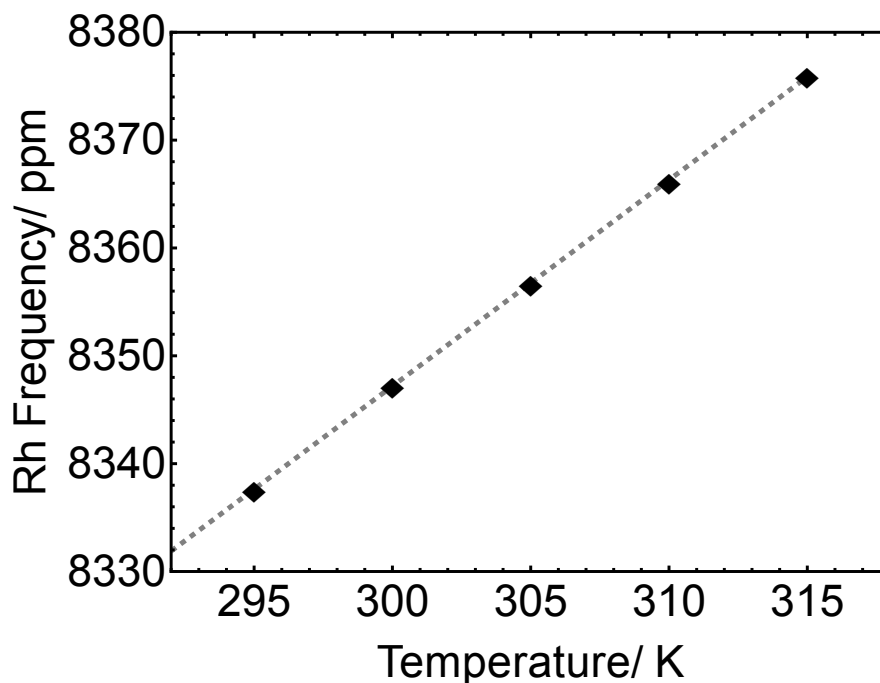


FIGURE 6.6: ^{103}Rh chemical shift of $\text{Rh}(\text{acac})_3$ at 9.4 T, as a function of temperature. The chemical shifts are referenced to the absolute frequency $\Xi(^{103}\text{Rh}) = 3.16\%$.

6.3 $\text{Rh}(\text{acac})_3$ ^{103}Rh T_2 measurement

6.3.1 Indirect ^{103}Rh T_2 pulse sequence

The sequence shown in figure 6.7 was used to measure the $\text{Rh}(\text{acac})_3$ ^{103}Rh T_2 relaxation time constant in the high field. The duration of individual spin echoes was kept at a constant duration of $\tau = 45$ ms.

Conversion of ^1H z-polarisation to ^{103}Rh z-polarisation is achieved via the DualPol sequence. ^{103}Rh transverse magnetisation is generated by a 90° pulse and allowed to decay during the subsequent train of m spin echoes, each of duration τ_{echo} . The ensuing 90° ^{103}Rh pulse returns the remaining transverse ^{103}Rh magnetisation back to longitudinal ^{103}Rh polarisation. A Proton destruction filter (figure 6.8) destroys any residual ^1H magnetisation before another DualPol cross-polarisation block transfers ^{103}Rh z-magnetisation back to ^1H z-magnetization. The proton z-filter (figure 6.9) selects for ^1H z-magnetization before observable transverse ^1H magnetisation is generated by the final 90° ^1H pulse. The pulse sequence is repeated varying the number of spin echoes m in order to follow the decay of ^{103}Rh transverse magnetization.

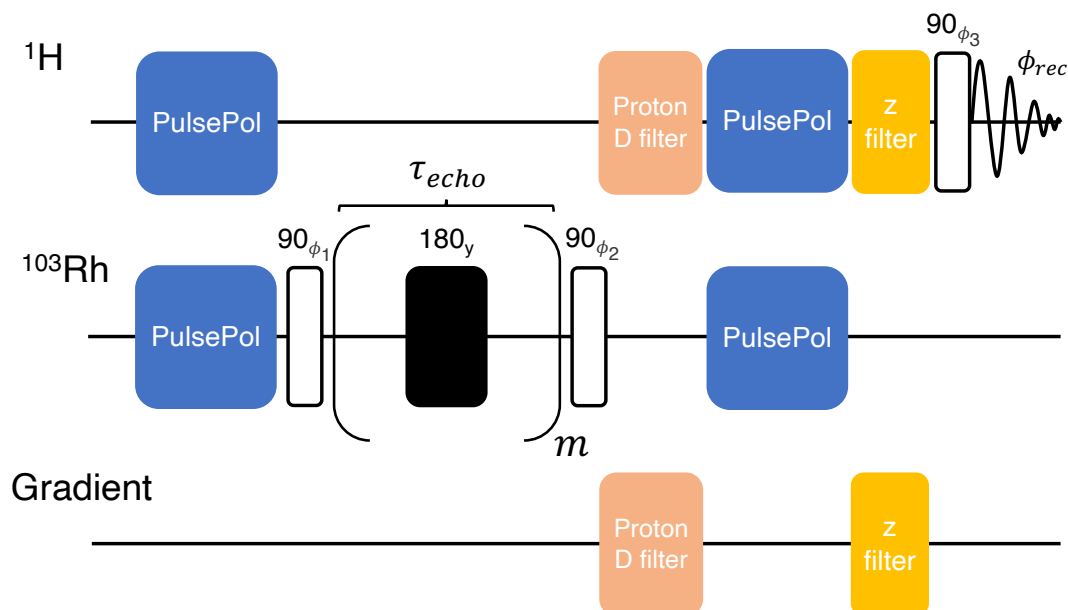


FIGURE 6.7: Sequence used for the indirect measurement of rhodium T_2 with detection on protons. Phase cycles are given by $\phi_1 = [x, x, -x, -x]$, $\phi_2 = [-x, x, -x, x]$, $\phi_3 = [x, x, x, x, y, y, y, y, -x, -x, -x, -x, -y, -y, -y, -y]$ and the receiver $\phi_{rec} = [x, -x, -x, x, y, -y, -y, y, -x, x, x, -x, -y, y, y, -y]$. The black rectangle indicates a BB1 composite π -pulse (equation 5.4).

The proton destruction filter (proton D filter) pulse sequence element is shown in figure 6.8 and has the net effect of dephasing residual proton transverse and longitudinal magnetisation (which may be generated by accidental excitation, and recovery during the decay interval respectively).

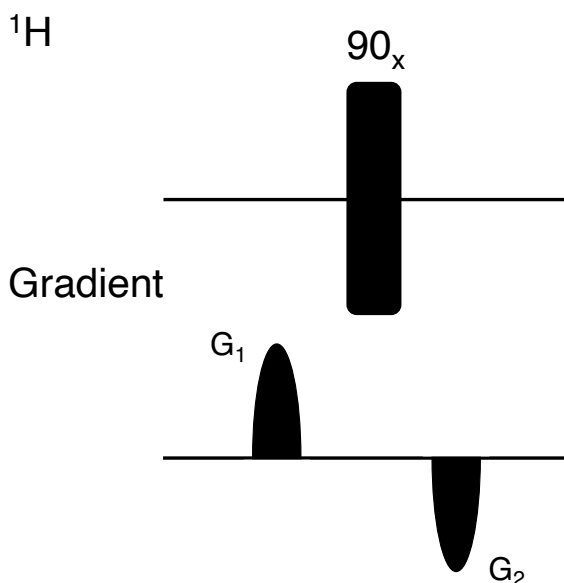


FIGURE 6.8: Proton destruction filter for the removal of residual proton magnetisation. The gradient strengths are given by $G_1=100\%$ and $G_2=-61.8\%$ with respect to the maximum gradient strength 50 G cm^{-1} . Each gradient has a duration of 2 ms. The black rectangle indicates a BB1 composite $\pi/2$ pulse (equation 5.3).

The proton z-filter pulse sequence element is shown in figure 6.9 and selects for longitudinal ^1H magnetisation. This filter employs a bipolar gradient scheme in order to reduce spectral distortions by eddy currents or residual gradient fields [115].

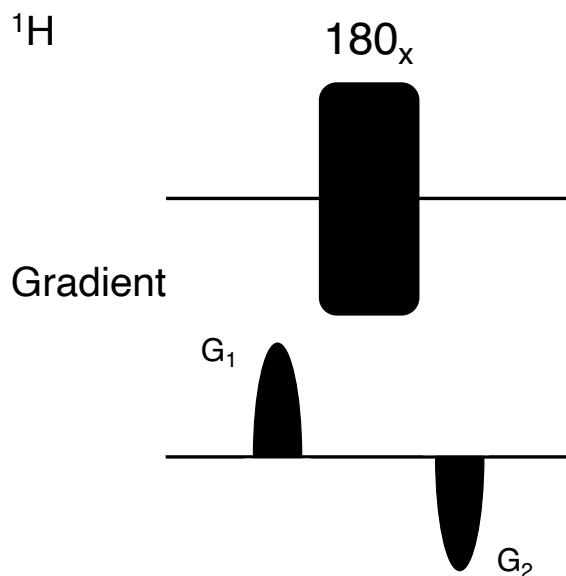


FIGURE 6.9: Proton z-filter for the selection of proton z-magnetisation, using bipolar gradients. The gradient strengths are given by $G_1=40\%$ and $G_2=-40\%$ with respect to the maximum gradient strength of 50 G cm^{-1} . Each gradient pulse has a duration of 2 ms. The black rectangle indicates a BB1 composite π -pulse (equation 5.4).

6.3.2 $\text{Rh}(\text{acac})_3$ ^{103}Rh T_2 decay curve

The trajectory of indirectly-detected ^{103}Rh transverse magnetization in a field of 9.4 T is shown in figure 6.10. The trajectory fits well to a single-exponential decay of the form $\langle \hat{I}_y \rangle(t) = I_y(0) \exp \{-t/T_2\}$ with time constant $T_2(^{103}\text{Rh}) = 18.36 \pm 0.92 \text{ s}$.

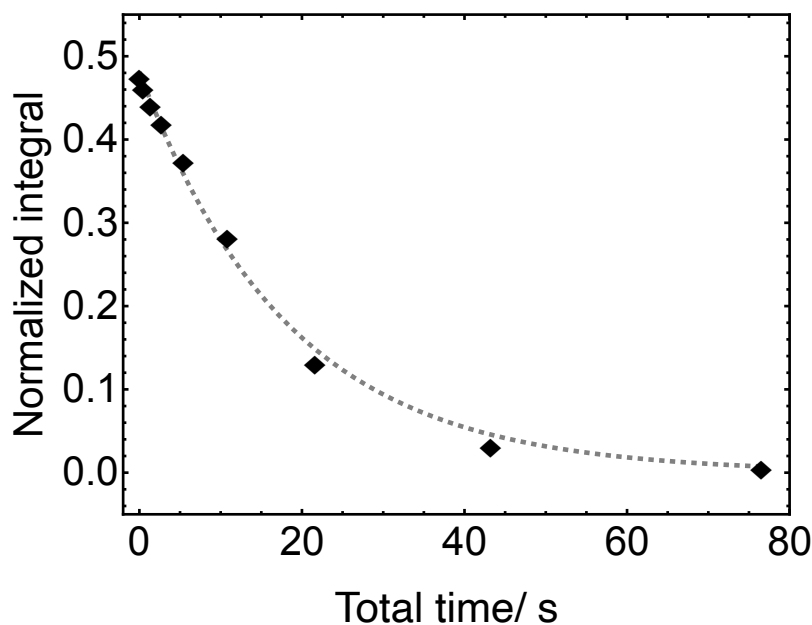


FIGURE 6.10: Decay curve for ^{103}Rh transverse magnetization at a field of 9.4 T, obtained using the pulse sequence in figure 6.7. The data fits well to an exponential decay with time constant $T_2 = 18.36 \pm 0.92$ s. The data was acquired in ~ 15 minutes. The integrals are normalised against the ^1H spectrum obtained by a single ^1H 90° pulse applied to a system in thermal equilibrium at 9.4 T and at 298K.

6.4 $\text{Rh}(\text{acac})_3$ ^{103}Rh T_1 relaxometry

6.4.1 Indirect ^{103}Rh T_1 pulse sequence

^{103}Rh T_1 relaxation time constants were measured indirectly through ^1H NMR signals using the sequence shown in figure 6.11.

A DualPol block sequence is used to transfer z-magnetization from the ^1H nuclei to the ^{103}Rh nuclei, and allowed to relax towards equilibrium during the relaxation interval τ_{relax} . For field-dependent relaxation measurements, the sample is shuttled to a region of lower magnetic field during this interval, and back again. A proton destruction filter is applied to eliminate any residual proton magnetisation, such as that generated during τ_{relax} through longitudinal relaxation towards equilibrium. Remaining ^{103}Rh z-magnetisation, selected for by the two 90° pulses, is now transferred back to ^1H z-magnetisation by a second DualPol block and is selected for by a proton z-filter. A final ^1H 90° pulse generates observable ^1H transverse magnetization. The sequence is repeated with variation of τ_{relax} in order to follow the equilibration of longitudinal ^{103}Rh magnetization.

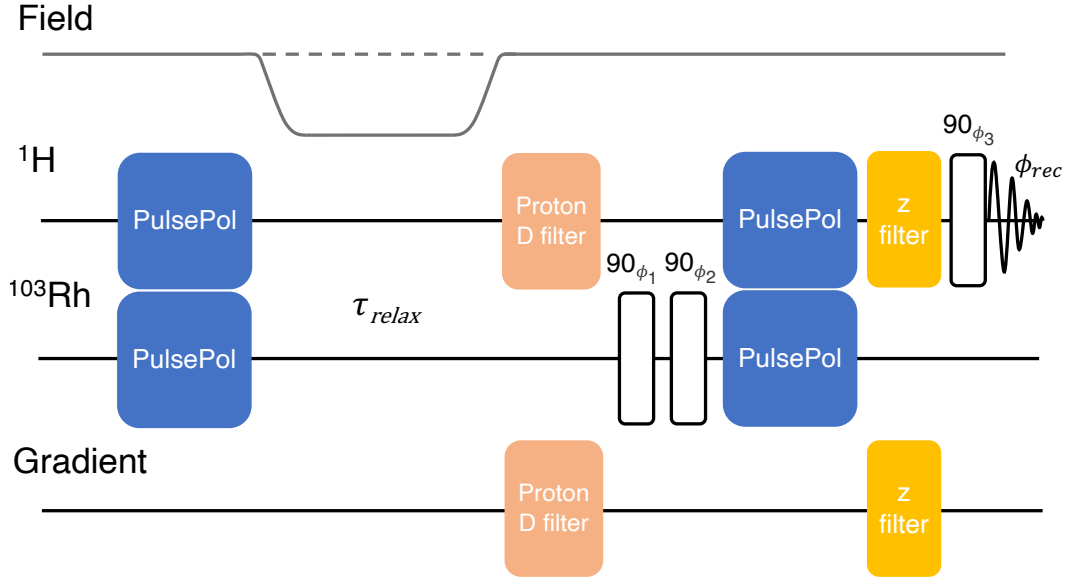


FIGURE 6.11: Sequence used for the indirect measurement of rhodium T_1 through ^1H NMR signals. Phase cycles are given by $\phi_1 = [x, x, -x, -x]$, $\phi_2 = [-x, x, -x, x]$, $\phi_3 = [x, x, x, x, y, y, y, y, -x, -x, -x, -x, -y, -y, -y, -y]$ and the receiver $\phi_{rec} = [x, -x, -x, x, y, -y, -y, y, -x, x, x, -x, -y, y, y, -y]$. The optional shuttling of the sample to low field, and back again, during the interval τ_{relax} , is indicated.

6.4.2 $\text{Rh}(\text{acac})_3$ ^{103}Rh T_1 relaxometry

The trajectory of indirectly-detected ^{103}Rh z-magnetization in a field of 9.4 T and temperature 295 K is shown in figure 6.12(a). The trajectory fits well to a single-exponential decay of the form $\langle \hat{I}_z \rangle(t) = I_z^{eq} + (I_z(0) - I_z^{eq}) \exp \{-t/T_1\}$ with time constant $T_1(^{103}\text{Rh}) = 41.8 \pm 0.9$ s. A trajectory in the low magnetic field of 10 mT and temperature 295 K is shown in figure 6.12(b). This was produced by shuttling the sample to low magnetic field during the interval τ_{relax} . The relaxation process is slower in low field, with a time constant of $T_1(^{103}\text{Rh}) = 57.8 \pm 1.7$ s. Note how in these experiments, contrary to conventional T_1 measurements (section 1.5.3.1), the ^{103}Rh polarisation *decreases* during τ_{relax} . This is because the initial ^{103}Rh longitudinal polarisation at the start of τ_{relax} has been ^1H enhanced by the preceding DualPol cross polarisation block; ergo, we observe the enhanced ^{103}Rh polarisation at the start of τ_{relax} decays to reach its lesser equilibrium value. Moreover, given the small gyromagnetic ratio of ^{103}Rh , the ^{103}Rh longitudinal equilibrium polarisation is very small, which manifests as the normalised integral being only marginally above zero for large values of τ_{relax} .

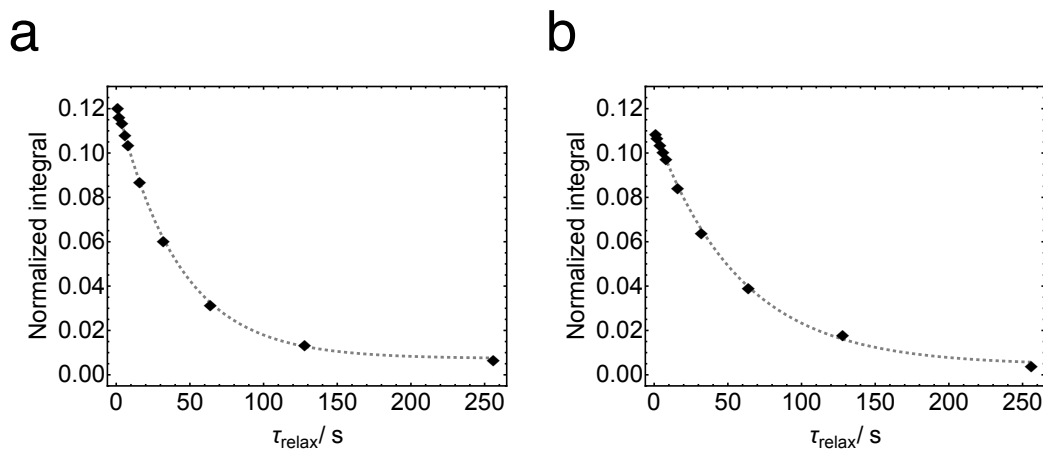


FIGURE 6.12: (a) Filled symbols: ^1H signal amplitudes for the pulse sequence in figure 6.11, at a magnetic field of 9.4 T and a temperature of 295 K. The data was acquired in ~ 2 hours. The integrals are normalised against the ^1H spectrum obtained by a single ^1H 90° pulse applied to a system in thermal equilibrium at 9.4 T and at 295 K. The data fits well to an exponential decay with time constant $T_1(^{103}\text{Rh}) = 41.8 \pm 0.9$ s. (b) As in (a), but shuttling the sample to a field of 10 mT during the relaxation delay τ_{relax} . The data fits well to an exponential decay with time constant $T_1(^{103}\text{Rh}) = 57.8 \pm 1.7$ s.

The rhodium T_1^{-1} increases weakly with the magnetic field strength at the higher field end, as shown in figure 6.13(a). The field-dependent relaxation rate constant is a reasonable fit to the quadratic function $T_1^{-1}(B) = T_1^{-1}(0) + aB^2$, where $T_1^{-1}(0) = (167 \pm 7) \times 10^{-4} \text{ s}^{-1}$ and $a = (7 \pm 2) \times 10^{-5} \text{ s}^{-1} \text{ T}^{-2}$. Conversely, the rhodium T_1^{-1} increases approximately linearly over the relevant temperature range, as shown in figure 6.13(b) and where at 315 K relaxation occurs with a time constant of $T_1(^{103}\text{Rh}) = 30.6 \pm 1.1$ s. A positive dependence of the rhodium T_1^{-1} on temperature for $\text{Rh}(\text{acac})_3$ has previously been suggested [116].

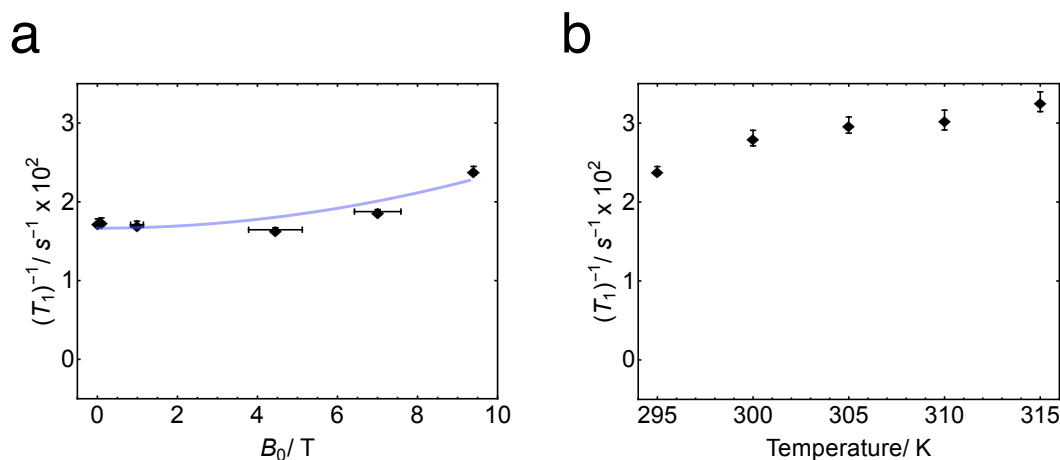


FIGURE 6.13: (a) ^{103}Rh relaxation rate constant T_1^{-1} as a function of magnetic field strength at a temperature of 295 K. The blue line shows the quadratic function $T_1^{-1}(B) = T_1^{-1}(0) + aB^2$, where $T_1^{-1}(0) = (167 \pm 7) \times 10^{-4} \text{ s}^{-1}$ and $a = (7 \pm 2) \times 10^{-5} \text{ s}^{-1} \text{ T}^{-2}$. (b) ^{103}Rh relaxation rate constant T_1^{-1} as a function of temperature at a field strength of 9.4 T.

We note that measurements performed at higher temperatures suffer from increased uncertainty. This is likely a consequence of increased thermal convection or a temperature gradient across the sample. Moreover, the large uncertainties in B_0 field strength for field cycling measurements between 4 and 8 Tesla is attributed to the rapidly changing stray field across the finite length of the NMR sample in this region of the high field magnet.

6.5 Discussion

6.5.1 DualPol performance

Neglecting losses due to relaxation, the computed maximum theoretical ^{103}Rh signal enhancement factor for $^1\text{H} \rightarrow ^{103}\text{Rh}$ polarisation transfer in the $\text{Rh}(\text{acac})_3$ spin system when using refocused-INEPT is given by: $\sim 1.15 |\gamma_{\text{H}}/\gamma_{\text{Rh}}| \simeq 36$. Whereas for DualPol, the theoretical enhancement factor is less and given by $\sim 1.05 |\gamma_{\text{H}}/\gamma_{\text{Rh}}| \simeq 33$.

However, theoretical arguments notwithstanding, experimentally the DualPol sequence outperformed refocused-INEPT. One possible explanation for this is that, because of its superior robustness (section 3.4.1), the DualPol sequence may suffer from fewer losses arising from pulse errors relative to refocused-INEPT; so is potentially more efficient. Additionally, it has been shown that Hartmann-Hahn cross polarisation sequences such as DualPol can outperform INEPT in the presence of transverse relaxation effects [117].

In any case, these enhancement factors fall short of the theoretical maximum for this transfer, which is given by: $\frac{3}{2} |\gamma_{\text{H}}/\gamma_{\text{Rh}}| \simeq 47$; as estimated using the symmetry constrained bounds for polarisation transfer in a AX_3 spin system [118, 119].

6.5.2 ^{103}Rh T_1 relaxometry

The weak field dependence of the ^{103}Rh T_1^{-1} as shown in figure 6.13(a) is suggestive of a minor CSA mechanism. This is consistent with the modest ^{103}Rh CSA of $|\Delta\sigma| \simeq 460$ ppm, as measured for $\text{Rh}(\text{acac})_3$ in the solid state [120].

The temperature dependence of the ^{103}Rh T_1^{-1} as shown in figure 6.13(b) is consistent with the spin-rotation relaxation mechanism. This is because, for small molecules in the extreme narrowing limit, the spin-rotation relaxation mechanism is the only mechanism that leads to a T_1^{-1} that is positively correlated to temperature [121]. This is because the amplitude of the local fluctuating fields at the nuclear site generated by the spin-rotation interaction depends on the root-mean-square molecular rotational angular momentum - a property that is linked to the mean rotational kinetic energy, which is proportional to temperature. Conversely, for other mechanisms, a reduction in rotational correlation time τ_c with increasing temperatures leads to a decrease in the relaxation rate.

We therefore tentatively attribute the relaxation of longitudinal ^{103}Rh spin order in the $\text{Rh}(\text{acac})_3$ complex to spin rotation with a significant contribution from the CSA at high fields.

Chapter 7

^{103}Rh NMR spectroscopy and relaxometry of the rhodium formate paddlewheel complex

In this chapter, we utilise the DualPol cross polarisation sequence in the proton enhanced ^{103}Rh NMR spectroscopy of the rhodium formate paddlewheel complex. Moreover, the ^{103}Rh T_1 spin-lattice relaxation in the rhodium formate paddlewheel complex is characterised.

In this implementation, the DualPol sequence (figure 3.5) uses an R-element duration of $\tau_R = 5$ ms and a repetition number of $L = 10$. The total DualPol sequence duration is $T = 2\tau_R L = 100$ ms. Moreover, all 180° pulses were composite and of the form shown in equation 5.4.

Experimental optimisation of the the DualPol sequence for ^1H to ^{103}Rh polarisation transfer in the rhodium formate paddlewheel complex is shown in Appendix B.

In this chapter, experiments were performed on a saturated (~ 10 mM) solution of rhodium formate ($\text{Rh}_2(\text{HCO}_2)_4$) dissolved in $500\ \mu\text{L}$ deuterated tetrahydrofuran ($\text{THF-}d_8$) and contained in a Wilmad LPV 5 ml sample tube. The rhodium formate was synthesised by Gamal Moustafa from rhodium chloride using a reported procedure [122]. The resulting rhodium formate powder was green in colour and dissolved in $\text{THF-}d_8$ to form a green solution. In solution, solvent $\text{THF-}d_8$ molecules coordinate to the axial positions of the rhodium formate complex; as shown in figure 7.1.

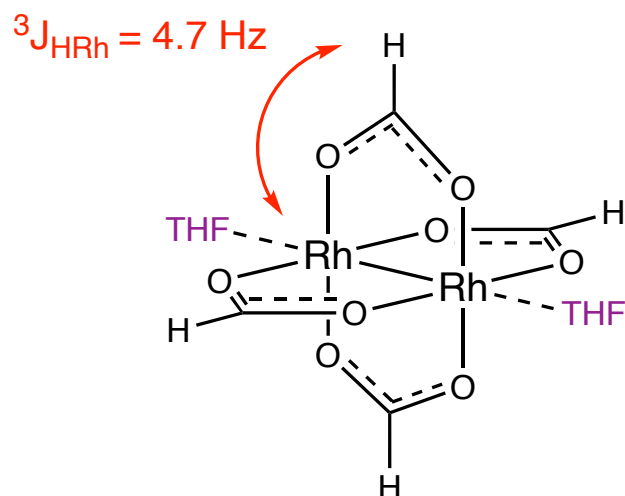


FIGURE 7.1: Molecular structure of the rhodium formate paddlewheel complex where the axial sites are ligated by solvent tetrahydrofuran (THF) molecules.

The rhodium formate molecule contains two equivalent ^{103}Rh nuclei weakly coupled to four equivalent protons - one on each bridging formate ligand. Hence, neglecting the presence of any ^{13}C nuclei, rhodium formate represents an A_2X_4 spin system, where A denotes ^{103}Rh and X denotes a proton.

For shuttling experiments described here the total shuttling duration was kept constant at 1 second, in both directions.

7.1 NMR spectra

7.1.1 ^1H

The rhodium formate ^1H spectrum is shown in figure 7.2 and features a single formate ^1H resonance split into a 1:2:1 triplet by coupling to the pair of magnetically equivalent ^{103}Rh nuclei. The three-bond ^1H - ^{103}Rh J-coupling is estimated to be $|^3J_{\text{RhH}}| = 4.7 \pm 0.1$ Hz.

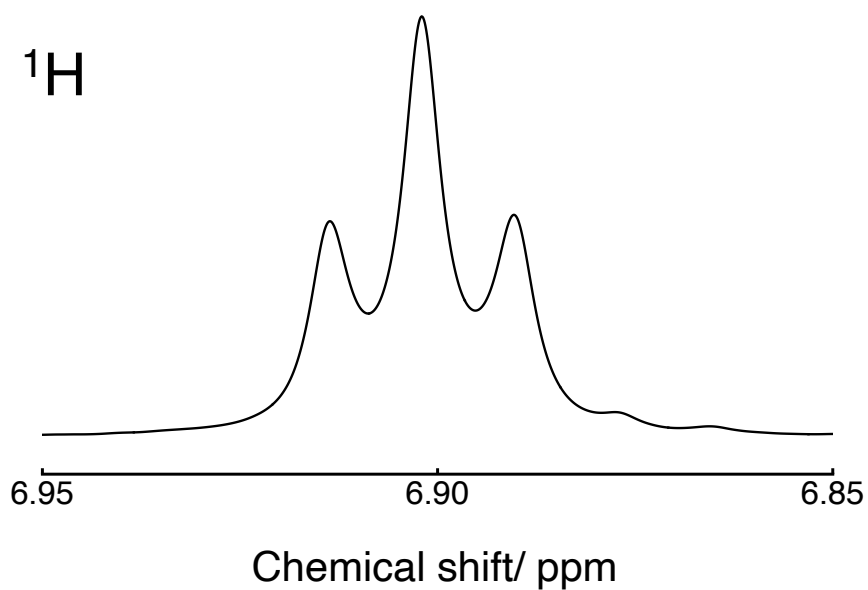


FIGURE 7.2: ^1H spectrum of a ~ 10 mM solution of rhodium formate in THF-d_8 , acquired at 9.4 T and at 298K in a single scan. Lorentzian line broadening (0.75 Hz) was applied.

7.1.2 $^{13}\text{C}\{^1\text{H},^{103}\text{Rh}\}$

The rhodium formate $^{13}\text{C}\{^1\text{H},^{103}\text{Rh}\}$ spectrum likewise features just a single resonance (figure 7.3).

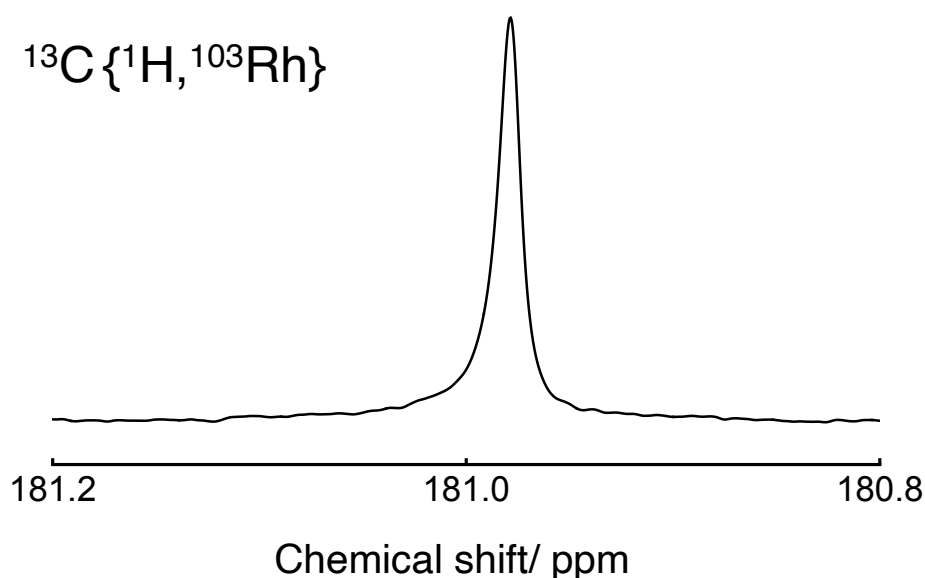


FIGURE 7.3: $^{13}\text{C}\{^1\text{H}, ^{103}\text{Rh}\}$ spectrum of a ~ 10 mM solution of rhodium formate in THF-d_8 , acquired at 14.1 T and at 298K in 4096 scans. Lorentzian line broadening (1 Hz) was applied.

7.1.3 Proton enhanced ^{103}Rh spectra

The sequence shown in figure 6.3 was used to acquire the directly detected rhodium formate ^{103}Rh spectra shown in figure 7.4, enhanced by polarisation transfer from ^1H nuclei via the DualPol sequence.

The spectrum shown in figure 7.4(a) features a single ^{103}Rh resonance split into a 1:4:6:4:1 quintet by couplings to the four equivalent ^1H nuclei on the formate ligands. The three-bond ^1H - ^{103}Rh J-coupling is estimated to be $|^3J_{\text{RhH}}| = 4.7 \pm 0.1$ Hz, which is in agreement with the ^1H spectrum. The ^{103}Rh resonances collapse into a single peak centred at 7516 ppm upon ^1H decoupling (figure 7.4(b)).

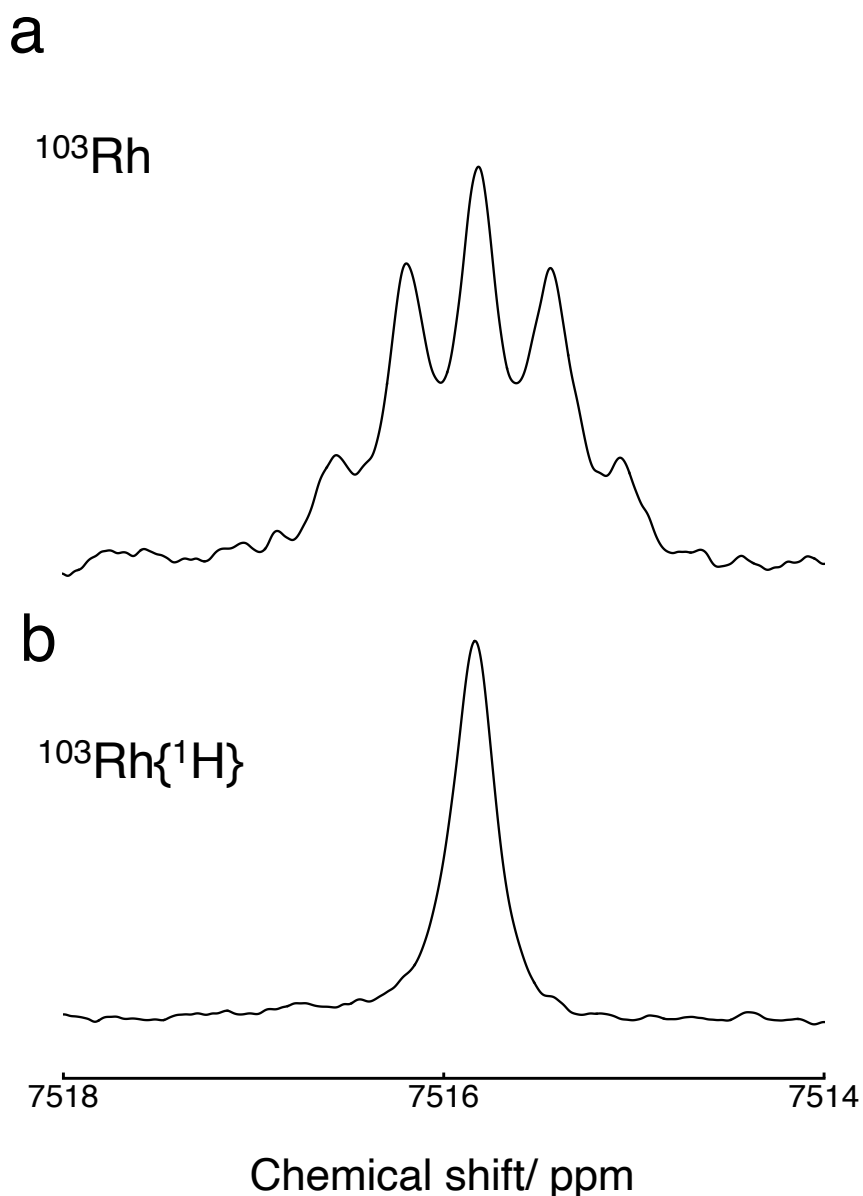


FIGURE 7.4: (a) ^{103}Rh spectrum of a ~ 10 mM solution of rhodium formate in THF-d_8 scaled 2.5 times, acquired using 128 scans at 9.4 T and at 298 K using the pulse sequence in figure 6.3 but without proton decoupling. (b) ^1H -decoupled ^{103}Rh spectrum acquired using 128 scans at 9.4 T and at 298 K using the pulse sequence in figure 6.3. Acquisition time for each spectrum was ~ 1 hour. Lorentzian line broadening (1 Hz) was applied to each spectrum.

The ^{103}Rh resonances are broadened by the short ^{103}Rh T_2 (see figure 7.8)

7.1.3.1 DualPol vs refocused-INEPT ^{103}Rh spectrum

The sequence shown in figure 6.4 was used to acquire a directly detected ^{103}Rh spectrum, enhanced by polarisation transfer from ^1H nuclei via the refocused-INEPT pulse

sequence. The optimal refocused-INEPT delays for $^1\text{H} \rightarrow ^{103}\text{Rh}$ polarisation transfer in the rhodium formate spin system were derived analytically (see appendix C) to yield: $\tau_1 = (1/8J)$ and $\tau_2 = (1/12J)$, which, assuming a ^1H - ^{103}Rh spin-spin coupling of $J_{\text{HRh}} = 4.7$ Hz, corresponds to the theoretical optimal delays: $\tau_1 = 26.6$ ms and $\tau_2 = 17.7$ ms. Upon experimental optimisation, we attained the following optimised values: $\tau_1 = 26.5$ ms and $\tau_2 = 17.0$ ms. The experimentally obtained values are hence in good agreement with those derived theoretically.

Figure 7.5 shows directly detected ^{103}Rh spectra as acquired using a single 90° ^{103}Rh pulse applied to ^{103}Rh polarisation at thermal equilibrium, DualPol and refocused-INEPT.

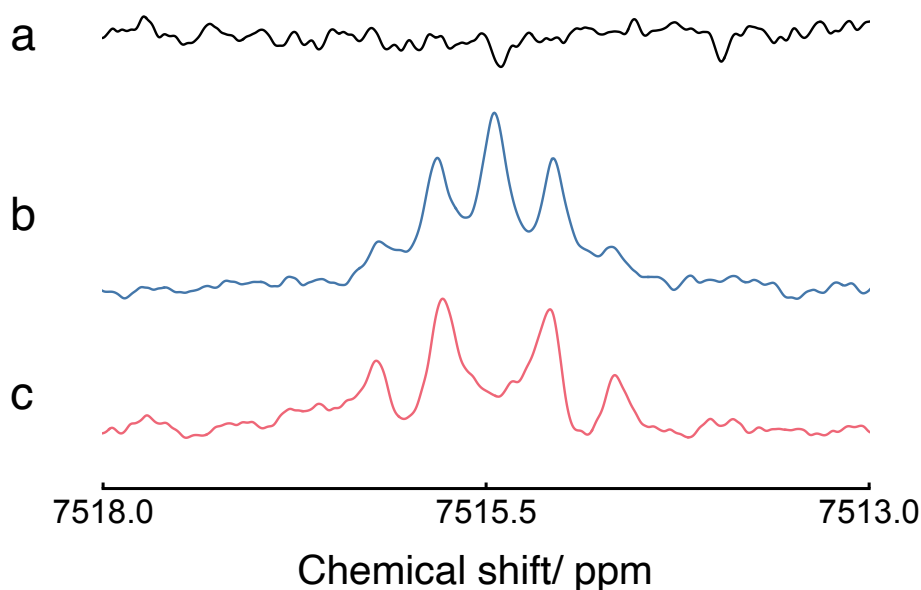


FIGURE 7.5: ^{103}Rh NMR spectra of a ~ 10 mM solution of rhodium formate in THF-d_8 , in a field of 9.4 T and a temperature of 298 K. Lorentzian line broadening (1 Hz) was applied to all spectra. ^{103}Rh chemical shifts are referenced to the absolute frequency ($\Xi(^{103}\text{Rh}) = 3.16\%$). (a) ^{103}Rh spectrum, acquired using 64 transients, each using a single ^{103}Rh 90° pulse. The total experimental duration was ~ 3 minutes. (b) ^{103}Rh spectrum, acquired using 64 scans and the DualPol pulse sequence shown in figure 6.3, but without proton decoupling. The total experimental duration was ~ 50 minutes. (c) ^{103}Rh spectrum, acquired using 64 scans and the refocused-INEPT pulse sequence shown in figure 6.4, but without proton decoupling. The total experimental duration was ~ 50 minutes.

The DualPol ^{103}Rh NMR spectrum (figure 7.5(b)) features a quintet peak structure centred at the frequency 7515.5 ppm. The refocused-INEPT ^{103}Rh NMR spectrum (figure 7.5(c)) exhibits noticeable peak distortions, including the entire absence of the central peak.

A refocused-INEPT NMR spectrum for $X \rightarrow A$ polarisation transfer in an A_2X_4 spin system simulated in SpinDynamica [110] is shown in figure 7.6 and is in good agreement with the experimentally derived refocused-INEPT sequence shown in figure 7.5(b).

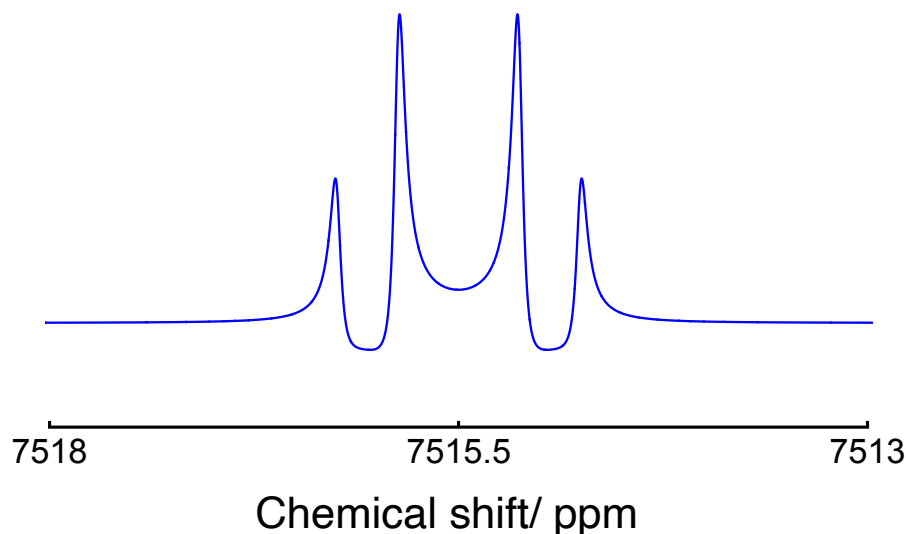


FIGURE 7.6: Simulated refocused-INEPT NMR spectrum of A-spins for $X \rightarrow A$ polarisation transfer in an A_2X_4 spin system where $J_{AX} = 4.7$ Hz. Note the absence of the central peak. Spectrum was produced using 1 Hz Lorentzian line broadening.

The observed distortions are therefore not experimental/hardware artifacts, but are instead a consequence of the refocused-INEPT sequence itself.

7.2 ^{103}Rh chemical shift temperature dependence

The temperature-dependence of the ^{103}Rh chemical shift is again demonstrated, this time for the rhodium formate paddlewheel complex. The temperature-dependence of the ^{103}Rh chemical shift is approximately linear over the relevant temperature range, with a gradient of $\sim 1.48 \text{ ppm K}^{-1}$. This is in general agreement with observations on other ^{103}Rh complexes [88, 92].

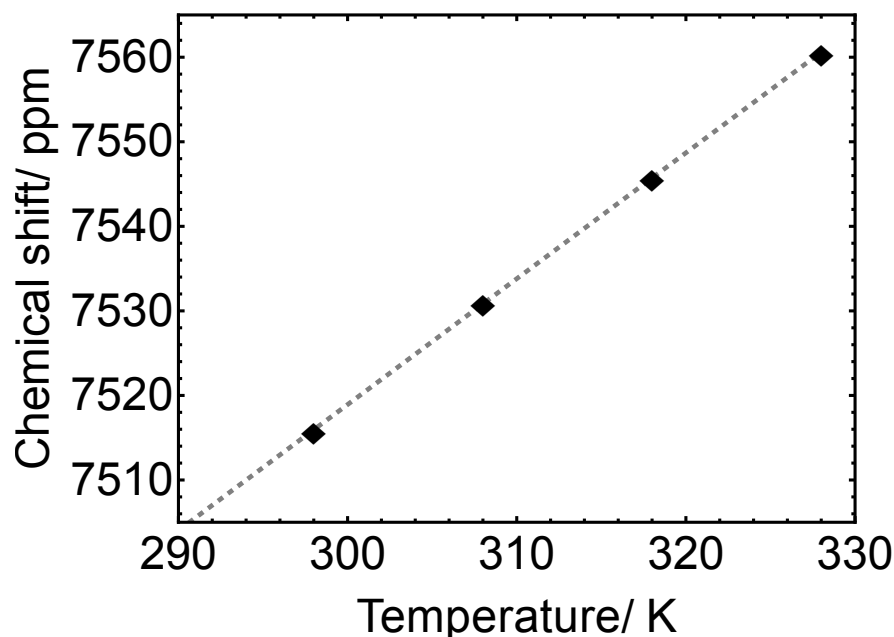


FIGURE 7.7: ^{103}Rh chemical shift of rhodium formate dissolved in THF-d_8 at 9.4 T, as a function of temperature. The chemical shifts are referenced to $\Xi(^{103}\text{Rh}) = 3.16\%$.

7.3 Rhodium formate ^{103}Rh T_2

The sequence shown in figure 6.7 was used to measure the rhodium formate ^{103}Rh T_2 relaxation time constant in the high field. The duration of the individual spin echoes were kept constant at: $\tau = 10$ ms.

7.3.1 Rhodium formate ^{103}Rh T_2 decay curve

The trajectory of indirectly-detected ^{103}Rh transverse magnetization in a field of 9.4 T is shown in figure 7.8. The trajectory fits well to a single-exponential decay of the form $\langle \hat{I}_y \rangle(t) = I_y(0) \exp \{-t/T_2\}$ with time constant $T_2 = 0.110 \pm 0.001$ s. This value is particularly short and contributes to broad lineshapes in directly detected ^{103}Rh spectra.

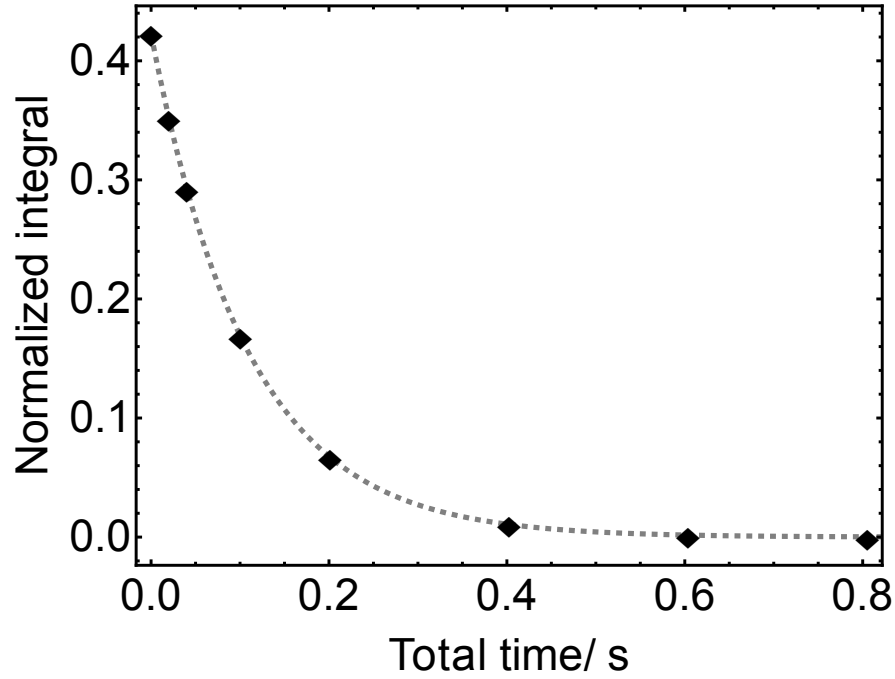


FIGURE 7.8: Decay curve for ^{103}Rh transverse magnetization at a field of 9.4 T and at 295 K, obtained using the pulse sequence in figure 6.7. The data fits well to an exponential decay with time constant $T_2 = 0.110 \pm 0.001$ s. The data was acquired in ~ 5 minutes. The integrals are normalised thermal ^1H polarisation at 9.4 T.

7.4 Rhodium formate ^{103}Rh T_1 relaxometry

7.4.1 Indirect ^{103}Rh T_1 pulse sequence

^{103}Rh T_1 relaxation time constants were measured indirectly through ^1H NMR signals using the sequence shown in figure 6.11.

7.4.2 Rhodium formate ^{103}Rh T_1 decay curves

The trajectory of indirectly-detected ^{103}Rh z-magnetization in a field of 9.4 T is shown in figure 7.9(a). The trajectory fits well to a single-exponential decay of the form $\langle \hat{I}_z \rangle(t) = I_z^{eq} + (I_z(0) - I_z^{eq}) \exp\{-t/T_1\}$ with time constant $T_1(^{103}\text{Rh}) = 0.483 \pm 0.002$ s. A trajectory in the low magnetic field of 1 mT is shown in figure 7.9(b). This was produced by shuttling the sample to low magnetic field during the interval τ_{relax} . The relaxation process is much slower in low field, with a time constant of $T_1(^{103}\text{Rh}) = 28.2 \pm 1.2$ s. Note that in these experiments, similarly to the preceding chapter, we again observe that the initial ^1H enhanced longitudinal ^{103}Rh polarisation decays towards its lesser equilibrium value during τ_{relax} .

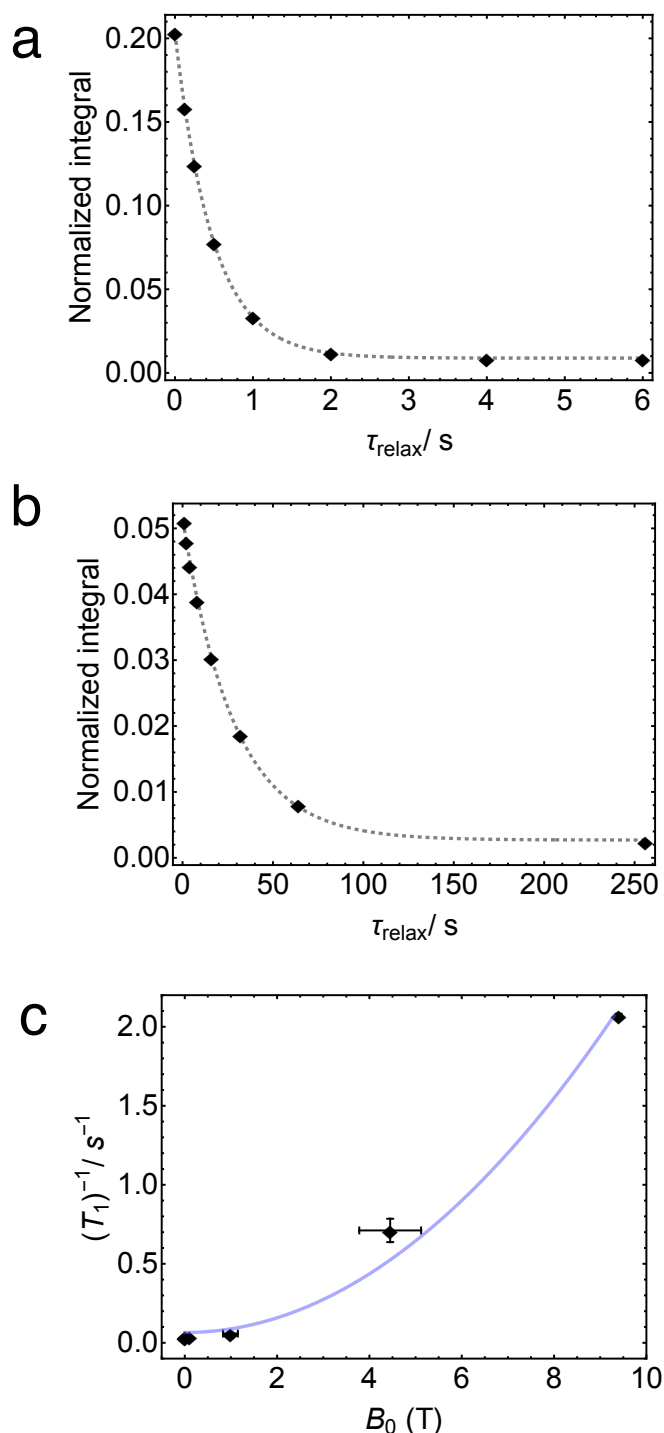


FIGURE 7.9: (a) Decay curve for ^{103}Rh longitudinal magnetization at a field of 9.4 T and at 298 K, obtained using the pulse sequence in figure 6.11, but without shuttling the sample to low field. The data was acquired in ~ 20 minutes. The data fits well to an exponential decay with time constant $T_1 = 0.483 \pm 0.002$ s. (b) Decay curve for ^{103}Rh longitudinal magnetization at a field of 1 mT, obtained using the pulse sequence in figure 6.11, including the shuttling of the sample to low field. The data fits well to an exponential decay with time constant $T_1 = 28.2 \pm 1.2$ s. The integrals are normalised against the ^1H spectrum obtained by a single ^1H 90° pulse applied to a system in thermal equilibrium at 9.4 T and at 298 K. (c) ^{103}Rh relaxation rate constant T_1^{-1} as a function of magnetic field strength. The blue line shows the quadratic function $T_1^{-1}(B) = T_1^{-1}(0) + aB^2$, where $T_1^{-1}(0) = (65 \pm 4) \times 10^{-3} \text{ s}^{-1}$ and $a = (23 \pm 1) \times 10^{-3} \text{ s}^{-1} \text{ T}^{-2}$.

The rhodium T_1^{-1} increases approximately quadratically with the magnetic field strength B_0 , as shown in figure 7.9(c). The field-dependent relaxation rate constant is a reasonable fit to the quadratic function $T_1^{-1}(B) = T_1^{-1}(0) + aB^2$, where $T_1^{-1}(0) = (65 \pm 4) \times 10^{-3} \text{ s}^{-1}$ and $a = (23 \pm 1) \times 10^{-3} \text{ s}^{-1} \text{ T}^{-2}$.

We note that the large uncertainty in B_0 field strength for the measurement at ~ 4.5 Tesla is attributed to the rapidly changing stray field across the finite length of the NMR sample in this region of the high field magnet.

7.5 Discussion

7.5.1 Spectral distortions in coupled spectra acquired via refocused-INEPT

The ^1H enhanced rhodium formate ^{103}Rh spectrum acquired via refocused-INEPT shown in figure 7.4(b) exhibits spectral distortions of which are corroborated by simulation (figure 7.6).

Distortions in coupled spectra acquired via refocused-INEPT are well known and there exists pulse sequence modifications to suppress them [123]. Distortions may also be suppressed by simply decoupling coupled nuclei - albeit at the cost of sacrificing splitting information. Regardless, the DualPol sequence is unaffected by this issue and, more importantly, is capable of transferring polarisation even in the strong coupling regime, which is required for the ^{103}Rh singlet order experiments presented later in this thesis.

7.5.2 ^{103}Rh T_1 relaxometry

The quadratic field dependence of the ^{103}Rh T_1^{-1} relaxation rate constant shown in figure 7.9(c) is consistent with a dominant chemical shift anisotropy (CSA) relaxation mechanism, as is commonly observed for the ^{103}Rh T_1 relaxation of rhodium complexes [91, 88].

7.5.3 Estimation of rhodium formate ^{103}Rh CSA

It is difficult to estimate the ^{103}Rh chemical shift anisotropy by solid-state NMR. The small gyromagnetic ratio of ^{103}Rh and the very large CSA value make solid-state ^{103}Rh NMR very difficult. Complicating matters further, in the rhodium formate complex, ^1H - ^{103}Rh dipolar couplings are very small (see appendix F.3), which greatly inhibits the use of dipolar-polarisation transfer techniques in the solid-state. However, although

the ¹⁰³Rh CSA may not be measured directly, it is possible to estimate it by a combination of field-dependent ¹⁰³Rh and ¹³C *T*₁ measurements.

The symmetry of the complex suggests that the ¹⁰³Rh CSA tensors should have uniaxial symmetry ($\eta = 0$); with their unique principal axis along the Rh-Rh bond. This property is assumed in the following discussion.

7.5.3.1 Estimation of rhodium formate τ_c using ¹³C *T*₁ relaxation data

The largely spherical cage structure of the rhodium formate complex (figure 7.1) suggests that, to a good approximation, the complex tumbles in solution as a near-rigid body, with a common rotational correlation time τ_c for all spin interactions. This approximation allows a correlation time estimate from ¹³C NMR to be applied in the context of ¹⁰³Rh NMR.

The rhodium formate ¹³C *T*₁ relaxation is dominated by its dipolar coupling to the adjacent formate proton. For point nuclei (i.e. ignoring the spatial spread of the nuclear wavefunctions), the ¹³C-¹H dipole-dipole coupling constant is given by $b_{CH} = -(\mu_0/4\pi)\hbar\gamma_C\gamma_H r_{CH}^{-3}$, where r_{CH} is the ¹³C-¹H internuclear distance [16].

Quantum chemical calculations[109] (see appendix F) predict an internuclear ¹³C-¹H distance of 1.097 Å, corresponding to a dipole-dipole coupling constant of $b_{CH} = -2\pi \times 22.8$ kHz. However, solid-state NMR studies have shown that the true dipole-dipole coupling is weakened by the angular spread of the ¹H wavefunctions, associated with the zero-point librational motion of the C-H bonds [124]. Hence, the predicted ¹³C-¹H dipole-dipole coupling constant is adjusted to $b_{CH} = -2\pi \times (20.4 \pm 0.5)$ kHz.

For isolated ¹³C-¹H spin systems in the extreme narrowing approximation (where $\omega_0\tau_c \ll 1$) and under proton decoupling, the ¹³C-¹H dipolar coupling contribution to the *T*₁⁻¹ relaxation rate constant for ¹³C is given by [14],

$$(T_1(^{13}\text{C}))_{CH}^{-1} = b_{CH}^2 \tau_c \quad (7.1)$$

The ¹³C *T*₁ was measured at natural abundance using reverse detection on the protons and was found to be 2.14 ± 0.15 s (see appendix E).

Using the ¹³C *T*₁ relaxation data and the estimated ¹³C-¹H dipolar coupling constant we arrive at the following estimate for the rhodium formate rotational correlation time: $\tau_c = 28.4 \pm 4$ ps. This estimate factors in both the uncertainty of the b_{CH} dipolar coupling constant; as well as the uncertainty of the ¹³C *T*₁ measurement.

7.5.3.2 Experimental estimate of the rhodium formate ^{103}Rh CSA

The ^{103}Rh relaxation may now be analyzed using the estimate of τ_c . As shown in figure 7.9, the ^{103}Rh T_1^{-1} relaxation rate constant is well-described by the function $T_1^{-1}(B) = T_1^{-1}(0) + aB^2$, with the field-independent term $T_1^{-1}(0) = 0.065 \pm 0.038 \text{ s}^{-1}$, and the quadratic coefficient $a = 0.023 \pm 0.001 \text{ s}^{-1} \text{ T}^{-2}$.

The quadratic field-dependent term may be attributed to the CSA mechanism. In the extreme narrowing limit and assuming ^{103}Rh shielding tensors have the same CSA, the CSA contribution to the T_1^{-1} relaxation rate constant for ^{103}Rh is given by [14]

$$\left(T_1(^{103}\text{Rh})\right)_{\text{CSA}}^{-1} = \frac{2}{15} B_0^2 \gamma_{\text{Rh}}^2 \Delta\sigma^2 \tau_c \quad (7.2)$$

where the shielding anisotropy $\Delta\sigma$ is defined as follows [14]:

$$\Delta\sigma = \frac{3}{2}(\sigma_{\text{ZZ}} - \sigma_{\text{iso}}) = -\frac{3}{2}\delta^{\text{aniso}} \quad (7.3)$$

Equation 7.2 implies that the quadratic field-dependent coefficient a for the ^{103}Rh T_1^{-1} relaxation rate constant is given by

$$a = \frac{2}{15} \gamma_{\text{Rh}}^2 \Delta\sigma^2 \tau_c \quad (7.4)$$

The experimental estimate of the quadratic coefficient $a = 0.023 \pm 0.001 \text{ s}^{-1} \text{ T}^{-2}$ may be combined with the correlation time estimate $\tau_c \simeq 28.4 \pm 4 \text{ ps}$ to obtain the following experimental estimate of the ^{103}Rh shielding anisotropy: $|\Delta\sigma| = 9200 \pm 940 \text{ ppm}$.

This value is consistent with CSA values for other heavy spin-1/2 nuclei in certain complexes [125, 126, 127, 128, 129, 130, 131, 132, 133, 134], with closely related platinum (II) compounds displaying ^{195}Pt CSA values on the order of 10,000 ppm [125, 127, 132, 134]. Reported ^{103}Rh CSAs are scarce in the literature; however, there does exist data measured in a handful of Rh(III) compounds, of which exhibited ^{103}Rh CSAs on the order of $\sim 500\text{--}8000 \text{ ppm}$ [135, 136, 120]. A large CSA range is not uncommon for many heavy spin-1/2 nuclei [129, 133, 128].

7.5.3.3 Computational estimate of the rhodium formate ^{103}Rh CSA

Rhodium formate ^{103}Rh shielding tensors were estimated computationally using the ORCA suite of software packages [109, 137, 138] (see Appendix F).

The rhodium formate ^{103}Rh CSA estimated using quantum chemistry was found to be: $|\Delta\sigma| = 7070$ ppm, which is in general agreement with the experimental estimate. The remaining discrepancy may be due to the ZORA method used in the computation. Underestimation of CSAs calculated using the ZORA method has been reported for other heavy spin-1/2 nuclei [139, 140, 141]. Better agreement might be obtained with higher-order four-component relativistic calculations [140].

7.5.4 Zero-field rhodium formate ^{103}Rh $T_1^{-1}(0)$ origin

The high field rhodium formate ^{103}Rh T_1 relaxation is dominated by the CSA; however, the origin of the zero-field $T_1^{-1}(0)$ contribution to the ^{103}Rh relaxation rate is less obvious.

The CSA relaxation mechanism is strongly field dependent; so is muted at low field strengths. Moreover, dipolar interactions are inefficient at inducing ^{103}Rh spin relaxation on account of the small ^{103}Rh gyromagnetic ratio. Therefore, we had anticipated that ^{103}Rh longitudinal magnetisation would subsist for a very long time when stored at low magnetic field strengths. However, the ^{103}Rh T_1 measured at just 1 mT is an underwhelming 28 seconds, which indicates the presence of an unaccounted for ^{103}Rh T_1 relaxation mechanism, which becomes dominant at low magnetic field strengths.

In the previous chapter, we attributed the ^{103}Rh T_1 relaxation in $\text{Rh}(\text{acac})_3$ to the spin-rotation mechanism. Moreover, spin-rotation has previously been proposed as a prominent ^{103}Rh spin relaxation mechanism in other compounds [142]. Similarly, spin-rotation may also be contributing to the low field ^{103}Rh T_1 relaxation in this complex.

Assuming the ^{103}Rh spin-rotation tensors are identical and uniaxial and that the molecule is a spherical top, the spin-rotation contribution to the ^{103}Rh T_1^{-1} relaxation rate is given, in the extreme narrowing approximation, by equation 2.20,

Using the calculated ^{103}Rh spin-rotation tensors (see appendix G) and the rotational correlation time estimated from the rhodium formate ^{13}C T_1 data, the calculated spin-rotation contribution to the ^{103}Rh T_1^{-1} is: $(T_1(^{103}\text{Rh}))_{SR}^{-1} = 0.107 \pm 0.011\text{s}^{-1}$, which is in rough agreement with the rhodium formate zero-field ^{103}Rh relaxation rate of: $T_1^{-1}(0) = 0.065 \pm 0.038\text{s}^{-1}$.

Experimental verification of a dominant low field spin-rotation ^{103}Rh T_1 relaxation mechanism necessitates the measurement of the ^{103}Rh T_1 as a function of temperature in the low field. Unfortunately, at present our shuttling setup lacks the ability to regulate temperature in the low field; thus this experiment is not currently accessible.

Chapter 8

^{103}Rh singlet-NMR spectroscopy and T'_S relaxometry of the rhodium formate paddlewheel complex

In this chapter, we study the possibility of nuclear singlet order in the rhodium formate paddlewheel complex wherein the symmetry across the ^{103}Rh spin pair has been broken by selective ^{18}O labelling of a singular formate ligand. We introduce and implement 2D pulse sequence methodology for the rapid indirect acquisition of ^{103}Rh spectra and NMR parameters - including the one-bond homonuclear ^{103}Rh - ^{103}Rh J-coupling and $^{103}\text{Rh}(^{18}/^{16}\text{O})$ secondary isotope shifts. Furthermore, pulse sequence methodology for the generation of long-lived ^{103}Rh spin order and for the rapid measurement of long-lived ^{103}Rh T'_S relaxation time constants over a range of magnetic field strengths is presented. Finally, the relaxation of long-lived ^{103}Rh spin order in the rhodium formate paddlewheel complex is characterised.

Experiments were performed on a saturated (~ 10 mM) solution of ^{18}O labelled rhodium formate ($\text{Rh}_2(\text{HCO}_2)_4$) dissolved in $500\ \mu\text{L}$ deuterated tetrahydrofuran (THF-d_8) contained in a Wilmad LPV 5 mL sample tube. The ^{18}O labelled rhodium formate was synthesised by Gamal Moustafa using the procedure outlined in appendix D.

Although rhodium formate paddlewheel molecules contain four formate ligands, only one of these was ^{18}O -labelled. The chosen synthetic route statistically labelled the two oxygen atoms of this single formate residue to $\sim 45\%$ with ^{18}O ; whereas; the oxygen atoms of the three other formate residues remained as the usual ^{16}O isotope. As a result, the sample contained a statistical mixture of three different major isotopologues, denoted here **I**, **II**, **III** as shown in figure 8.1. As determined below, the statistical abundances in solution are approximately (30%, 50%, 20%) for the isotopologues (**I**, **II**, **III**) respectively.

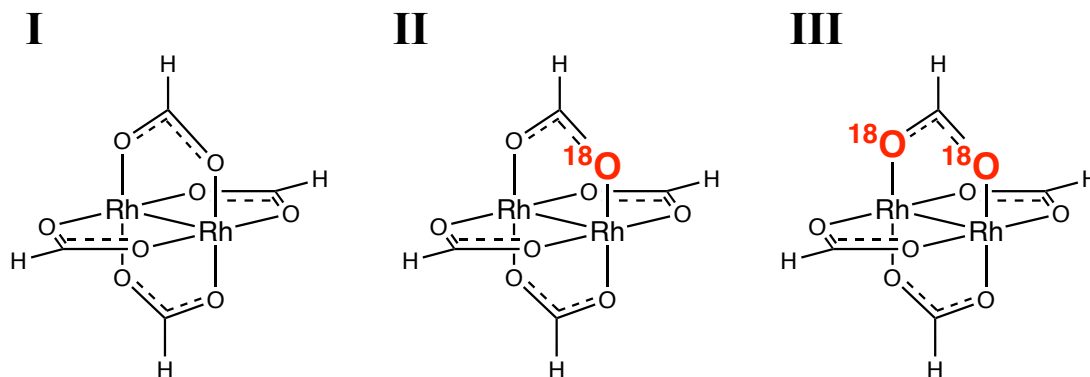


FIGURE 8.1: Molecular structures for the three rhodium formate isotopologues present in solution. Oxygen atoms with no annotation are the usual ^{16}O isotope. THF- d_8 ligands at axial sites omitted for clarity.

The increased mass of the ^{18}O alters the vibrational wavefunctions and induces secondary isotope shifts of ^{103}Rh and ^{13}C resonances [99]. Relevant to this work is the asymmetric $^1\Delta^{103}\text{Rh}(^{18/16}\text{O})$ secondary isotope shift seen for isotopologue **II** that breaks the symmetry across the dirhodium bond - rendering the ^{103}Rh sites chemically inequivalent and granting access to the ^{103}Rh - ^{103}Rh J-coupling and rhodium singlet state.

Isotopologue **II** represents an ABX_4 spin system, where AB denotes the chemically inequivalent, strongly coupled, ^{103}Rh spin pair. Whereas, isotopologues **I** and **III** represent A_2X_4 spin systems.

In this work, the ^{103}Rh ^{18}O secondary isotope shift is defined as the ^{103}Rh chemical shift difference caused by the substitution of ^{16}O by ^{18}O ,

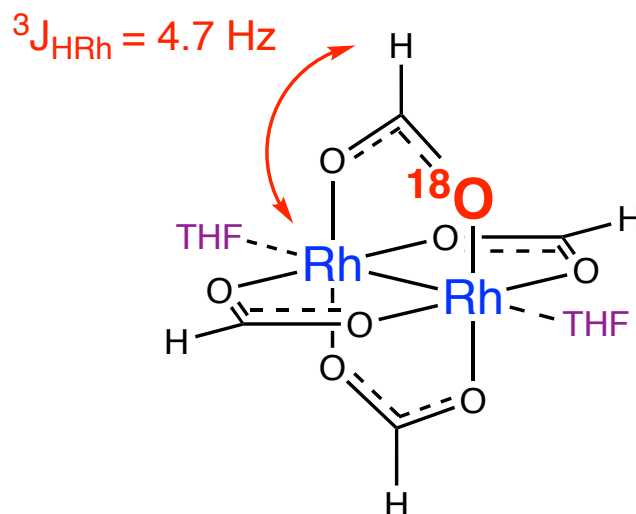
$$^n\Delta^{103}\text{Rh}(^{18}\text{O}) = \delta_{^{103}\text{Rh}}(^{16}\text{O}) - \delta_{^{103}\text{Rh}}(^{18}\text{O}) \quad (8.1)$$

Where ' n ' is the number of bonds between ^{18}O and the ^{103}Rh nucleus.

This is the same convention as used in the work by Hansen [99].

The parameters of the spin system of **II**, as estimated through the experiments described below, are given in table 8.1.

TABLE 8.1: Chemical structure of the singly ^{18}O labelled rhodium formate paddle-wheel complex (isotopologue **II** in figure 8.1) with its relevant NMR parameters in a magnetic field of 9.4 T. The chemical shift difference $\Delta\delta$ between the two ^{103}Rh nuclei in units of ppb is equal to the sum of the one-bond and two-bond ^{18}O -induced secondary isotope shifts. The ^{103}Rh - ^{103}Rh spin pair shown in blue. Solvent THF- d_8 molecules occupy axial sites. ω_Δ is the spin pair chemical shift difference in Hz at 9.4 T.



$^3J_{\text{RhH}}/\text{Hz}$	4.7 ± 0.1
$^1J_{\text{RhRh}}/\text{Hz}$	26.0 ± 0.1
$\Delta\delta/\text{ppb}$	1450 ± 1
$\omega_\Delta/\text{Hz} [@9.4 \text{ T}]$	18.5 ± 0.1
$\theta_{\text{ST}}/^\circ$	35.4 ± 0.2

The strong ^{103}Rh - ^{103}Rh J-coupling exhibited by isotopologue **II** precludes the use of the refocused-INEPT pulse sequence for $^1\text{H} \leftrightarrow ^{103}\text{Rh}$ polarisation transfer in the ^{18}O labelled rhodium formate sample. Conversely, the DualPol sequence is invariant to strong couplings and operates identically regardless of isotopologue.

Identically to the previous chapter, the DualPol sequences described here use an R-element duration of $\tau_R = 5 \text{ ms}$ and a repetition number of $L = 10$. The total DualPol sequence duration is $T = 2\tau_R L = 100 \text{ ms}$.

For shuttling experiments described here the total shuttling duration was kept constant at 1 second, in both directions.

8.1 NMR spectra

8.1.1 ^1H

The ^{18}O labelled rhodium formate proton spectrum yields the same triplet structure as seen in the non- ^{18}O labelled rhodium formate proton spectrum (figure 7.2) and likewise the three-bond ^1H - ^{103}Rh J-coupling is estimated to be $|^3J_{\text{RhH}}| = 4.7 \pm 0.1$ Hz.

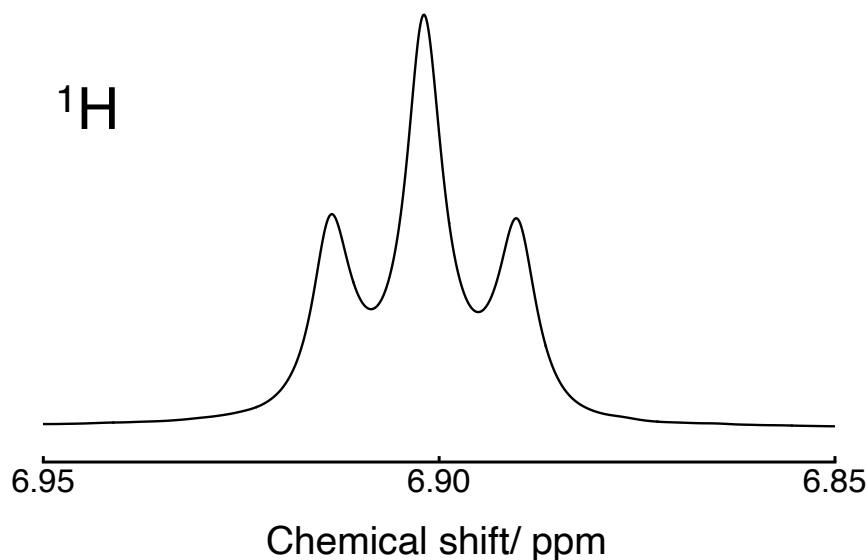


FIGURE 8.2: ^1H spectrum of a ~ 10 mM solution of ^{18}O labelled rhodium formate in $\text{THF-}d_8$, acquired at 9.4 T and at 298K. Spectrum was acquired in one scan. Lorentzian line broadening (0.75 Hz) was applied

8.1.2 $^{13}\text{C}\{^1\text{H}, ^{103}\text{Rh}\}$

The $^{13}\text{C}\{^1\text{H}, ^{103}\text{Rh}\}$ spectrum exhibits three peaks in a 13:2:1 ratio, corresponding to the different carbon environments formed by varying numbers of ^{18}O labels. The peak at ~ 180.950 ppm arises from a carbon environment consisting of a ^{13}C nucleus bound to two ^{16}O nuclei. This is the most common carbon environment and is present in *every* isotopologue; hence this peak exhibits the largest relative intensity. The peak at ~ 180.925 ppm corresponds to **II**. Finally, the peak at ~ 180.900 ppm arises from **III**.

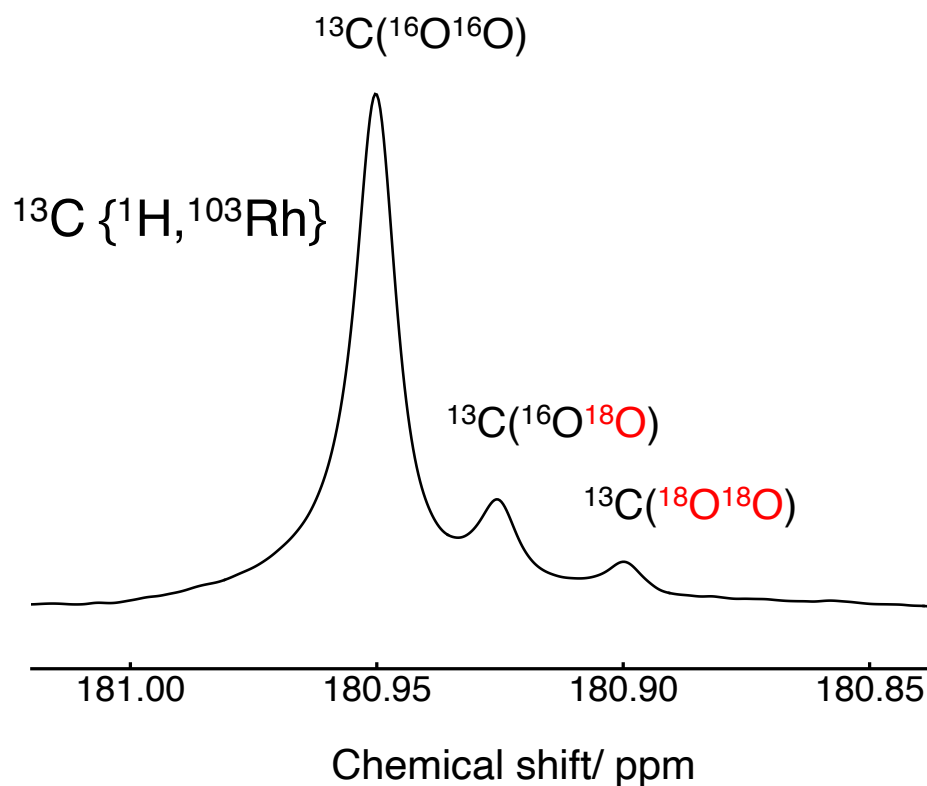


FIGURE 8.3: Annotated $^{13}\text{C}\{^1\text{H}, ^{103}\text{Rh}\}$ spectrum of a ~ 10 mM solution of ^{18}O labelled rhodium formate in $\text{THF-}d_8$, acquired at 14.1 T and at 298 K. Spectrum was acquired using 4096 scans. Lorentzian line broadening (1 Hz) was applied.

The $^1\Delta^{13}\text{C}(^{16}\text{O}, ^{18}\text{O})$ secondary isotope shift is approximately equal to 3.8 Hz or 25 ppb, which is similar to $^1\Delta^{13}\text{C}(^{16}\text{O}, ^{18}\text{O})$ secondary isotope shifts reported previously in certain organic molecules.[107, 143]

8.1.3 Proton enhanced ^{103}Rh spectra

Numerous rhodium formate isotopologues give rise to multiple ^{103}Rh environments with individual ^{103}Rh resonances that are comparably less intense than those arising from the single ^{103}Rh environment seen in the non ^{18}O labelled rhodium formate sample. Therefore, to maximise sensitivity for measurements on the ^{18}O labelled sample, 2D pulse sequence methodology was developed for the indirect acquisition of ^{103}Rh spectra.

The sequence shown in figure 8.4 was used in the acquisition of 2D ^1H - ^{103}Rh Heteronuclear Single Quantum Coherence (HSQC) spectra. ^1H to ^{103}Rh cross polarisation is achieved via a DualPol block. Next, rhodium transverse magnetisation is generated by a ^{103}Rh 90° pulse and which then evolves under continuous wave ^1H decoupling during the incremented t_1 interval. Transverse rhodium magnetisation is returned to ^{103}Rh

z-magnetisation by another 90° pulse before being transferred to proton z magnetisation by an additional DualPol block. A final 90° pulse on the proton channel generates observable transverse ^1H magnetisation, which is detected during the ensuing t_2 detection interval. The subsequent double Fourier Transform of the $s(t_1, t_2)$ signal matrix yields a 2D spectrum with ^{103}Rh frequencies in the indirectly detected F1 dimension and ^1H frequencies in the directly detected F2 dimension.

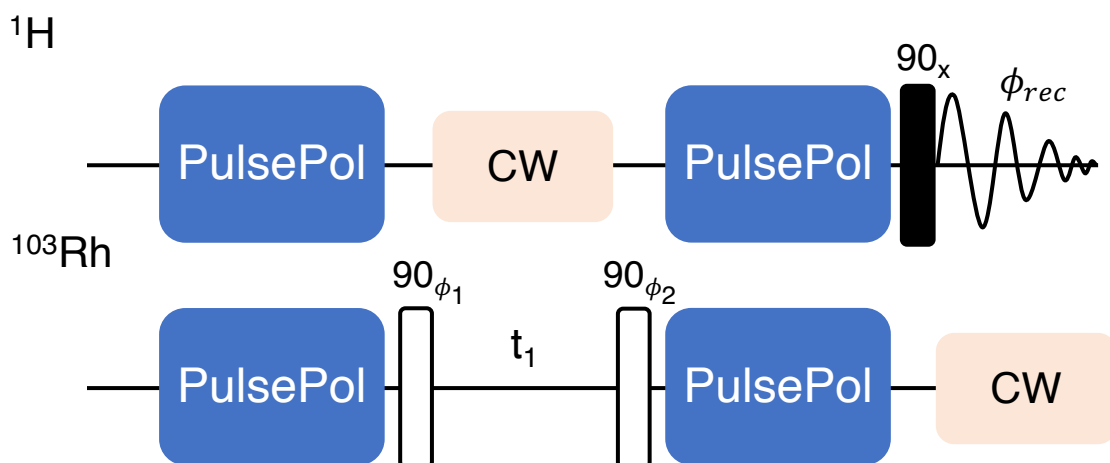


FIGURE 8.4: Pulse sequence for the acquisition of 2D ^1H - ^{103}Rh spectra. Phase cycles are given by $\phi_1 = [x, x, -x, -x]$, $\phi_2 = [-x, x]$ and the receiver $\phi_{rec} = [x, -x, -x, x]$. The black rectangle indicates a BB1 composite 90° pulse (equation 5.3).

The 2D spectrum shown in figure 8.5 shows a single peak in the ^1H dimension and six peaks heralding from the three rhodium formate isotopologues in the ^{103}Rh dimension. This spectrum was acquired using two scans for each $s(t_1, t_2)$ signal component and with an FID size of 65 k points in the direct $^1\text{H}\{^{103}\text{Rh}\}$ dimension and 512 points in the indirect $^{103}\text{Rh}\{^1\text{H}\}$ dimension. The spectral width in the indirect dimension was 20 ppm (254 Hz).

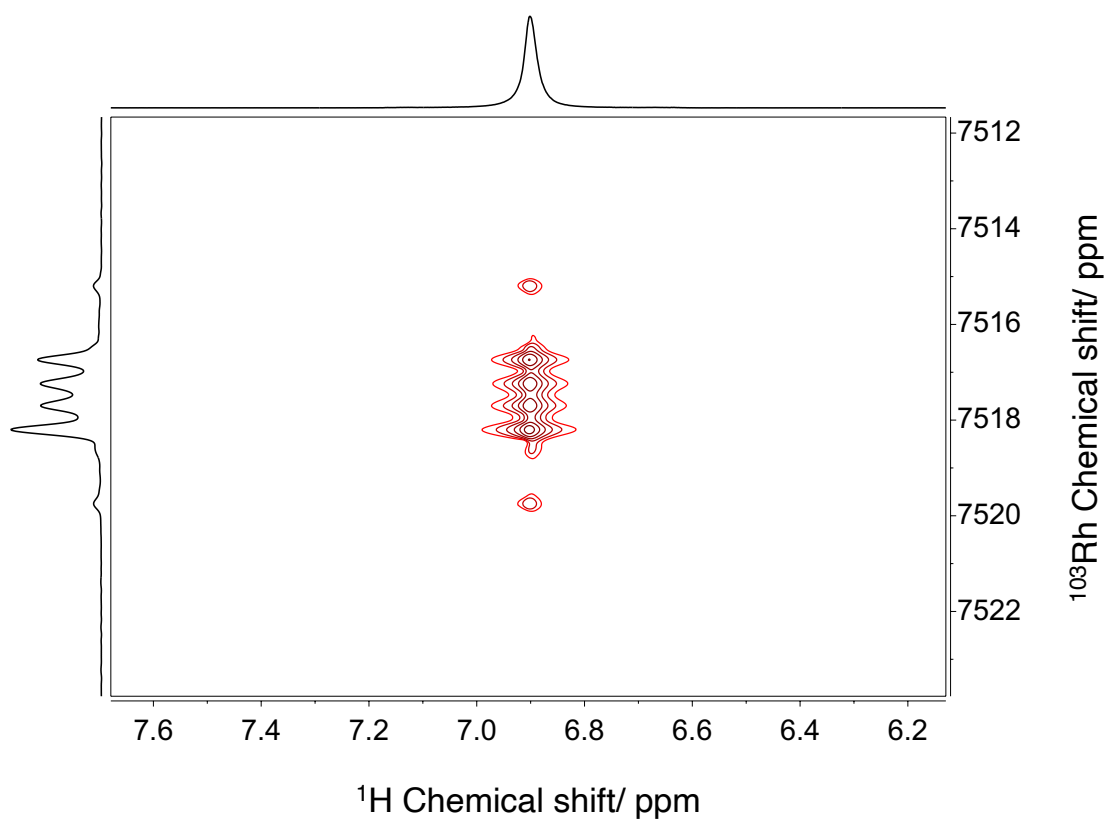


FIGURE 8.5: Rhodium formate 2D HSQC spectrum of a ~ 10 mM solution of ^{18}O labelled rhodium formate in $\text{THF-}d_8$ acquired at 9.4 T and at 298 K. Spectrum was processed with 2 Hz Lorentzian line broadening in the directly detected F2 ^1H dimension and 0.75 Hz Lorentzian line broadening in the F1 indirect ^{103}Rh dimension. The ^{103}Rh chemical shift is relative to the centre of the ^{103}Rh peaks at 7517.5 ppm and the ^1H chemical shift is relative to the peak at 6.9 ppm. The acquisition time for this spectrum was ~ 11 hours.

The indirectly detected $^{103}\text{Rh}\{^1\text{H}\}$ spectrum is examined in closer detail in figure 8.6.

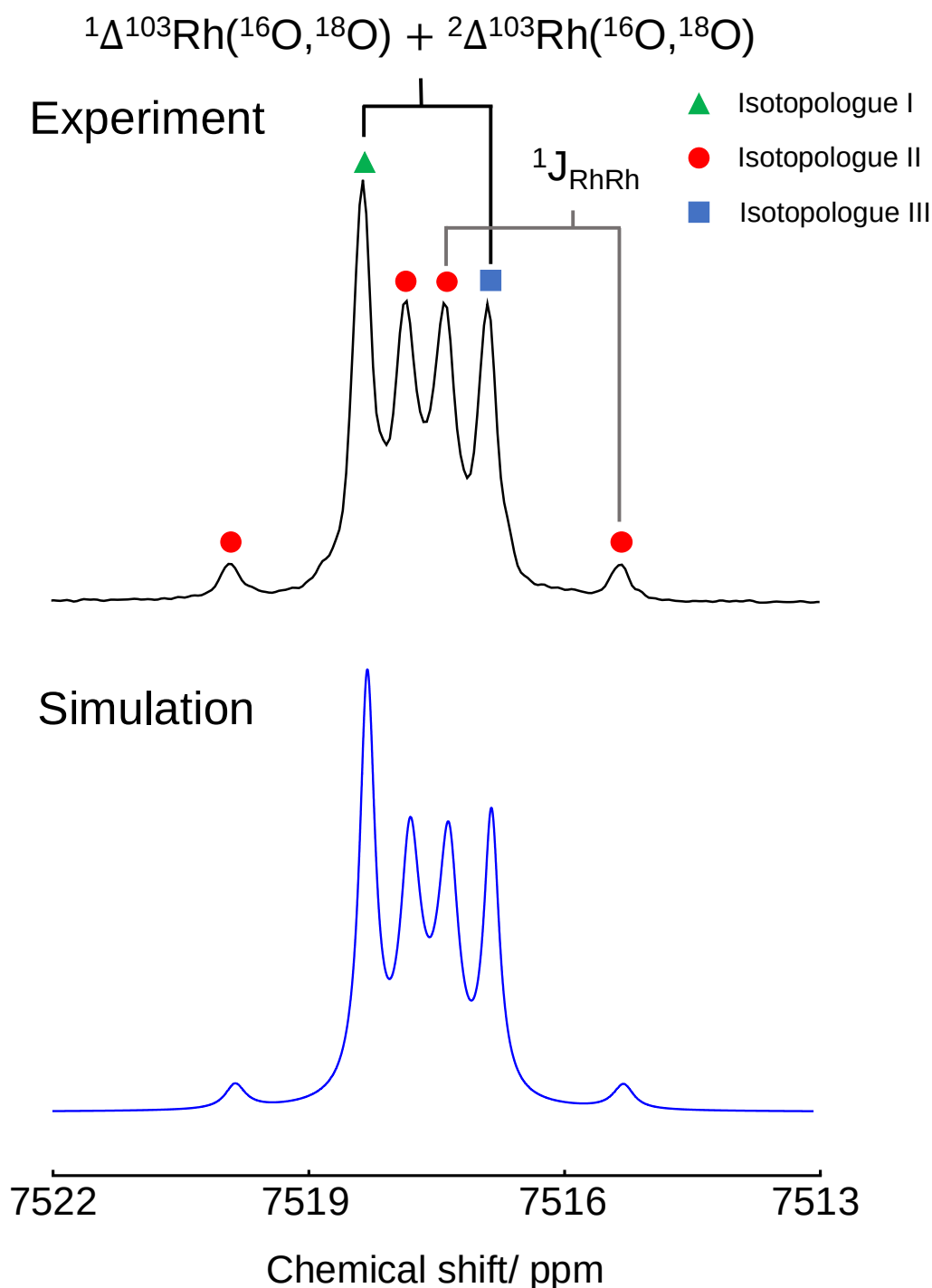


FIGURE 8.6: Rhodium formate $^{103}\text{Rh}\{^1\text{H}\}$ experimental and simulated spectra. The experimental spectrum is a single slice of the indirect dimension of the 2D HSQC spectrum shown in figure 8.5 and was processed using 0.75 Hz Lorentzian line broadening. The simulated spectrum was produced using an effective ^{103}Rh T_2 of 180 ms, 1 Hz Lorentzian line broadening, a ^{103}Rh spin pair chemical shift difference of 18.5 Hz, a $|^1J_{\text{RhRh}}|$ of 26 Hz and an ^{18}O enrichment factor of 45%. The proportion of each isotopologue is given by equations 8.2. The ^{103}Rh chemical shift is referenced to $(\Xi(^{103}\text{Rh}) = 3.16\%)$.

The $^{103}\text{Rh}\{^1\text{H}\}$ spectrum features singlet peaks originating from equivalent ^{103}Rh environments in **I** and **III** respectively; as well as an AB quartet originating from the inequivalent, coupled, ^{103}Rh spin pair in **II**.

Inspection of the bonding structure in figure 8.6 tells us that the frequency difference between isotopologues **I** and **III** is given as the sum of of the $^1\Delta^{103}\text{Rh}(^{16}\text{O},^{18}\text{O})$ and $^2\Delta^{103}\text{Rh}(^{16}\text{O},^{18}\text{O})$ secondary isotope shifts. Moreover, the centre of the AB quartet of isotopologue **II** is at the midpoint of isotopologues **I** and **III**, which precludes the independent measurements of the one bond and two bond secondary isotope shifts. The spectrum therefore only permits the measurement of the sum of secondary isotope shifts, which are estimated to be $^1\Delta^{103}\text{Rh}(^{16}\text{O},^{18}\text{O}) + ^2\Delta^{103}\text{Rh}(^{16}\text{O},^{18}\text{O}) = 1450 \pm 1$ ppb.

In solution, the probabilities of each isotopologue are given by:

$$\begin{aligned} p(\text{I}) &= p(^{16}\text{O})^2 \\ p(\text{II}) &= 2p(^{18}\text{O})p(^{16}\text{O}) \\ p(\text{III}) &= p(^{18}\text{O})^2 \end{aligned} \tag{8.2}$$

where $p(^{16}\text{O}) + p(^{18}\text{O}) = 1$ and $p(^{18}\text{O})$ is the ^{18}O enrichment level of the single labelled formate ligand.

From the relative peak intensities in the experimental spectrum shown in figure 8.6 (top pane), we can deduce that the solution contains an approximate 3:5:2 mixture of **I**, **II** and **III** respectively, corresponding to $\sim 45\%$ ^{18}O enrichment. Furthermore, the simulated $^{103}\text{Rh}\{^1\text{H}\}$ spectra with $p(^{18}\text{O}) = 0.45$ shown in figure 8.6 (lower pane) is in good agreement with the experimental spectrum.

The ^{103}Rh - ^{103}Rh homonuclear J-coupling, $|^1J_{\text{RhRh}}|$, can be taken directly from the outer splitting in the AB quartet corresponding to **II** and is equal to 26.0 ± 0.1 Hz.

The AB quartet pertaining to isotopologue **II** in the indirectly detected $^{103}\text{Rh}\{^1\text{H}\}$ spectrum demonstrates the successful breaking of magnetic equivalence across the dirhodium bond via selective ^{18}O labelling in the rhodium formate paddlewheel complex; and with knowledge of the ^{103}Rh - ^{103}Rh homonuclear J-coupling and ^{103}Rh chemical shift difference (assuming that $^1\Delta^{103}\text{Rh}(^{16}\text{O},^{18}\text{O}) \gg ^2\Delta^{103}\text{Rh}(^{16}\text{O},^{18}\text{O})$), we can now calculate the singlet-triplet mixing angle of the ^{103}Rh spin pair in isotopologue **II**: $\theta_{ST} = \arctan\left(\frac{\omega_{\Delta}}{J}\right) \simeq \arctan\left(\frac{18.5}{26}\right) \simeq 35^\circ$. This places the ^{103}Rh spin pair in approximately the intermediate coupling regime.

8.2 Generating rhodium singlet order

With the measurement of the homonuclear ^{103}Rh - ^{103}Rh J-coupling, we may now utilise the $\text{R}4_1^1$ PulsePol sequence (figure 3.4) to generate rhodium singlet order in the magnetically inequivalent ^{103}Rh spin pair of isotopologue **II**.

8.2.1 Rhodium SO build up curves

Rhodium singlet order derived signals were indirectly detected on the protons using the sequence shown in figure 8.7. DualPol is used to transfer z-magnetization from the ^1H nuclei to the ^{103}Rh nuclei. After which the $\text{R}4_1^1$ PulsePol sequence is used to convert ^{103}Rh z-magnetisation into rhodium singlet order. A dual T_{00} filter (figure 8.8) selects for rhodium singlet order whilst simultaneously eliminating any residual proton magnetisation (see below). An additional $\text{R}4_1^1$ PulsePol block returns rhodium singlet order back into rhodium z-magnetisation. A proton destruction filter is then applied to eliminate any residual proton magnetisation that may have formed during the $\text{R}4_1^1$ PulsePol block. ^{103}Rh z-magnetisation, selected for by the two 90° pulses, is now transferred back to ^1H z-magnetisation by a second DualPol block and is selected for by a proton z-filter. A final ^1H 90° pulse generates observable ^1H transverse magnetization. The sequence is repeated with variation of the $\text{R}4_1^1$ PulsePol block's loop count L in order to optimise the $\text{R}4_1^1$ PulsePol block parameters for optimal rhodium singlet order generation.

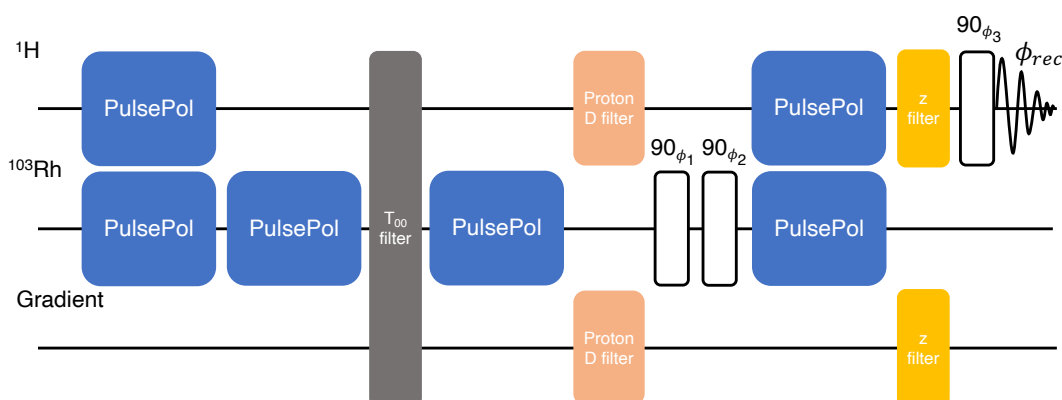


FIGURE 8.7: Pulse sequence for the acquisition of ^{103}Rh singlet filtered ^1H spectra. Phase cycles are given by $\phi_1 = [-x, x, -x, x]$, $\phi_2 = [x, x, -x, -x]$, $\phi_3 = [x, x, x, x, y, y, y, y, -x, -x, -x, -x, -y, -y, -y, -y]$ and the receiver $\phi_{rec} = [x, -x, x, -x, y, -y, -y, -x, x, -x, x, -y, y, y]$.

The conventional single-channel T_{00} filter is a sequence of rf and field-gradient pulses designed to select for spin operators which transform as a rank-0 spherical operator.

These rank-0 spin operators are invariant to three-dimensional rotations [143] and, for spin-1/2 systems, correspond to the unity operator and the scalar coupling operator, which corresponds to singlet order. This work utilises a dual-channel T_{00} filter featuring simultaneous T_{00} sequences on both the ^1H and ^{103}Rh channels as shown in figure 8.8. This filter selects for spin order terms that are invariant to rotations of both the ^{103}Rh and ^1H spin states - such as the unity operator and rhodium/proton singlet order. In the context of this work, the effect of this filter is two fold, (i) rhodium singlet order is selected for, whilst (ii) residual ^1H longitudinal and transverse magnetisation is destroyed. The destruction of ^1H magnetisation is particularly pertinent for the suppression of background signals in rhodium singlet filtered ^1H spectra.

The parameters of the dual T_{00} filter sequence used here are as follows: The gradient strengths are given by $G_1=100\%$, $G_2=61.8\%$ and $G_3=38.2\%$ with respect to the maximum gradient strength of 50 G cm^{-1} . The duration of the gradients was 2 ms. The flip angle β is given by the magic angle (54.74°).

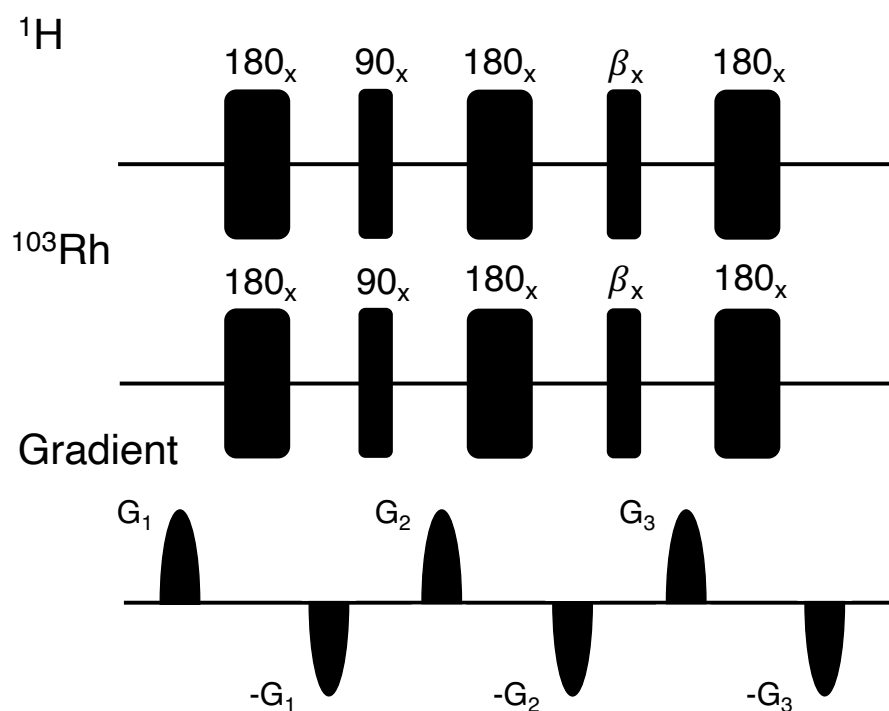


FIGURE 8.8: Dual T_{00} filter for the selection of rank-0 spin order, using bipolar gradient pulses and rf pulses. β_x denotes a pulse with phase 0 with a flip angle of 54.74° (i.e the magic angle). The gradient strengths are given by $G_1=100\%$, $G_2=61.8\%$ and $G_3=38.2\%$ with respect to the maximum gradient strength of 50 G cm^{-1} . Each gradient pulse has a duration of 2 ms. The black rectangles indicate BB1 composite pulses (equations 5.2, 5.3 and 5.4).

The generation of rhodium singlet order as a function of R4_1^1 PulsePol R-element duration for the rhodium formate paddlewheel complex is shown in figure 8.9.

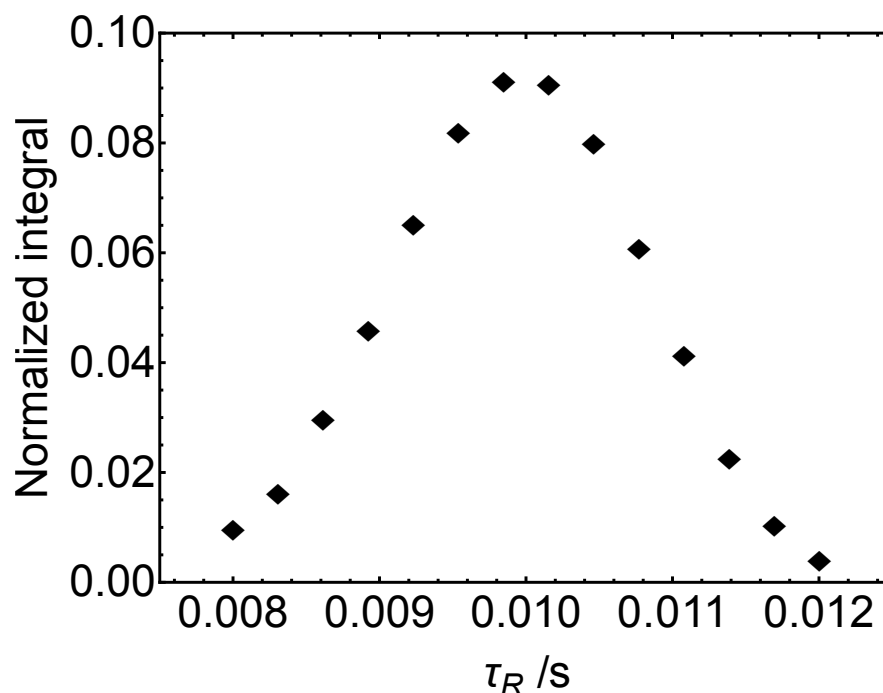


FIGURE 8.9: Plot showing rhodium SO derived ^1H signal intensity as a function of R4_1^1 PulsePol R-element duration at 9.4 T and at 298 K. The R4_1^1 PulsePol repetition number L was kept constant at 10. The integrals are normalised against a ^1H spectrum obtained by a single ^1H 90° pulse applied to a system in thermal equilibrium at 9.4 T.

The experimentally optimised R-element duration of 9.8 ms is in good agreement with the theoretical optimum of $\tau_R = n/NJ_{RhRh} = 9.6$ ms (assuming $J_{RhRh} = 26$ Hz).

The generation of rhodium singlet order as a function of the number of R4_1^1 PulsePol R-elements for the rhodium formate paddlewheel complex is shown in figure 8.10

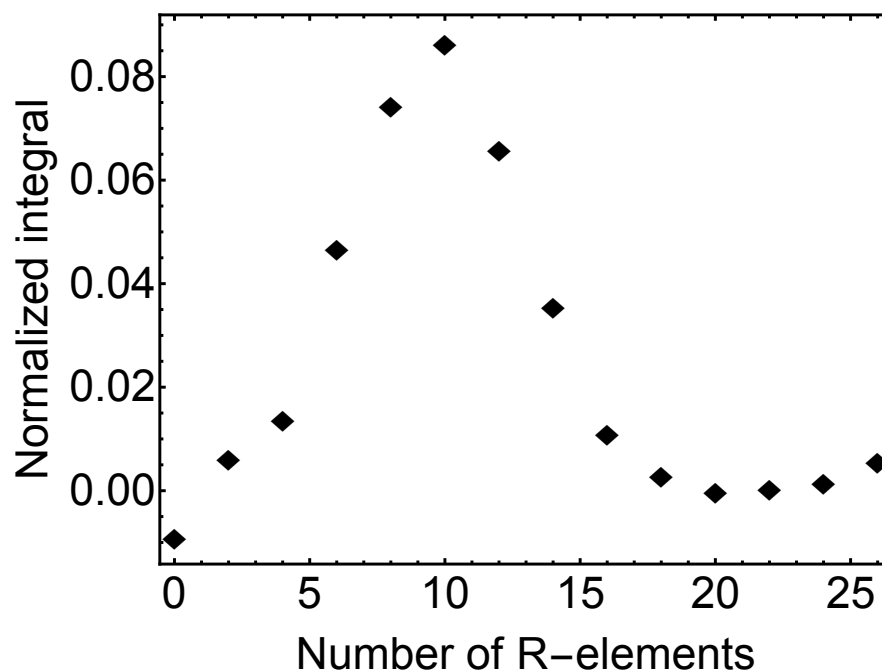


FIGURE 8.10: Plot showing rhodium SO derived ^1H signal intensity as a function of the number of R4_1^1 PulsePol R-elements at 9.4 T and at 298 K. The R4_1^1 PulsePol R-element duration was kept constant at $\tau_R = 9.8$ ms. The integrals are normalised against a ^1H spectrum obtained by a single ^1H 90° pulse applied to a system in thermal equilibrium at 9.4 T.

The optimal number of R4_1^1 PulsePol R-elements for the generation of rhodium singlet order in the rhodium formate paddlewheel complex is 10, which corresponds to a total duration of: $10 \times \tau_R = 98$ ms.

8.2.2 Singlet filtered $^{103}\text{Rh}\{^1\text{H}\}$ spectrum

The sequence shown in figure 8.11 was used to acquire a directly detected ^{103}Rh singlet filtered ^{103}Rh spectrum.

The sequence operates as follows: An initial pair of phase cycled 90° pulses on the ^1H channel select for ^1H z-magnetisation whilst simultaneously suppressing acoustic ringing artefacts from the ^{103}Rh channel (this is the same acoustic ringing suppression scheme as described in section 7.1.3). A DualPol block converts ^1H z-magnetisation into ^{103}Rh z-magnetisation, which is then converted into ^{103}Rh singlet order by a R4_1^1 PulsePol block. ^{103}Rh singlet order is selected for by a dual T_{00} filter before being converted back into ^{103}Rh z-magnetisation by an additional R4_1^1 PulsePol block. Finally, observable ^{103}Rh magnetisation is generated by a 90° pulse. The dual T_{00} filter ensures that only signals derived from ^{103}Rh singlet order are present in the resulting spectrum.

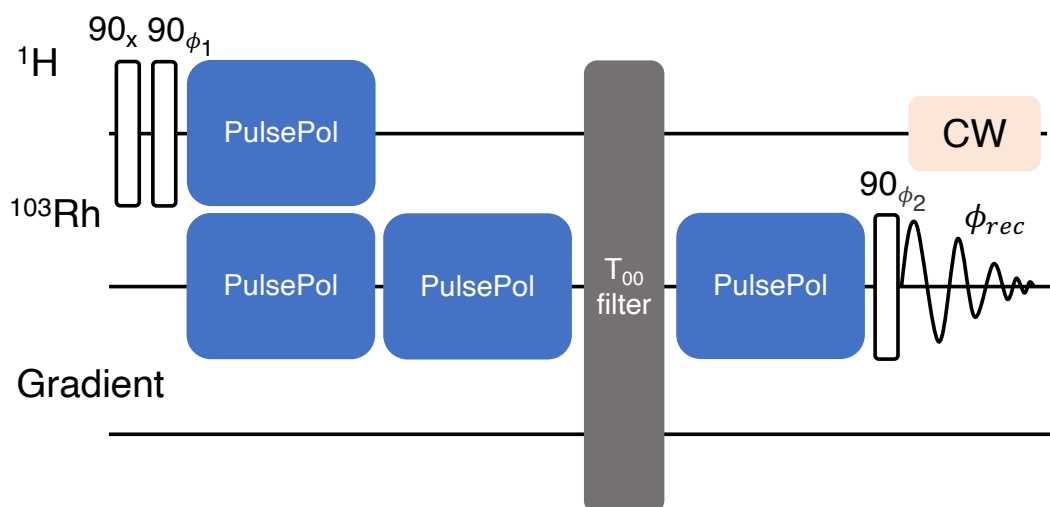


FIGURE 8.11: Sequence used for the acquisition of ^{103}Rh singlet filtered ^{103}Rh spectra. Initial pair of ^1H pulses filter out acoustic ringing generated by subsequent ^{103}Rh pulses. The phase cycles are given by, $\phi_1 = [-x, x, -x, x]$, $\phi_2 = [x, x, x, x, y, y, y, y, -x, -x, -x, -x, -y, -y, -y, -y]$ and the receiver $\phi_{rec} = [x, -x, x, -x, y, -y, y, -y, y, -x, x, -x, x, -y, y, -y, y]$

The singlet filtered $^{103}\text{Rh}\{^1\text{H}\}$ spectrum, shown in figure 8.12, only exhibits the AB quartet belonging to isotopologue **II**. This is because only isotopologue **II** has the prerequisite molecular geometry for the generation of rhodium singlet order. Signals originating from isotopologues **I** and **III** are suppressed by the dual T_{00} filter. Curiously, a 1 ppm shift difference is observed between the spectra in figures 8.6 and 8.12. This shift may be attributed to minor differences in sample temperature during the two experiments. Using the known temperature dependence of the ^{103}Rh chemical shift (figure 7.7), a temperature change of ~ 0.7 K is sufficient to account for this shift difference. Since this spectrum was obtained by direct detection of the ^{103}Rh NMR signal, its signal-to-noise ratio is poor relative to the ^1H -detected ^{103}Rh spectrum shown in figure 8.6. Consequently, the outer peaks of the AB quartet are concealed by an abundance of background noise and are thus difficult to discern.

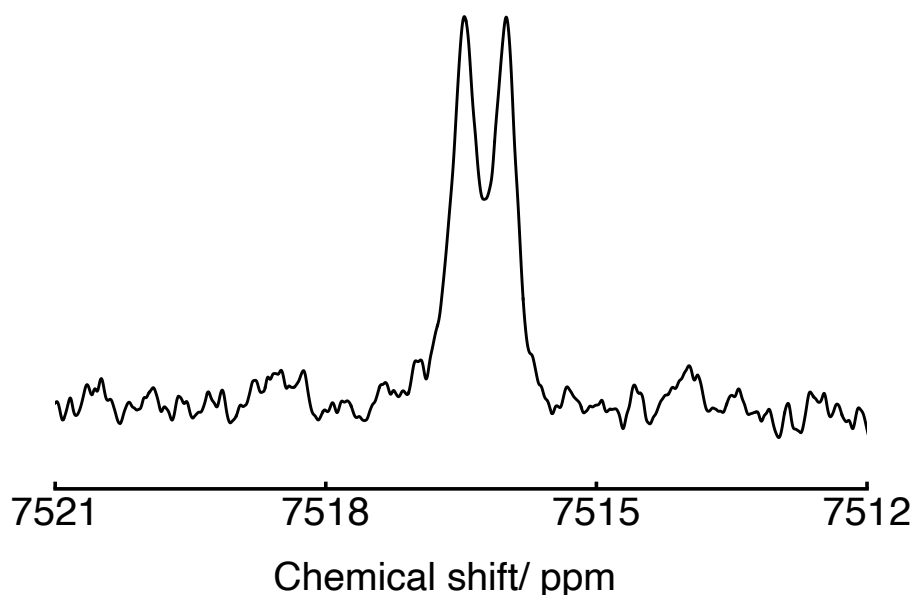


FIGURE 8.12: Singlet filtered $^{103}\text{Rh}\{^1\text{H}\}$ spectrum of a ~ 10 mM solution of ^{18}O labelled rhodium formate in $\text{THF-}d_8$ acquired at 9.4 T and at 298 K using 2048 scans. Spectrum was processed with 1 Hz Lorentzian line broadening. ^{103}Rh chemical shift referenced to $(\Xi(^{103}\text{Rh}) = 3.16\%)$.

8.3 Rhodium formate ^{103}Rh T'_S relaxometry

Despite succeeding in the generation of rhodium singlet order, the rhodium formate coupled ^{103}Rh spin pair resides in the intermediate coupling regime ($\theta_{ST} = 35^\circ$) wherein singlet order is *not* eigenorder of the corresponding ^{103}Rh spin pair Hamiltonian. Thus, rhodium singlet order generated in this complex at high fields is vulnerable to the singlet-triplet leakage relaxation mechanism and is invariably short lived.

We therefore opted to convert high field rhodium singlet order into high field Quasi-Singlet EigenOrder (section 2.1.5), which *does* represent eigenorder of the ^{103}Rh spin Hamiltonian, so is immune to singlet-triplet leakage. Furthermore, upon adiabatic sample transport to low magnetic fields, and as $\Delta \rightarrow 0$, QSEO is converted into pure singlet order.

In this work, we use the symbol T'_S to denote the relaxation time constant for the decay of QSEO.

8.3.1 Indirect ^{103}Rh T'_S pulse sequence

^{103}Rh T'_S relaxation time constants were measured indirectly on the protons using the sequence in figure 8.13

Due to its significant length, and for convenience to the reader, this pulse sequence has been partitioned into three parts. In part A (shown in figure 8.13b) rhodium QSEO is generated. Part B consists of optional shuttling of the sample to and from a region of lower magnetic field strength either side of a relaxation interval τ_{relax} . Finally, part C (shown in figure 8.13c) converts the remaining rhodium QSEO into observable ^1H magnetisation.

Part A functions as follows: The initial pair of proton 90° pulses select for proton z-magnetisation. A DualPol block is used to transfer z-magnetisation from the protons onto the ^{103}Rh nuclei, after which a pair of rhodium 90° pulses select for ^{103}Rh z-magnetisation. Rhodium singlet order is generated via a $\text{R}4_1^1$ PulsePol block and selected for by a dual T_{00} filter. singlet order is then converted into high field rhodium QSEO by a $\text{S}2\text{S}'$ block (figure 8.14).

Part B is comprised of a variable waiting interval τ_{relax} that occurs in between two optional transport intervals in which the sample is transported to and from a region of low magnetic field.

In part C, remaining eigenorder is converted back into rhodium singlet order by a $\text{S}'2\text{S}$ block and selected for by another dual T_{00} filter. Rhodium singlet order is converted back into ^{103}Rh z-magnetisation by another $\text{R}4_1^1$ PulsePol block before being transferred to the protons by a second DualPol block. ^1H z-magnetisation is selected for by a proton z-filter and converted into observable magnetisation by a final 90° pulse.

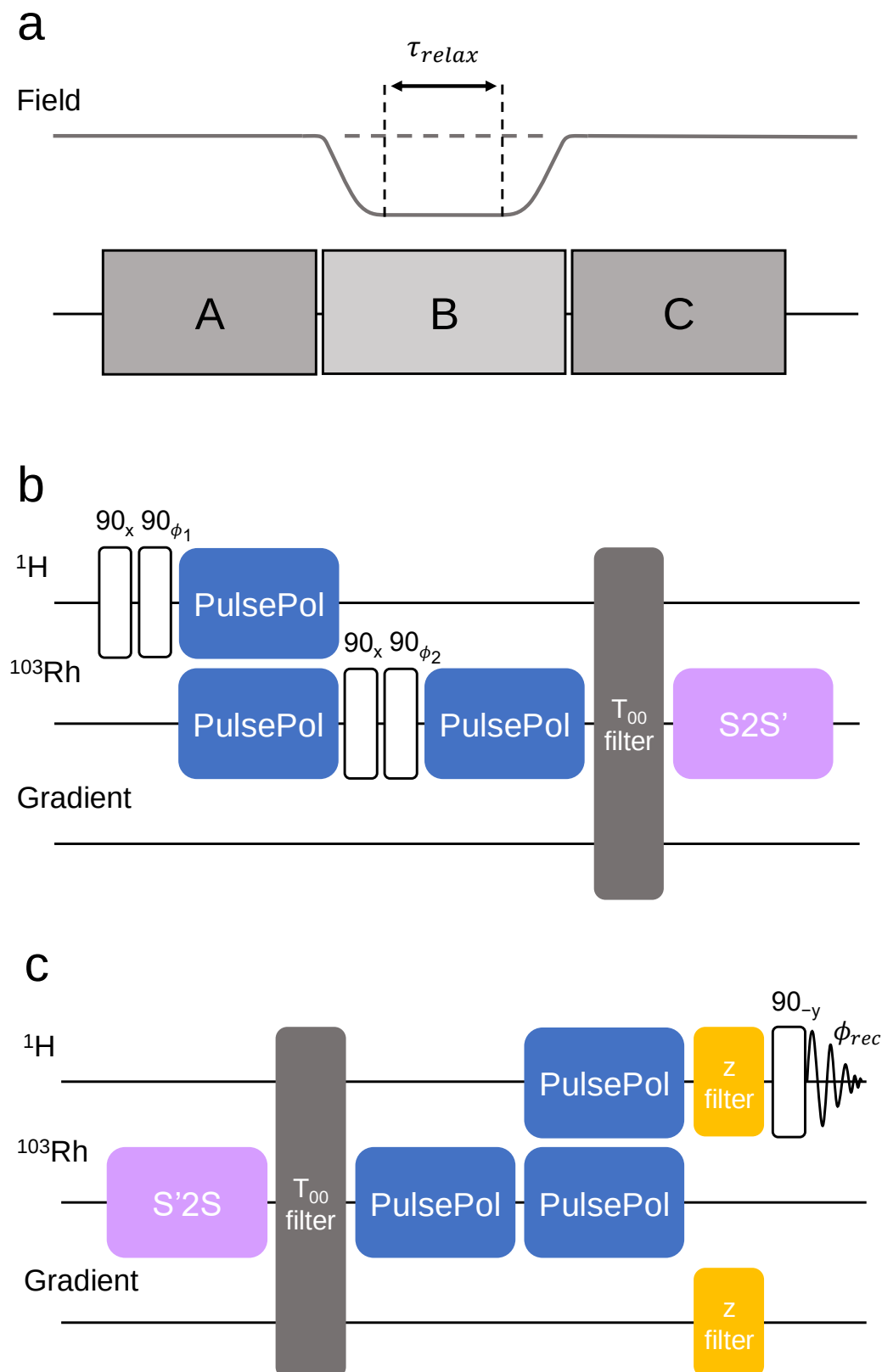


FIGURE 8.13: Sequence used for the indirect measurement of rhodium T'_S with detection on protons. Due to significant length, pulse sequence is partitioned into blocks a and b. Block a is for the excitation of rhodium quasi-singlet eigen order; whereas block b reads out remaining rhodium quasi-singlet eigen order after the decay interval τ_{relax} . Phase cycles are given by $\phi_1 = [-x, x]$, $\phi_2 = [-x, -x, -x, -x, x, x, x, x]$ and the receiver $\phi_{rec} = [y, -y, y, -y, -y, y, -y, y]$.

Designed by Mohamed Sabba and Christian Bengs, The S2S' pulse sequence element, shown in figure 8.14 converts singlet order into QSEO. This transformation is achieved using a sequence of two pulses and three evolution intervals, of the form:

$$\text{S2S}' = (\tau_1 - \pi_x - \tau_1 - \tau_2 - \pi_x - \tau_2) \quad (8.3)$$

For the experiments described here, the delay intervals were optimised numerically and are given by $\tau_1 = 7.3$ ms and $\tau_2 = 27.6$ ms.

To accomplish the reverse transformation (i.e. $|S'_0\rangle \rightarrow |S_0\rangle$) the same sequence is applied but in reverse chronological order, for example:

$$\text{S}'2\text{S} = (\tau_2 - \pi_x - \tau_2 - \tau_1 - \pi_x - \tau_1) \quad (8.4)$$

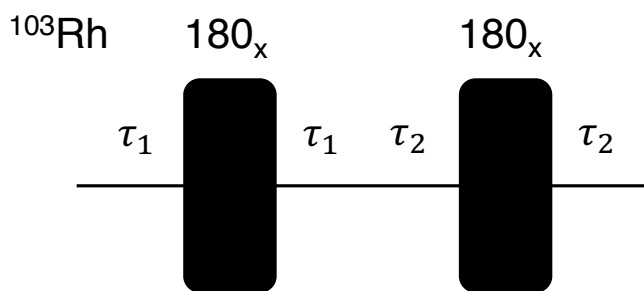


FIGURE 8.14: S2S' block for the transformation of rhodium singlet order into highfield rhodium QSEO where $\tau_1 = 7.3$ ms and $\tau_2 = 27.6$ ms. The black rectangles indicate BB1 composite π -pulses (equation 5.4).

8.3.2 Rhodium formate ^{103}Rh $T_{S'}$ decay curves

The trajectory of indirectly-detected ^{103}Rh QSEO in a field of 9.4 T is shown in figure 8.15(a) and was obtained by the pulse sequence in figure 8.13, but without the sample transport into low field. The trajectory fits well to a single-exponential decay with time constant $T_{S'}(^{103}\text{Rh}) = 0.359 \pm 0.001$ s. We recall that the T_1 time constant for the equilibration of ^{103}Rh longitudinal magnetisation at the same field was $T_1(^{103}\text{Rh}) = 0.483 \pm 0.002$ s. Therefore, the high field ^{103}Rh QSEO clearly does not constitute a long-lived mode of spin order. Upon sample transport to the low field, high-field QSEO is converted into low-field singlet order, which decays with the time constant T_S . An experimental relaxation trajectory of ^{103}Rh singlet order in the low magnetic field of 1 mT is shown in figure 8.15(b). This was produced by shuttling the sample to and from low magnetic field before and after the interval τ_{relax} . Here the

trajectory is a bi-exponential decay of the form $A \exp \{-t/T_a\} + B \exp \{-t/T_b\}$ where $A = 0.0026 \pm 0.0008$, $B = 0.0055 \pm 0.0008$, $T_a = 229 \pm 94$ s and $T_b = 25.2 \pm 5.8$ s. We attribute the longer decay constant T_a to the decay of rhodium singlet order ($T_a = T_{S'}(^{103}\text{Rh})$). This may be compared with the time constant for the equilibration of longitudinal magnetisation in the same field: $T_1(^{103}\text{Rh}) = 28.2 \pm 1.2$ s (figure 7.9(b)). The low field rhodium singlet lifetime is approximately 8 times longer than the corresponding rhodium T_1 ; and thus constitutes a long-lived mode of spin order in the low field.

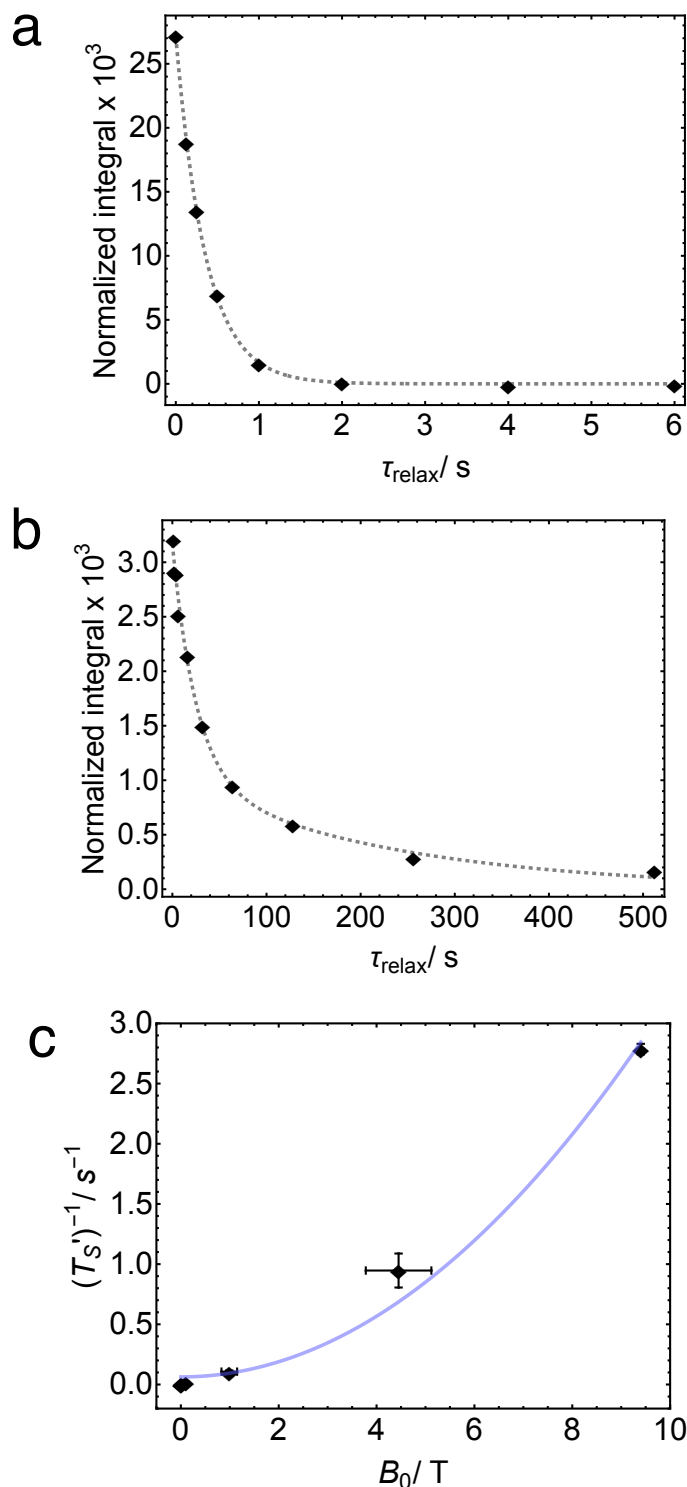


FIGURE 8.15: (a) Decay curve for ^{103}Rh QSEO at a field of 9.4 T and at 298 K, obtained using the pulse sequence in figure 8.13, but without shuttling the sample to low field. The data was acquired in ~ 20 minutes. The data fits well to a monoexponential decay with time constant $T'_S = 0.359 \pm 0.01$ s. (b) Decay curve for ^{103}Rh QSEO at a field of 1 mT and at 298 K, obtained using the pulse sequence in figure 8.13, including the shuttling of the sample to low field. The data fits well to a bi-exponential decay of the form $A \exp\{-t/T_a\} + B \exp\{-t/T_b\}$ where $A = 0.0026 \pm 0.0008$, $B = 0.0055 \pm 0.0008$, $T_a = 229 \pm 94$ s and $T_b = 25.2 \pm 5.8$ s. The integrals are normalised against the ^1H spectrum obtained by a single ^1H 90° pulse applied to a system in thermal equilibrium at 9.4 T. (c) ^{103}Rh QSEO relaxation rate constant $(T'_S)^{-1}$ as a function of magnetic field strength B . The blue line shows the quadratic function $(T'_S)^{-1}(B) = (T'_S)^{-1}(0) + aB^2$, where $(T'_S)^{-1}(0) = (63 \pm 55) \times 10^{-3} \text{ s}^{-1}$ and $a = (31 \pm 2) \times 10^{-3} \text{ s}^{-1} \text{ T}^{-2}$.

The rhodium T_S^{-1} increases approximately quadratically with the magnetic field strength B_0 , as shown in figure 8.15(c). The field-dependent relaxation rate constant is a reasonable fit to the quadratic function $(T_S')^{-1}(B) = (T_S')^{-1}(0) + aB^2$, where $(T_S')^{-1}(0) = (63 \pm 55) \times 10^{-3} \text{ s}^{-1}$ and $a = (31 \pm 2) \times 10^{-3} \text{ s}^{-1} \text{ T}^{-2}$.

8.4 Discussion

8.4.1 ^{103}Rh ^{18}O secondary isotope shift

Assuming the two bond isotope shift is negligible (i.e. $^2\Delta^{103}\text{Rh}(^{16}\text{O},^{18}\text{O}) = 0$), the one bond $^1\Delta^{103}\text{Rh}(^{16}\text{O},^{18}\text{O})$ secondary isotope shift is ~ 60 times larger than the corresponding $^1\Delta^{13}\text{C}(^{16}\text{O},^{18}\text{O})$ secondary isotope shift, which reflects the extreme sensitivity of the ^{103}Rh chemical shift to its local chemical environment. To the best of this author's knowledge, whilst the effects of other isotopes on ^{103}Rh shifts has previously been reported [79, 144], this work encompasses the first measurement of $^{103}\text{Rh}(^{16}\text{O},^{18}\text{O})$ isotope shifts.

8.4.2 ^{103}Rh - ^{103}Rh homonuclear J-coupling

Although previous measurements of ^{103}Rh - ^{103}Rh couplings have been measured in *asymmetric* complexes [145, 146, 147, 81, 148], the measured $^1J_{\text{RhRh}} = 26 \pm 0.1 \text{ Hz}$ coupling presented here represents the first measurement of the ^{103}Rh - ^{103}Rh homonuclear J-coupling in a symmetric paddlewheel complex (i.e where ^{103}Rh nuclei occupy chemically equivalent sites).

8.4.3 ^{103}Rh singlet order generation

The singlet filtered $^{103}\text{Rh}\{^1\text{H}\}$ spectrum shown in figure 8.12 demonstrates the first reported instance of singlet order generated in a ^{103}Rh spin pair. This also represents the first time singlet order has been accessed for nuclei outside of the first three rows of the periodic table.

8.4.4 ^{103}Rh singlet relaxometry

The reduced signal amplitude for the measurement of ^{103}Rh T_S in the low field relative to the high field T_S' measurement is well accounted for by relaxation losses during shuttling as shown in appendix H. Whereas, the bi-exponentiality of the decay of ^{103}Rh spin order in the low field is currently unexplained. Although, we note that bi-exponential

low field decay of long lived spin order has previously been reported in certain ^1H and ^{13}C spin pairs [149, 26]. It is possible that non-adiabatic transitions are occurring during sample transport, and which contribute to the observed bi-exponentiality; however, as shown in appendix I, the adiabaticity condition is well satisfied for the experiments presented here.

The quadratic field dependence of the ^{103}Rh singlet relaxation rate is consistent with a dominant high field CSA relaxation mechanism. Indeed we estimated the ^{103}Rh CSA to be ~ 9200 ppm for this complex (section 7.5.3). However, the high symmetry of the rhodium formate paddlewheel complex suggests that the two ^{103}Rh shielding tensors are equal in both magnitude and orientation; so, given the sensitivity to the *difference* in shielding tensors, the CSA contribution to the relaxation of ^{103}Rh singlet order is anticipated to be minor. This notwithstanding, deviations to the fixed geometry through thermal modulation or ligand exchange at axial sites may still prevent the complete cancellation of this mechanism.

The high-field ^{103}Rh QSEO relaxation time constant of $T_{S'}(^{103}\text{Rh}) = 0.359 \pm 0.01$ s is shorter than the corresponding high-field ^{103}Rh longitudinal relaxation time constant of $T_1(^{103}\text{Rh}) = 0.482 \pm 0.002$ s. This observation suggests that chemical exchange is occurring at the axial sites, which can be a potent singlet relaxation mechanism - even when the exchange kinetics are slow [107]. It is plausible that the reversible exchanging of solvent molecules at the axial sites breaks the symmetry across the ^{103}Rh - ^{103}Rh spin pair and modulates the isotropic chemical shifts of the ^{103}Rh nuclei; thus providing an avenue to ^{103}Rh singlet order relaxation at high fields.

We had anticipated, because of the high symmetry of the rhodium formate paddlewheel complex; as well as the low gyromagnetic ratio of ^{103}Rh , that the ^{103}Rh singlet lifetime would exhibit significant longevity - especially at low fields where the field dependent mechanisms are muted. However, although technically long-lived, the low field ^{103}Rh singlet lifetime of $T_S(^{103}\text{Rh}) \sim 230$ seconds for the rhodium formate paddlewheel complex is ultimately unremarkable. In the absence of field dependent or dipolar mechanisms, the modest low-field ^{103}Rh singlet lifetime is instead curtailed by a currently unaccounted for relaxation mechanism. Similar to our analysis of the low field ^{103}Rh T_1 , we may again invoke spin-rotation to rationalise the shorter-than-expected low field ^{103}Rh T_S . The modulation of ^{103}Rh spin-rotation tensors by chemical exchange or other dynamic processes could feasibly break the symmetry across the dirhodium bond and give rise to a significant field independent spin-rotation contribution to the ^{103}Rh singlet relaxation rate $(T_S)^{-1}$. Alternatively, it's possible that chemical exchange at axial sites may also induce fluctuations of the ^{103}Rh - ^{103}Rh J-coupling, which at low fields can induce singlet-triplet transitions and hence singlet relaxation [14].

In any case, these arguments are currently unsubstantiated; and the low field ^{103}Rh singlet relaxation behaviour of the rhodium formate paddlewheel complex remains unexplained. We can however conclude that the rhodium formate paddlewheel complex is not a suitable vehicle for sustaining ultra long-lived ^{103}Rh spin-order as was initially anticipated.

Chapter 9

Closing Remarks

The NMR of ^{103}Rh is often associated with onerous technical difficulties and prohibitively low sensitivity, and as such has received minimal attention relative to the NMR of more sensitive, easier to work with, nuclei such as ^1H and ^{13}C . This notwithstanding, through the application of certain methodologies, such as those presented in this thesis, one stands to greatly improve the sensitivity and accessibility of the ^{103}Rh NMR technique. Accordingly, it is this author's expressed hope that the work presented in this thesis may help dispel the stigmas surrounding the NMR of ^{103}Rh and demonstrate the relative ease of the practice – even when without purpose-built hardware.

The methodologies presented here, although demonstrated just in the context of ^{103}Rh NMR, also pertain to the broader field of low gamma NMR in general. However, I would be remiss not to mention the major limitation of this work: the methodologies are reliant on the presence of scalar couplings between the low gamma nucleus and more sensitive nuclei and thus are not suitable for use in all types of spin system, which limits the scope of future work somewhat.

Although the rhodium formate paddlewheel complex was ultimately an unsuitable vehicle for sustaining ultra long-lived spin order, we have successfully broadened the scope of low gamma NMR to now encompass singlet NMR. And in doing so, we are now able to study the potential of ultra long-lived spin order across a range of previously unconsidered candidate complexes.

To summarise, and in keeping with the analogy established by Brian Mann, it is high time that the Cinderella nuclei found their Prince Charming and rise up from the depths of obscurity, up to the realm of mainstream NMR; where they may thrive - living evermore, *happily ever after!*

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Appendix A

DualPol optimisation in an AX_3 spin system

The DualPol sequence for polarisation transfer between proton and ^{103}Rh nuclei in the AX_3 $\text{Rh}(\text{acac})_3$ spin system was optimised experimentally using the pulse sequence shown in figure 6.3 but where the sequence is repeated with variation of DualPol loop counter L , to control the DualPol sequence total duration.

$^1\text{H} \rightarrow ^{103}\text{Rh}$ polarisation transfer efficiency as a function of DualPol total duration is shown in figure A.1.

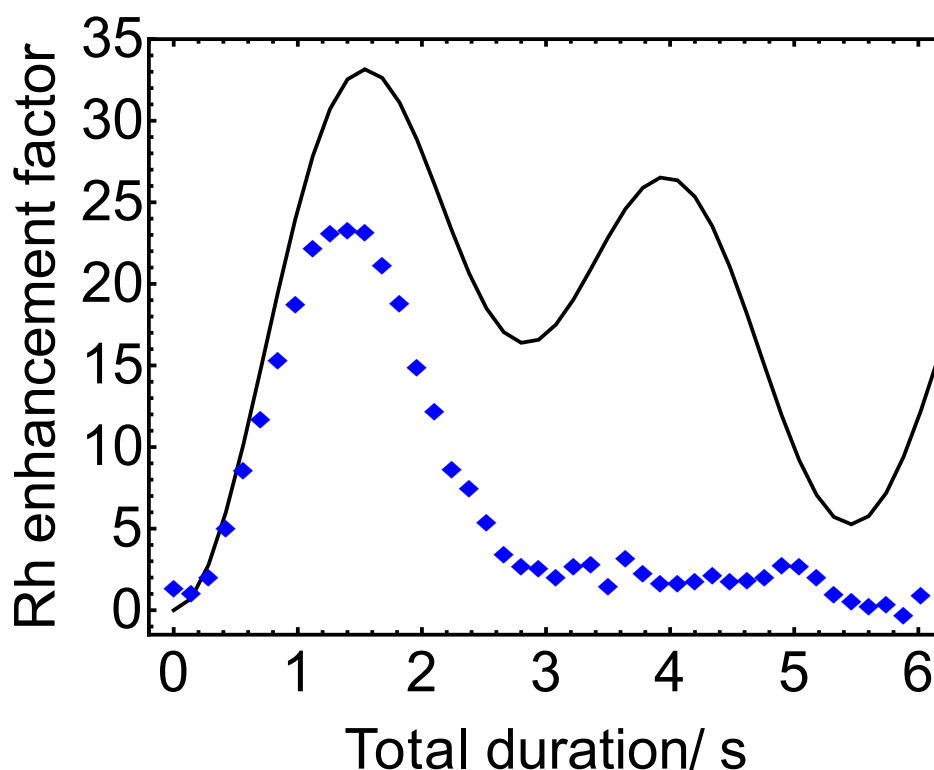


FIGURE A.1: DualPol build up curve for ^1H - ^{103}Rh polarisation transfer amplitude as a function of DualPol total duration. Blue diamonds denote experimental data points; whereas the black line represents numerical simulation. Numerical simulation was performed with $J_{RhH} = 0.39$ Hz and a DualPol R-element duration of $\tau = 70$ ms. Curves are normalised against thermal ^{103}Rh polarisation.

Optimal polarisation transfer using the DualPol sequence in the rhodium formate spin system achieved after $L = 11$ repeats (total duration = 1.54 s). The additional loss in polarisation; as seen for the experimental data points, is likely due to ^1H and ^{103}Rh transverse relaxation during the polarisation transfer process.

Appendix B

DualPol optimisation in an A_2X_4 spin system

The DualPol sequence for polarisation transfer between proton and ^{103}Rh nuclei in the A_2X_4 rhodium formate spin system was optimised experimentally using the pulse sequence shown in figure 6.3 but where the sequence is repeated with variation of DualPol loop counter L , to control the DualPol sequence total duration.

$^1\text{H} \rightarrow ^{103}\text{Rh}$ polarisation transfer efficiency as a function of DualPol total duration is shown in figure B.1

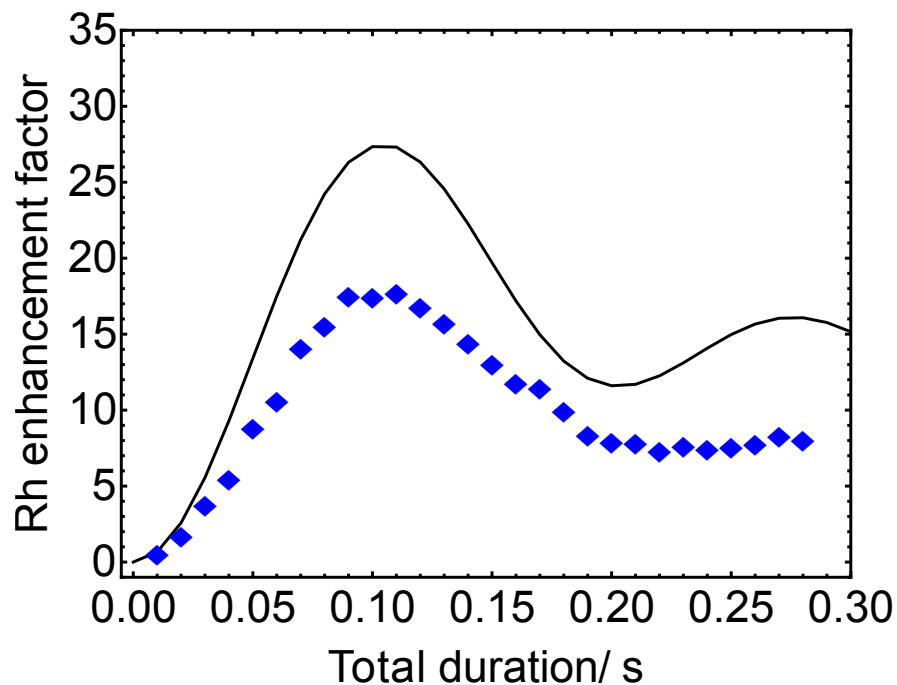


FIGURE B.1: DualPol build up curve for ^1H - ^{103}Rh polarisation transfer amplitude as a function of DualPol total duration. Blue diamonds denote experimental data points; whereas the black line represents numerical simulation. Numerical simulation was performed with $J_{\text{RhH}} = 4.7$ Hz and a DualPol R-element duration of $\tau = 5$ ms. Curves are normalised against thermal ^{103}Rh polarisation.

Optimal polarisation transfer using the DualPol sequence in the rhodium formate spin system achieved after $L = 10$ repeats (total duration = 100 ms). The additional loss in polarisation; as seen for the experimental data points, is likely due to ^1H and ^{103}Rh transverse relaxation during the polarisation transfer process.

Although this optimisation was performed on the non ^{18}O labelled sample, the DualPol sequence is invariant to the strong coupling regime, and so this optimisation is applicable for both A_2X_4 and ABX_4 rhodium formate isotopologues.

Appendix C

Refocused-INEPT analytical delay derivation in an A_2X_4 spin system

The refocused-INEPT sequence for $^{103}\text{Rh} \rightarrow ^1\text{H}$ polarisation transfer in the A_2X_4 rhodium formate spin system is shown in figure C.1 and which contains two delay parameters - one for the INEPT block (τ_1) and another for the refocusing echo (τ_2).

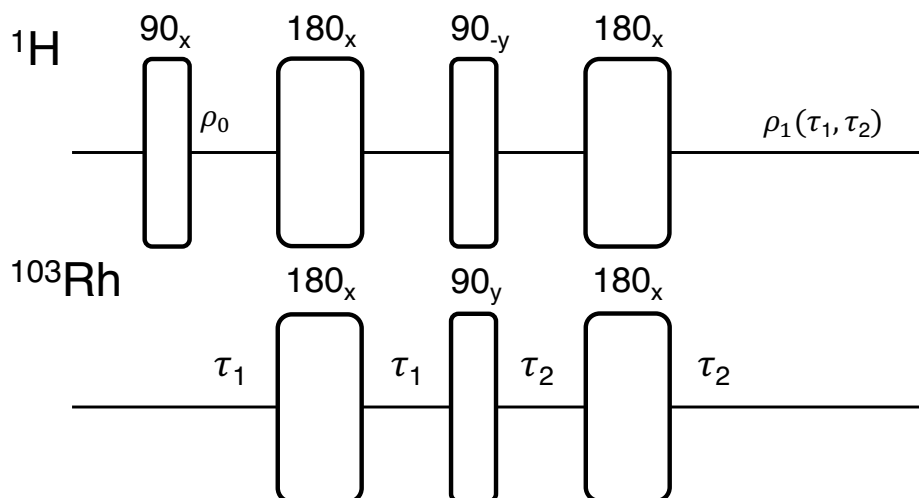


FIGURE C.1: Refocused-INEPT sequence for $^{103}\text{Rh} \rightarrow ^1\text{H}$ polarisation transfer.

One may solve analytically for the optimum values of both τ_1 and τ_2 as follows,

The refocused-INEPT final density operator $\rho_1(\tau_1, \tau_2)$ is a function of both τ_1 and τ_2 and is given by,

$$\rho_1(\tau_1, \tau_2) = U(\tau_1, \tau_2) \rho_0 U^\dagger(\tau_1, \tau_2) \quad (\text{C.1})$$

where $\rho_0 = -\hat{H}_y$ and U represents the propagator of the sequence.

U may be written as a product of propagators as follows:

$$U = U^{(\tau_2-180_x-\tau_2)} U^{(90_y^H 90_y^{Rh})} U^{(\tau_1-180_x-\tau_1)} \quad (C.2)$$

where,

$$\begin{aligned} U^{(\tau_1-180_x-\tau_1)} &= \exp \{-i\hat{H}\tau_1\} \exp \{-i\pi\hat{H}_x\} \exp \{-i\pi\hat{R}h_x\} \exp \{-i\hat{H}\tau_1\} \\ U^{(90_y^H 90_y^{Rh})} &= \exp \{-i\frac{\pi}{2}\hat{H}_{-y}\} \exp \{-i\frac{\pi}{2}\hat{R}h_y\} \\ U^{(\tau_2-180_x-\tau_2)} &= \exp \{-i\hat{H}\tau_2\} \exp \{-i\pi\hat{H}_x\} \exp \{-i\pi\hat{R}h_x\} \exp \{-i\hat{H}\tau_2\} \end{aligned} \quad (C.3)$$

and where $\hat{H}$ is the $^1H \leftrightarrow ^{103}Rh$ weak coupling Hamiltonian, $\hat{H} = 2\pi J \hat{R}h_z \cdot \hat{H}_z$

The desired density operator at the end of the refocused-INEPT sequence is $-\hat{R}h_y$. And taking the amplitude of $-\hat{R}h_y$ within $\rho_1(\tau_1, \tau_2)$ yields,

$$\frac{Tr\{-\hat{R}h_y^\dagger, \rho_1(\tau_1, \tau_2)\}}{Tr\{-\hat{R}h_y^\dagger, \hat{R}h_y\}} = \cos(2\pi J\tau_2)^3 \sin(4\pi J\tau_1) \sin(2\pi J\tau_2) \quad (C.4)$$

where Tr denotes the trace mathematical operation.

Through maximisation of equation C.4 one can attain the optimal values of $1/8J$ and $1/12J$ for τ_1 and τ_2 respectively. For the reverse transfer, i.e $^{103}Rh \rightarrow ^1H$, the delays are reversed.

Appendix D

Synthesis of rhodium formate with singly ^{18}O labelled formate ligand

The following synthesis procedure was kindly provided by Gamal Moustafa:

Dirhodium tetraformate $[\text{Rh}_2(\text{HCO}_2)_4]$ (1) and dirhodium(II)tris(formate)trifluoroacetate $[\text{Rh}_2(\text{HCO})_3(\text{OTfa})]$ (2) were prepared according to literature procedure [150, 122]. ^{18}O -enriched formic acid was prepared via the heating of formic acid with H_2^{18}O (98% ^{18}O enrichment) in a sealed tube for one hour to get a statistical mixture of formates bearing $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$ in 1.0 : 1.8 : 0.9 ratio, respectively.

To a stirred solution of dirhodium(II)tris(formate)trifluoroacetate $[\text{Rh}_2(\text{HCO})_3(\text{OTfa})]$ (2) (100 mg, 0.24 mmol) in MeCN (8 mL) were added ^{18}O -enriched formic acid (15 μL , 0.36 mmol) and DIPEA (105 μL , 0.60 mmol). The mixture was heated at 50 $^\circ\text{C}$ for 2 h, and then concentrated under reduced pressure. The residue was purified by column chromatography using MeCN: PhCH_3 (1:3 to 1:1) as an eluent to afford the title compound (92.8 mg, 0.22 mmol, 92% yield) as a statistical mixture of isotopologues. See figure 8.6.

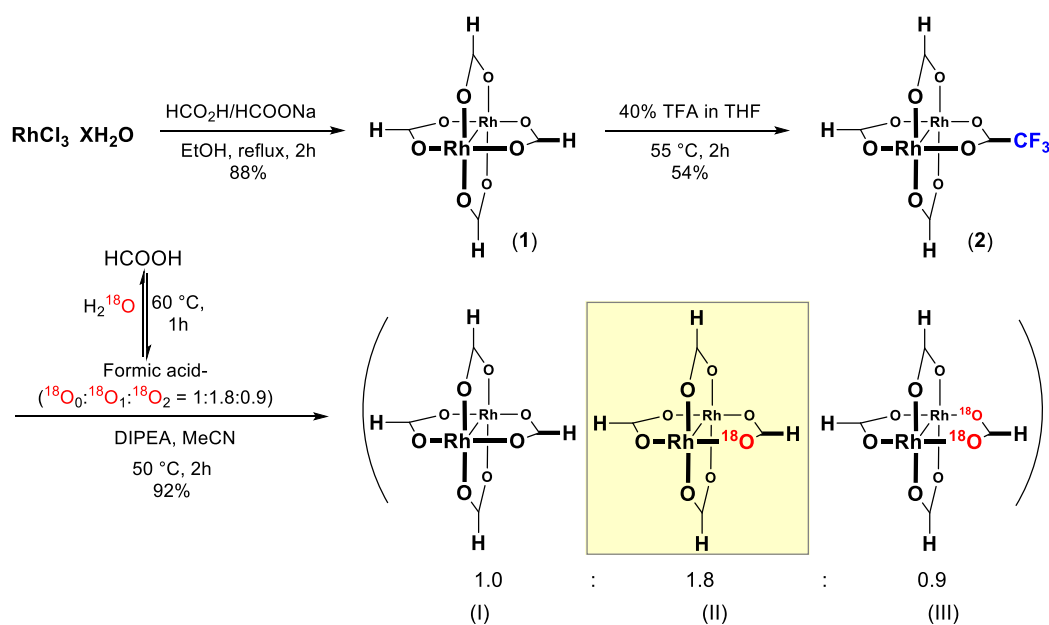


FIGURE D.1: Reaction scheme for the synthesis of ^{18}O labelled rhodium formate.

Appendix E

Rhodium formate ^{13}C T_1

E.1 Pulse sequence

^{13}C T_1 relaxation time constants were measured indirectly through ^1H NMR signals using the sequence shown in figure E.1. Longitudinal ^{13}C magnetisation is inverted by an initial 180° pulse, and allowed to relax towards equilibrium during the waiting interval τ_{relax} . During this interval, protons are decoupled to prevent cross-relaxation. A proton destruction filter is applied to eliminate any residual proton magnetisation generated during the waiting interval. Remaining ^{13}C z-magnetisation, selected for by the two 90° pulses, is now transferred back to ^1H z-magnetisation by a DualPol block and is selected for by a proton z-filter. A final ^1H 90° pulse generates observable ^1H transverse magnetization. The sequence is repeated with variation of the waiting interval τ_{relax} in order to follow the equilibration of longitudinal ^{13}C magnetization.

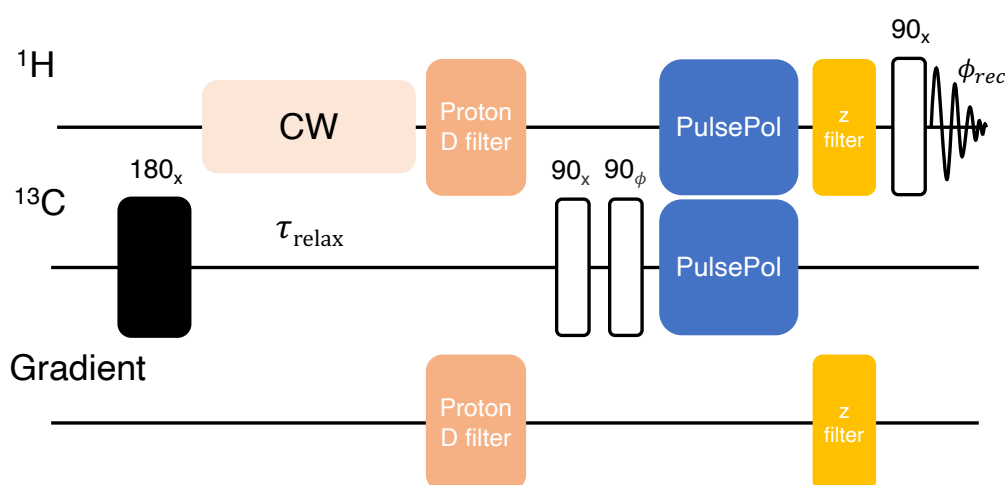


FIGURE E.1: Sequence used for the indirect measurement of carbon T_1 through ^1H NMR signals. Phase cycles are given by $\phi = [-x, x]$ and the receiver $\phi_{\text{rec}} = [x, -x]$. Black rectangle indicates a BB1 composite 180° pulse of the form shown by equation 5.4.

E.2 Rhodium formate ^{13}C decay curve

The trajectory of indirectly-detected ^{13}C z-magnetization in a field of 9.4 T is shown in figure E.2. The trajectory fits well to a single-exponential decay with a time constant of $T_1(^{13}\text{C}) = 2.14 \pm 0.15$ seconds.

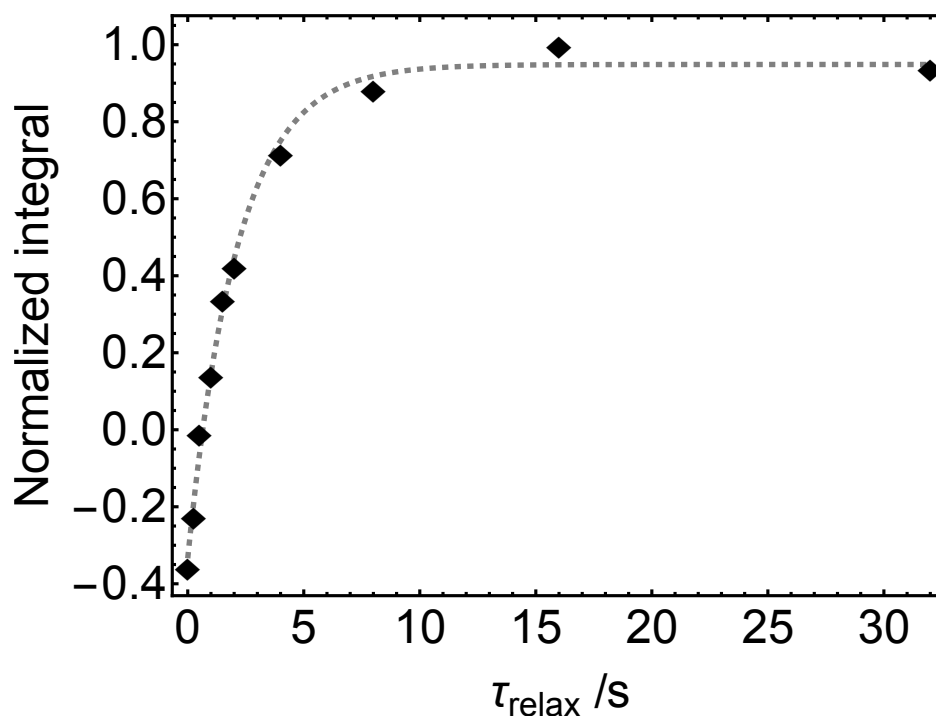


FIGURE E.2: Experimental ^{13}C longitudinal magnetization recovery for rhodium formate dissolved in THF- d_8 at a field of 9.4 T. Integrals are normalised against largest point.

Appendix F

Rhodium formate quantum chemical calculations

F.1 Geometry optimisation

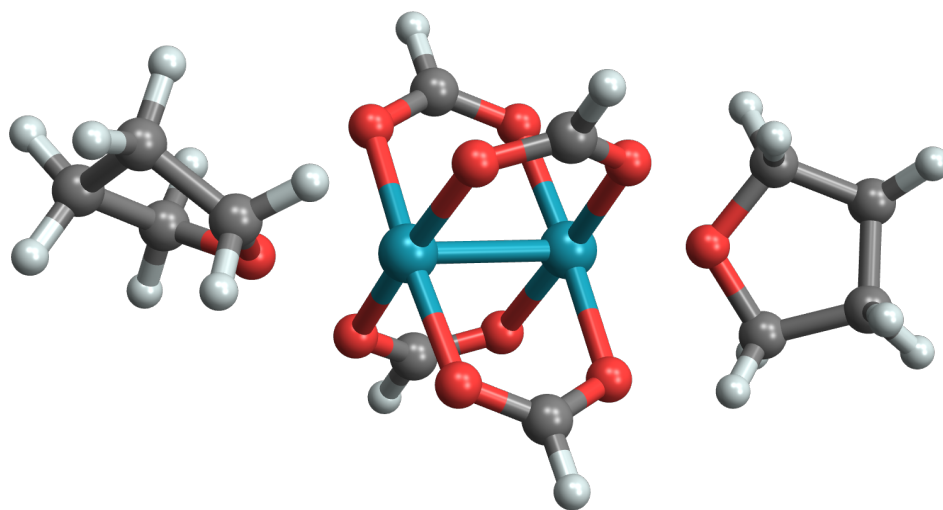


FIGURE F.1: Rhodium formate with axial ligation by THF molecules geometry optimised structure.

The geometry of the rhodium formate complex axially ligated by solvent THF molecules was optimised using the ORCA program package version 5.0.3 [109]. Calculations were performed at the B3LYP/SARC-ZORA-TZVP level of theory.

F.2 Shielding tensor calculation

The ^{103}Rh shielding tensors were computed at the TPSSh/SARC-ZORA-TZVPP level of theory using implicit solvation (CPCM[151, 152] for THF), the zeroth-order regular approximation (ZORA)[153, 154] for the inclusion of relativistic effects, GIAOs, the RI approximation[138] and the tau-dependent correction as suggested by Dobson[155, 156, 157].

$$^{103}\text{Rh}_0(\text{Total/ ppm}) = \begin{pmatrix} -12607.2 & -15.5 & -908.9 \\ -36.3 & -5622.9 & 79.0 \\ -900.0 & 91.327 & -5821.6 \end{pmatrix} \quad (\text{F.1})$$

$$^{103}\text{Rh}_1(\text{Total/ ppm}) = \begin{pmatrix} -12617.6 & -107.5 & -919.8 \\ -38.4 & -5751.1 & -27.4 \\ -912.0 & -53.8 & -5709.4 \end{pmatrix}$$

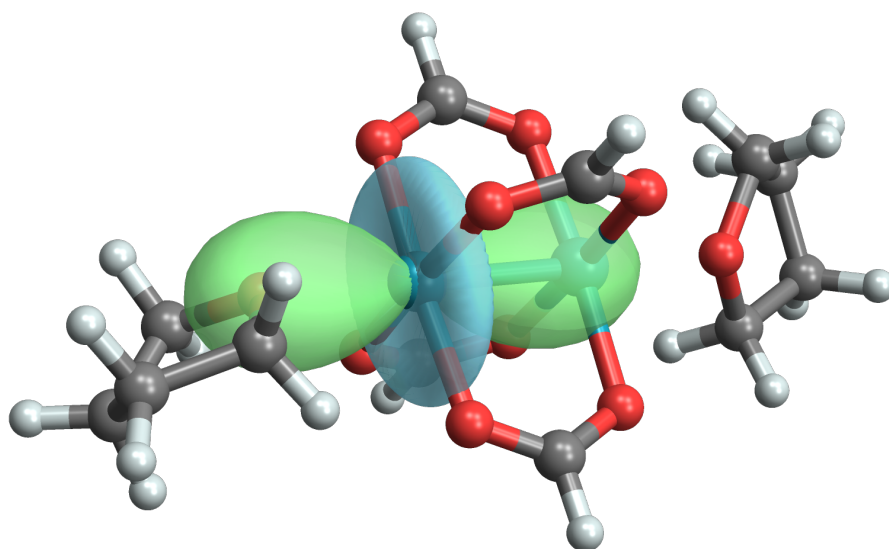


FIGURE F.2: Axially ligated rhodium formate structure with shielding tensor ovaloid shown on a ^{103}Rh site.

F.3 Dipolar contributions to the $^{103}\text{Rh } T_1^{-1}$

In the extreme narrowing limit, the contribution of a heteronuclear dipolar coupling to the $^{103}\text{Rh } (T_1)^{-1}$ relaxation rate constant (when the heteronucleus is decoupled) is given by,

$$(T_1(^{103}\text{Rh}))_{\text{RhX}}^{-1} = b_{\text{RhX}}^2 \tau_c \quad (\text{F.2})$$

Where b_{RhX} represents the dipolar coupling constant between the ^{103}Rh and the heteronucleus X and τ_c is the rotational correlation time. In contrast, the contribution of the homonuclear ^{103}Rh dipolar coupling to the $^{103}\text{Rh } (T_1)^{-1}$ relaxation rate constant is given by,

$$(T_1(^{103}\text{Rh}))_{\text{RhRh}}^{-1} = \frac{3}{2} b_{\text{RhRh}}^2 \tau_c \quad (\text{F.3})$$

Where b_{RhX} represents the dipolar coupling constant between the ^{103}Rh nuclei and τ_c is again the rotational correlation time. Using the optimised geometry in figure F.1, the $^{103}\text{Rh}-^1\text{H}$ dipolar coupling was estimated to be $\sim 2\pi 61$ Hz; whereas the $^{103}\text{Rh}-^{103}\text{Rh}$ homonuclear dipolar coupling constant was estimated to be $\sim 2\pi 8$ Hz. These are extremely small numbers - the $^{103}\text{Rh}(T_1)$ resulting purely from the dipolar mechanism is predicted to be on the order of a day for typically values of τ_c .

Appendix G

Rhodium formate ^{103}Rh spin-rotation tensors

The following ^{103}Rh spin-rotation and moment of inertia tensors for the rhodium formate paddlewheel complex axially ligated by solvent THF molecules were very kindly provided by Alexej Jerschow and were calculated at the TPSSH def2-TZVPP level of theory.

^{103}Rh spin-rotation tensors:

$$^{103}\text{Rh}_0(\text{Total/ kHz}) = \begin{pmatrix} 1.375 & 0.014 & 0.360 \\ 0.003 & 0.222 & 0.004 \\ 0.372 & 0.008 & 0.338 \end{pmatrix}$$

$$^{103}\text{Rh}_0(\text{eigenvalues/ kHz}) = (1.493, \quad 0.225, \quad 0.219)$$

(G.1)

$$^{103}\text{Rh}_1(\text{Total/ kHz}) = \begin{pmatrix} 1.375 & 0.012 & 0.362 \\ 0 & 0.222 & 0.003 \\ 0.375 & 0.007 & 0.338 \end{pmatrix}$$

$$^{103}\text{Rh}_1(\text{eigenvalues/ kHz}) = (1.493, \quad 0.224, \quad 0.218)$$

Spin-rotation tensors are very similar at both ^{103}Rh sites.

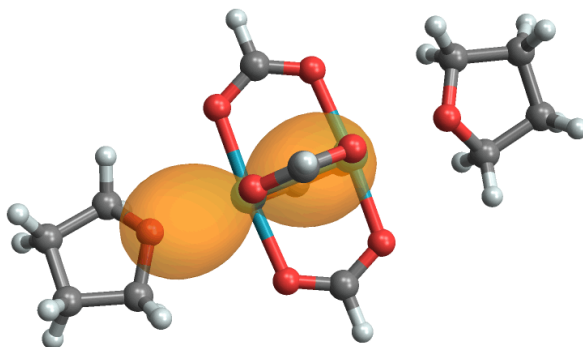


FIGURE G.1: Axially ligated rhodium formate structure with spin-rotation tensor ovaloid shown on a ^{103}Rh site.

It was assumed that the moment of inertia tensors at both ^{103}Rh sites are equivalent.

The ^{103}Rh moment of inertia tensor eigenvalues are: $(7.14, 7.05, 1.85) \times 10^{-44} \text{ Kg m}^2$; hence the corresponding isotropic moment of inertia is: $5.35 \times 10^{-44} \text{ Kg m}^2$.

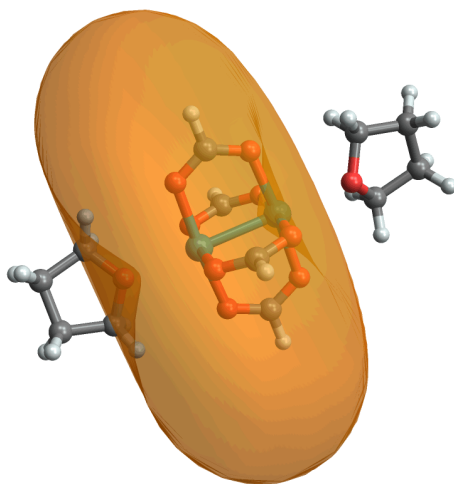


FIGURE G.2: Axially ligated rhodium formate structure with moment of inertia tensor ovaloid shown on a ^{103}Rh site.

Appendix H

Loss of signal amplitude during shuttling experiments to 1 mT

H.1 Magnetic field as a function of time

By combining the shuttle trajectory with the magnet field profile shown in figures 5.1 and 5.3 respectively, we obtain the magnetic field as a function of time. Therefore, for shuttling experiments to a field of 1 mT and where the sample is transported 113.8 cm above the magnet bore in 1 second, the corresponding magnetic field as a function of time experienced by the sample is given by:

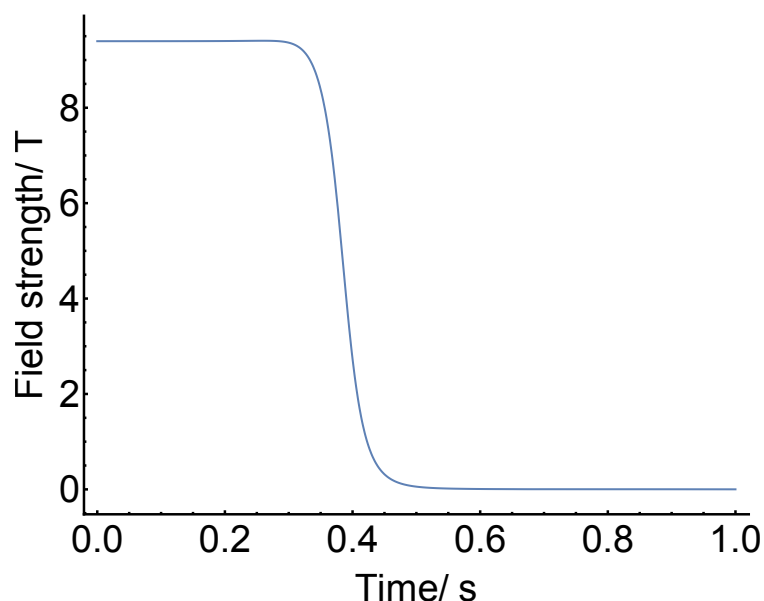


FIGURE H.1: Magnetic field strength experienced by sample as a function of time during shuttling to 1 mT.

To a good approximation, the experienced magnetic field time evolution is bimodal. It may be divided into an initial period lasting 0.33 s; where the sample is static in the high field and a second period lasting 0.56 s; in which the sample is static in the low field. The shuttling between the high and low field occurs very quickly over 0.11 s.

The experienced magnetic field time evolution for the reverse transfer from 1 mT to high field is identical to that shown in figure H.1 but where the trajectory is reversed.

H.2 Loss of QSEO spin order during shuttling

The $^{103}\text{Rh } T'_S$ is field dependent; therefore we may approximate *relaxation losses during shuttling* as occurring solely during the intervals in which the sample is stationary in the high field, and neglect the short period in which the sample moves rapidly through the field; as well as the time spent in the low field - where spin order lifetimes are much longer.

When measuring T_S at 1 mT, the sample spends approximately 0.66 seconds stationary in the high field bore of the magnet during field cycling. Therefore, using the high field $^{103}\text{Rh } T'_S$ of ~ 0.359 s, we may estimate the relaxation losses during shuttling as follows:

$$\exp\left(-\frac{0.66}{0.359}\right) = 0.16 \quad (\text{H.1})$$

Hence, only $\sim 16\%$ of initial ^{103}Rh spin order is retained after shuttling. This estimation is in good agreement with the observed reduced signal amplitude for the measurement of $^{103}\text{Rh } T_S$ in the low field relative to the high field T'_S measurement.

Appendix I

Validation of the adiabatic approximation

Complete conversion of quasi-singlet eigenorder (QSEO) into singlet order (SO) upon field cycling from high-to-low field is only achieved if the evolution of the Hamiltonian is *adiabatic*.

We satisfy the adiabatic condition when the rate of change of the time-dependent singlet-triplet mixing angle (θ_{ST}) of the ^{103}Rh spin pair is small relative to the energy difference between the universal $|S'_0\rangle$ and $|T'_0\rangle$ states, expressed as the frequency Ω i.e:

$$\left| \frac{d}{dt} \theta_{ST}(t) \right| \ll |\Omega(t)| \quad (\text{I.1})$$

where the singlet-triplet energy difference $\Omega_{ST}(t)$ is given by [25, 158]:

$$\Omega(t) = 2\pi \sqrt{(B(t)\Delta)^2 + J^2} \quad (\text{I.2})$$

where $B(t)\Delta$ is the field-dependent chemical shift difference of the ^{103}Rh spin pair, while J is the one bond ^{103}Rh - ^{103}Rh J-coupling.

The relative magnitudes of $(d/dt)\theta_{ST}$ vs Ω during shuttling to 1 mT are compared below:

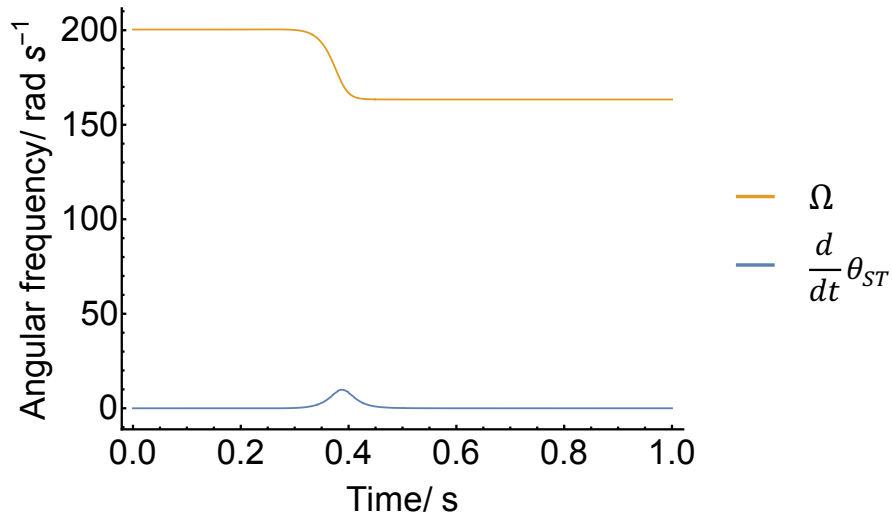


FIGURE I.1: A plot of $(d/dt)\theta_{ST}$ vs Ω during shuttling of ^{103}Rh QSEO to 1 mT

One observes that $(d/dt)\theta_{ST}$ is, at all times, much smaller than the singlet-triplet energy difference Ω ; hence, the adiabaticity of the field cycling of ^{103}Rh QSEO into SO is well satisfied in this work.