Using a Lindbladian approach to model decoherence in two coupled nuclear spins via correlated phase-damping and amplitude damping noise channels

Harpreet Singh∗
Department of Physical Sciences, Indian Institute of Science Education & Research Mohali,
Sector 81 SAS Nagar, Manauli PO 140306 Punjab India. and
Fakultät Physik, Technische Universität Dortmund D-44221, Dortmund, Germany.

Arvind† and Kavita Dorai‡
Department of Physical Sciences, Indian Institute of Science Education & Research Mohali,
Sector 81 SAS Nagar, Manauli PO 140306 Punjab India.

In this work, we studied the relaxation dynamics of coherences of different order present in a system of two coupled nuclear spins. We used a previously designed model for intrinsic noise present in such systems which considers the Lindblad master equation for Markovian relaxation. We experimentally created zero-, single- and double-quantum coherences in several two-spin systems and performed a complete state tomography and computed state fidelity. We experimentally measured the decay of zero- and double-quantum coherences in these systems. The experimental data fitted well to a model that considers the main noise channels to be a correlated phase damping channel acting simultaneously on both spins in conjunction with a generalized amplitude damping channel acting independently on both spins. The differential relaxation of multiple-quantum coherences can be ascribed to the action of a correlated phase damping channel acting simultaneously on both the spins.

PACS numbers: 03.65.Yz, 76.60.-k, 03.67.a

I. INTRODUCTION

Quantum coherence can be associated with a transition between the eigenstates of a quantum system and most spectroscopic signals crucially rely on the manipulation, transfer and detection of such coherences [1]. In nuclear magnetic resonance (NMR), spin coherence resides in the off-diagonal elements of the density operator of the system and a system of coupled spin-1/2 nuclei can have coherences of different orders \( n (n = 0, 1, 2, \ldots) \) [2]. NMR is able to directly access only those off-diagonal elements of the density matrix whose difference in magnetic quantum number is \( \pm 1 \) (the single quantum transitions). The direct observation of multiple quantum transitions \( (\Delta m \neq \pm 1) \) is forbidden by quantum-mechanical selection rules (in the dipole approximation). Multiple quantum coherences have found several useful applications in NMR including spectral simplification, spin-locking and cross-polarization experiments [3].

The interaction with the environment of a quantum system causes loss of coherence and forces the system to relax back towards a time-invariant equilibrium state. This limits the time over which coherences live and leads to poor signal sensitivity [4]. In solution NMR the problem is exaggerated when dealing with larger spin systems such as those encountered in proteins, where slower rotational tumbling of the molecules leads to faster rates of relaxation, and consequently larger losses in signal [5]. Coherence preservation is hence of supreme importance in NMR experiments and several schemes have been designed to suppress spin relaxation including using longlived two-spin order states which have lifetimes much longer than \( T_1 \), termed singlet states [6, 7]. Links between NMR coherence orders and decoherence have been recently investigated [8]. Several NMR techniques have benefited from cross-fertilization of ideas from other fields of research such as quantum information processing. For instance, several methods that suppress spin relaxation such as optimal control theory [9] and dynamical decoupling [10, 11], have all drawn on insights from their initial application to general problems of quantum decoherence, algorithm implementation [12] and quantum entanglement [13]. Recently, certain special types of correlation functions termed out-of-time-order correlations (OTOC) have been used to characterize the delocalization of quantum information and have been linked to multiple-quantum coherences [14–17]. Optimal control techniques have also been used to control coupled heteronuclear spin dynamics in the presence of general relaxation mechanisms and to explore how closely a quantum system can be steered to a target state [18–22]. Synthesizer noise can lead to severe dephasing effects akin to a decohering environment and new methods have been recently proposed to eliminate such noise using two single-spin systems in opposite static magnetic fields [23, 24]. Transverse relaxation times in systems of coupled spins have been accurately measured and the noise profiles of multi-spin coherences and their scaling with respect to coherence order has been studied [25, 26]. In order

∗ harpreet.singh@tu-dortmund.de
† arvind@iisermohali.ac.in
‡ kavita@iisermohali.ac.in
to devise techniques to obviate the deleterious effects of spin relaxation, one first needs to gain a deeper understanding of the mechanisms underlying this complex phenomenon. Molecules in a liquid freely tumble and undergo stochastic Brownian motion which is the main source of NMR spin relaxation, where the spin lattice degrees of freedom include all the molecular rotational and translational motions. The semi-classical Redfield approach is typically used to describe NMR spin relaxation which uses the density matrix formalism and second order perturbation theory; the noisy spin environment is treated classically by a spin lattice model while the spins are treated as quantum mechanical objects and a weak system-environment coupling is assumed [27]. The bath correlations decay much more rapidly than the evolution of the spins and the Markovian approximation remains valid. For two coupled spins 1/2, the major relaxation mechanisms in NMR are the dipole-dipole (DD) relaxation and the relaxation arising from the chemical shift anisotropy (CSA) of each spin. In general, interference terms between the DD and CSA relaxation mechanisms can give rise to another mechanism for relaxation termed as cross-correlated spin relaxation [28, 29]. Extensions of Bloch-Redfield relaxation theory have developed a unified picture by including contributions from dipolar coupling between remote spins [30, 31] and by considering a two-state Markov process which includes lattice fluctuations and chemical exchange dynamics [32]. The most general form for the nonunitary evolution of the density operator of an open quantum system can be described by a master equation [33]. In the master equation approach, both the environment and the spins are assumed to be quantum mechanical in character. The Redfield approach is a “bottom-up” approach which begins with the allowed degrees of freedom and the relaxation mechanisms which are specific to the system under consideration and then builds a model from them. The master equation approach on the other hand, is a “top-down” approach which begins by considering all possible allowed relaxation processes and then concludes from the data which is the noise channels that are dominant. The insights gained from the Redfield and the master equation methods are complementary in character, and using a combined approach can help build a complete picture of coupled spin relaxation.

In the master equation formalism, the NMR longitudinal \( T_1 \) and transverse \( T_2 \) relaxation processes are described by two different noise channels, namely the amplitude damping and the phase damping channel, respectively [34]. The effect of the phase damping channel on a single spin is to nullify the coherences stored in the off-diagonal elements of the spin density matrix. The generalized amplitude damping channel leads to energy loss through dissipative interactions between the spin and the lattice at finite temperatures, where the spin in the excited state decays to its ground state. The Lindblad operators were delineated for a system of two coupled spin-1/2 nuclei by measuring the density operator at multiple time points [35]. The phase damping, amplitude damping and depolarizing noise channels have been implemented in NMR using two and three heteronuclear coupled spins [36].

It has long been known in NMR that the relaxation of multiple quantum transitions contains useful information about correlated fluctuations occurring at different nuclear sites as well about molecular motions [2]. In contrast to single quantum experiments on coupled spins, the relaxation dispersion profiles of multiple-quantum relaxation rates are sensitive to the chemical environment of the involved nuclei and can hence be used to gain insights about millisecond time-scale dynamics in large biomolecules [37]. Multiple quantum relaxation has been used to probe protein-ligand interactions, conformational exchange processes and side-chain motions in proteins [38].

A spin system consisting of coupled spins of the same nuclear species is termed a homonuclear system while a coupled spin system consisting of different nuclear species is called a heteronuclear system. In this work, we focus on studying the relaxation dynamics of quantum coherences in homonuclear systems of coupled spin-1/2 nuclei. On the other hand, in a heteronuclear coupled two-spin system, the noise was fitted using several noise models and it was shown that such systems can be treated as being acted upon by independent noise channels [39]. We use the Lindblad master equation for Markovian relaxation to set up and analyze the relaxation of coherences of different order, namely zero-, single-, and double-quantum coherences. We first experimentally prepared states with different orders of quantum coherences, tomographed the state, and computed state fidelity. We then allowed the state to decay and experimentally measured the decay rates of different quantum coherences. The experimentally determined evolution of the density matrices for the states prepared as pure double-, single-, or zero-quantum coherence were obtained via a generalized master equation formalism. We modeled the inherent noise in the system by assuming that a correlated phase damping quantum channel acts on both spins and that a generalized amplitude damping quantum channel acts independently on each spin. We obtained good fits of the theoretical model to the experimental data within reasonable experimental errors. It has been shown that cross-correlated spin relaxation terms arising both from auto-correlation spectral densities for dipolar relaxation as well as from a “remote” CSA-CSA cross-correlation mechanism, contribute differentially to the relaxation of zero- and double-quantum coherences in a coupled two-spin system [40]. We conjecture that the Redfield description of CSA-CSA cross-correlated spin relaxation is analogous to the correlated phase damping channel in the generalized master equation description of relaxation. The distinctly different relaxation dynamics of multiple-quantum coherences in homonuclear coupled spin systems as opposed to heteronuclear systems is clearly evident from our analysis. The relaxation be-
havior of homonuclear coupled spin-1/2 nuclei can be explained on the basis of a correlated phase damping noise channel acting on both spins and ties in well with the standard Redfield method of studying spin relaxation.

II. MODELING INTRINSIC NOISE IN NMR

The operator-sum representation is typically used to describe quantum decoherence [41]. A noisy channel acting on an input density matrix $\rho$ is given by a completely positive trace preserving map

$$ E(\rho) = \Sigma_i E_i \rho E_i^\dagger $$

where $E_i$ are Kraus operators describing a noisy channel in the sum-operator approach and $\Sigma_k E_k E_k^\dagger = 1$ ensures that unit trace is preserved. The final noisy state is $[42, 43]$

$$ E(\rho) = (1 - \mu)\Sigma_{i,j} E_{i,j} \rho E_{i,j}^\dagger + \mu \Sigma_k E_{k,k} \rho E_{k,k}^\dagger $$

where $\mu$ is probability for noise to be correlated and $(1 - \mu)$ is the probability for uncorrelated noise.

For a special class of noisy channels where the Markovian approximation is valid, one can write the master equation governing decoherence in a Lindblad form $[33, 44-46]$

$$ \frac{\partial \rho}{\partial t} = \sum_{i,\alpha} \left[ L_{i,\alpha} \rho L_{i,\alpha}^\dagger - \frac{1}{2} \{ L_{i,\alpha}^\dagger L_{i,\alpha}, \rho \} \right] $$

where $L_{i,\alpha} \equiv \sqrt{\kappa_{i,\alpha}} \sigma_{\alpha}^{(i)}$ is the Lindblad operator and $\sigma_{\alpha}^{(i)}$ is the Pauli operator of the $i$th spin ($\alpha = x, y, z$) and the constant $\kappa_{i,\alpha}$ has the units of inverse time. It has been proved that a linear operator on a finite $N$-dimensional Hilbert space is the generator of a completely positive dynamical semigroup [47] and hence the Lindbladian is the generator of the semigroup which governs the dissipation of the density operator.

In the language of the master equation approach to decoherence, the relaxation of an NMR spin tumbling isotropically in a solution can be described by two noise channels: a phase damping channel and an amplitude damping channel $[48-51]$. Due to molecular tumbling the average magnetic field experienced by a spin over time is the same but it varies across the sample at a particular time which causes identical spins to slowly lose phase coherence, which is the process of phase damping. The Kraus superoperator for the phase damping (PD) channel acting on a single spin density operator $\rho$ can be written as

$$ E^\text{PD}(\rho) = \begin{pmatrix} \rho_{00} & \rho_{01} e^{-\gamma t} \\ e^{-\gamma t} \rho_{10} & \rho_{11} \end{pmatrix} $$

for a damping rate $\gamma$. The generator of PD channel on a single spin can be written as

$$ Z^\text{PD}(\rho) = -\gamma \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\gamma & 0 \\ 0 & 0 & -\gamma \end{pmatrix} $$

Ordering the matrix elements of $\rho$ in the vector $(\rho_{00}, \rho_{01}, \rho_{10}, \rho_{11})^T$, we have

$$ Z^\text{PD} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\gamma & 0 \\ 0 & 0 & -\gamma \\ 0 & 0 & 0 \end{pmatrix} $$

The generalized amplitude damping channel (GAD) for a single spin models the process where the spin exchanges energy with a reservoir at some fixed temperature

$$ E^\text{GAD}(\rho) = \begin{pmatrix} k_1 \rho_{00} + k_2 \rho_{11} & e^{-\gamma t/2} \rho_{01} \\ e^{-\gamma t/2} \rho_{10} & k_3 \rho_{00} + k_4 \rho_{11} \end{pmatrix} $$

where $k_2 \equiv (1 - \bar{n})(1 - e^{-\gamma t})$, $k_3 \equiv \bar{n}(1 - e^{-\gamma t})$, $k_1 \equiv 1 - k_3$, and $k_4 \equiv 1 - k_2$, $\Gamma$ is the damping rate and $\bar{n}$ is a temperature parameter

$$ \log \frac{1 - \bar{n}}{\bar{n}} = \frac{\Delta E}{k_B T} $$

with $\Delta E$ being the energy level difference between the ground and excited states of the system.

An ensemble of NMR spins in thermal equilibrium at room temperature has a Boltzmann distribution of spin populations and in this high-temperature limit, the generator of the GAD channel is given by

$$ Z^\text{GAD}^\infty = -\Gamma \begin{pmatrix} \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ -\frac{1}{2} & 0 & 0 & \frac{1}{2} \end{pmatrix} $$

The simplest extension of these single-spin decoherence processes to a two-spin system is to consider a phase damping and an generalized amplitude damping channel acting independently on each spin. However, since the spin systems we have studied are homonuclear, with two proton nuclear species having slightly different Larmor resonance frequencies, we hypothesize that each spin decoheres under the concerted action of a phase-damping channel which is correlated with that of the other spin. Hence, the naturally occurring decoherence for this system can be modeled as a correlated dephasing channel acting on both spins and a generalized amplitude damping channel acting independently on each spin $[39]$. The generator of the correlated phase damping channel acting on both spins is given by

$$ Z^\text{CPD} = \text{diag}[0, -\gamma_2, -\gamma_1, -(\gamma_1 + \gamma_2 + \gamma_3), -\gamma_2, 0, -(\gamma_1 + \gamma_2 - \gamma_3), -\gamma_1, -\gamma_1, -(\gamma_1 + \gamma_2 - \gamma_3), 0, -\gamma_2, -\gamma_1, -\gamma_2, 0] $$

where $\gamma_1$ and $\gamma_2$ are decay rates for independent phase damping on spins 1 and 2, and $\gamma_3$ can be interpreted as a rate for correlated phase damping. The full generator to describe two-spin decoherence has the form

$$ Z = Z^\text{CPD} + Z_1^\text{GAD}^\infty + Z_2^\text{GAD}^\infty $$

with $Z_1^\text{GAD}^\infty$ and $Z_2^\text{GAD}^\infty$ being the generators for the correlated phase damping channels acting on spins 1 and 2, respectively.
Under the action of the full decoherence generator \( \mathcal{Z} \), the state \( \rho \) decoheres to:

\[
\mathcal{E}^{2\text{spin}}(\rho) = \begin{pmatrix} \alpha_1 & \beta_1 & \beta_2 & \beta_3 \\ \beta_1 & \alpha_2 & \beta_4 & \beta_5 \\ \beta_2 & \beta_4 & \alpha_3 & \beta_6 \\ \beta_3 & \beta_5 & \beta_6 & \alpha_4 \end{pmatrix}
\] (12)

The parameters \( \alpha_i, \beta_i \) can be written in terms of the decay rates \( \gamma_i, i = 1, 2, 3 \) and \( \Gamma_i, i = 1, 2 \) of the correlated PD channel and the independent GAD channels, respectively. In the next section, we will proceed towards the explicit calculation of the superoperator \( \mathcal{E}^{2\text{spin}}(\rho) \) for different input states.

### III. RESULTS AND DISCUSSION

#### A. System Details

In high field NMR, the Zeeman interaction causes a splitting of the energy levels according to the field direction and the difference between magnetic quantum numbers \( \Delta m_r = m_r - m_s \) defines the order of the coherence [2]. For two-spin systems, if \( \Delta m_r = 0 \) the coherence is a zero quantum (ZQ) coherence, if \( \Delta m_r = \pm 1 \) the coherence is a single quantum (SQ) coherence, and if \( \Delta m_r = \pm 2 \) the coherence is a double quantum (DQ) coherence.

#### TABLE I. NMR parameters of homonuclear two-spin systems used in this study.

| Molecule      | \( \nu_1, \nu_2 \) (Hz) | \( \Delta \nu \) (Hz) | \( J_{12} \) (Hz) |
|---------------|-------------------------|----------------------|-------------------|
| BTC acid     | (4602.4, 4287.0)        | 315.4                | 4.2               |
| Cytosine     | (4407.3, 3490.8)        | 916.9                | 7.1               |
| Coumarin     | (4734.0, 3807.9)        | 926.1                | 9.5               |

The Hamiltonian of a weakly-coupled two-spin system in a frame rotating at \( \omega_{rf} \) in a static magnetic field \( B_0 \) is given by

\[
H = - (\omega_1 - \omega_{rf}) I_{1z} - (\omega_2 - \omega_{rf}) I_{2z} + 2\pi J_{12} I_{1z} I_{2z} \]

(13)

where \( I_{iz} \) is the \( z \)th component of the spin angular momentum operator, the first two terms in the Hamiltonian denote the Zeeman interaction between each spin and the static magnetic field \( B_0 \), and the last term represents the spin-spin interaction with \( J_{ij} \) being the scalar coupling constant. We used the \( ^1H \) spins of 5-bromo-2-thiophenecarboxylic (BTC) acid, Cytosine, and Coumarin as model homonuclear two-spin systems. The molecular structure of these two-spin systems and the NMR spectra of the spins at thermal equilibrium are shown in Figs. 1(a), (b), and (c), respectively. The experiments were performed at an ambient temperature of 298 K on a Bruker Avance III 600 MHz NMR spectrometer equipped with a QXI probe.

![5-Bromo-2-thiophenecarboxylic acid](image)

![Cytosine](image)

![Coumarin](image)

**FIG. 1.** NMR spectra obtained after a \( \pi/2 \) readout pulse on the thermal equilibrium state of (a) 5-bromo-2-thiophenecarboxylic (BTC) acid, (b) Cytosine and (c) Coumarin.

#### B. State initialization schemes

We initialize our system into a “pseudopure” state, wherein all the energy levels except one, are uniformly populated. Such special quantum states have interesting properties and have recently found several applications in the area of quantum information processing [41]. While standard schemes for pseudopure state preparation involve a large number of experiments and lead to reduced signal, recently a few schemes have been proposed that use only one ancilla spin and fewer number of experiments [52, 53]. The relaxation behavior of two-spin pseudopure states have been investigated and it was noted that cross-correlated spin relaxation plays an important role in accelerating or retarding the lifetimes of such states [54]. The relaxation of pseudopure states in an oriented spin-3/2 system has been described using Redfield theory and reduced spectral densities [55].

The two-spin equilibrium density matrix (in the high temperature and high field approximations) is in a highly
mixed state given by:
\[ \rho_{eq} = \frac{1}{4} (I + \epsilon \Delta \rho_{eq}) \]
\[ \Delta \rho_{eq} \propto \sum_{i=1}^{2} I_{iz} \]  
(14)

with a thermal polarization \( \epsilon \sim 10^{-5} \), \( I \) being an \( 4 \times 4 \) identity operator and \( \Delta \rho_{eq} \) being the deviation part of the density matrix.

\[ \rho_{eq} = \frac{1}{4} (I + \epsilon \Delta \rho_{eq}) \]
\[ \Delta \rho_{eq} \propto \sum_{i=1}^{2} I_{iz} \]

The pulse sequence for the preparation of \( |00\rangle \) states from thermal equilibrium. The sequence of pulses before the vertical dashed red line achieves state initialization into the \( |00\rangle \) pseudopure state. Filled and unfilled rectangles represent \( \pi/2 \) and \( \pi \) pulses respectively, while all other rf pulses are labeled with their respective flip angles. The phase of the rf pulse is written below each pulse, with the phase \( \phi \) kept along x(-x), depending on the desired coherence order; \( \tau_{12} \) denotes a delay fixed at \( 1/2J_{1z} \).

**FIG. 2.** Pulse sequence for the preparation of \( \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle) \) and \( \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle) \) states from thermal equilibrium. The sequence of pulses before the vertical dashed red line achieves state initialization into the \( |00\rangle \) pseudopure state. Filled and unfilled rectangles represent \( \pi/2 \) and \( \pi \) pulses respectively, while all other rf pulses are labeled with their respective flip angles. The phase of the rf pulse is written below each pulse, with the phase \( \phi \) kept along x(-x), depending on the desired coherence order; \( \tau_{12} \) denotes a delay fixed at \( 1/2J_{1z} \).

We use the notation \( |0\rangle \) to denote the eigenstate of a spin-1/2 particle in the ground state (spin “up”) and \( |1\rangle \) to denote the eigenstate of the excited state (spin “down”). The two-spin systems were initialized into the \( |00\rangle \) pseudopure state using the spatial averaging technique [56], with the density operator given by
\[ \rho_{00} = \frac{1 - \epsilon}{4} I + \epsilon |00\rangle \langle 00| \]  
(15)

The pulse sequence for the preparation of \( |00\rangle \) from thermal state is shown in the first part of Fig.2. The pulse propagators for selective excitation were constructed using the GRAPE algorithm [9] to design the amplitude and phase modulated RF profiles. Numerically generated GRAPE pulse profiles were optimized to be robust against RF inhomogeneity and had an average fidelity of \( 0.995 \). Selective excitation was typically achieved with pulses of duration 10 ms for BTC acid and 1 ms for both coumarin and cytosine molecules.

C. Final density matrix reconstruction

We interrogate our final density matrix via a useful technique called quantum state tomography, which uses a set of measurements of the expectation values of spin angular momentum operators, to independently quantify all the real and imaginary elements of the density matrix. One can hence specifically follow the relaxation rates of different elements of the density matrix [57]. All experimental density matrices were reconstructed using a reduced tomographic protocol [58, 59], with the set of operations given by \( \{ I, X, Y, XX \} \) being sufficient to determine all 15 variables for the two-spin system. Here \( I \) is the identity (do-nothing operation) and \( X(Y) \) denotes a single spin operator that can be implemented by applying a spin-selective \( \pi/2 \) pulse on the corresponding spin.

D. Measuring state fidelity

The fidelity is an estimate of the “closeness” between two pure states or between two density matrices. The fidelity of an experimental density matrix was computed by measuring the projection between the theoretically expected and experimentally measured states using the Jozsa and Uhlmann fidelity measure [60, 61]:
\[ F = Tr \left( \sqrt{\rho_{\text{theory}} \rho_{\text{expt}}} \sqrt{\rho_{\text{theory}}} \right)^2 \]  
(16)

where \( \rho_{\text{theory}} \) and \( \rho_{\text{expt}} \) denote the theoretical and experimental density matrices, respectively. In our experiments, we use fidelity as a measure to evaluate how well our experimental schemes were able to achieve the theoretically expected final density matrices.

E. Experimental creation of multiple-quantum coherences

The desired order of multiple-quantum coherence i.e. zero- or double- was prepared using the latter part (after red dashed line) of the pulse sequence given in Fig.2. A non-selective \( \pi/2 \) pulse was applied along the \( y \)-axis, which rotates both spins onto the \( x \)-axis, followed by a delay of \( \tau = \frac{1}{2J_{1z}} \) (along with refocusing pulses being applied at the center and at the end of the delay). A GRAPE-optimized spin-selective \( \pi/2 \) pulse is applied along \( -x \) (a) axis in order to prepare either the zero-quantum coherence \( \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle) \) or the double-quantum coherence \( \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle) \). We were able to achieve final state fidelities of \( \approx 0.99 \) for all the three homonuclear spin systems studied.

Figs. 3-5 (a)-(b) depict the real (left panel) and imaginary (right panel) parts of the experimentally reconstructed density matrices of the zero-quantum coherence (\( \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle) \) state) and the double-quantum
FIG. 3. The real (left) and imaginary (right) parts of the experimentally tomographed density matrix of the BTC acid molecule in the (a) $\frac{1}{\sqrt{2}}(|01\rangle + |10\rangle)$ state, with a fidelity of 0.98 and in the (b) $\frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)$ state, with a fidelity of 0.99. The rows and columns encode the computational basis in binary order from $|00\rangle$ to $|11\rangle$.

coherence ($\frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)$ state), respectively, for the BTC acid, coumarin and cytosine molecules. Computed state fidelities were $0.982 \pm 0.011$, $0.983 \pm 0.017$, and $0.983 \pm 0.015$ for the zero-quantum coherence and $0.994 \pm 0.013$, $0.991 \pm 0.015$, and $0.979 \pm 0.016$ for the double-quantum coherence.

States with single-quantum coherences, $\frac{1}{\sqrt{2}}(|00\rangle + |10\rangle)$ or $\frac{1}{\sqrt{2}}(|00\rangle + |01\rangle)$ were prepared by applying a $\frac{\pi}{2}$ selective pulse along the $y$-axis on the first (second) spin, respectively, with computed state fidelities of $\approx 0.99$.

F. Decay of populations and single-quantum coherences

Spin-lattice relaxation rates $\Gamma = 1/T_1$ was measured using the standard $180^\circ - \tau - 90^\circ$ inversion recovery pulse sequence. The spin-spin relaxation rate $\gamma = 1/T_2$ which is the rate at which a single-quantum coherence decays, was experimentally measured by first rotating the magnetization of the spin into the transverse plane by a $\frac{\pi}{2}$ rf pulse followed by a delay and fitting the resulting magnetization decay.

The decay of single-quantum coherences with time is shown in Figs. 6-8(a)-(b), for the two-spin homonuclear systems of BTC acid, cytosine and coumarin, respectively. The experimentally measured values of spin-lattice relaxation rates $\Gamma_1$ and $\Gamma_2$ in these systems were obtained to be: $\Gamma_1 = 1/T_1^\text{H} = 0.264 \pm 0.004$ s$^{-1}$ and $\Gamma_2 = 1/T_2^\text{H} = 0.255 \pm 0.003$ s$^{-1}$ for the BTC molecule,

FIG. 4. The real (left) and imaginary (right) parts of the experimentally tomographed density matrix of the coumarin molecule in the (a) $\frac{1}{\sqrt{2}}(|01\rangle + |10\rangle)$ state, with a fidelity of 0.98 and in the (b) $\frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)$ state, with a fidelity of 0.99. The rows and columns encode the computational basis in binary order from $|00\rangle$ to $|11\rangle$.

FIG. 5. The real (left) and imaginary (right) parts of the experimentally tomographed density matrix of the cytosine molecule in the (a) $\frac{1}{\sqrt{2}}(|01\rangle + |10\rangle)$ state, with a fidelity of 0.98 and in the (b) $\frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)$ state, with a fidelity of 0.99. The rows and columns encode the computational basis in binary order from $|00\rangle$ to $|11\rangle$. 

\[ \Gamma_1 = 1/T_1^{1H} = 0.153 \pm 0.002 \text{ s}^{-1} \] and \[ \Gamma_2 = T_1^{2H} = 0.152 \pm 0.014 \text{ s}^{-1} \] for the cytosine molecule, and \[ \Gamma_1 = 1/T_1^{1H} = 0.210 \pm 0.004 \text{ s}^{-1} \] and \[ \Gamma_2 = 1/T_2^{2H} = 0.135 \pm 0.002 \text{ s}^{-1} \] for the coumarin molecule. The single-quantum coherence decay rates turned out to be \[ \gamma_1 = 1/T_2^{1H} = 3.741 \pm 0.242 \text{ s}^{-1} \] and \[ \gamma_2 = 1/T_2^{2H} = 3.048 \pm 0.376 \text{ s}^{-1} \] for spin 1 and spin 2, respectively in the BTC molecule. In the cytosine molecule, the single-quantum coherence decay rates were obtained as \[ \gamma_1 = 1/T_2^{1H} = 1.618 \pm 0.080 \text{ s}^{-1} \] and \[ \gamma_2 = 1/T_2^{2H} = 1.891 \pm 0.096 \text{ s}^{-1} \] for spin 1 and spin 2, respectively. In the coumarin molecule, the single-quantum coherence decay rates were obtained as \[ \gamma_1 = 1/T_2^{1H} = 6.813 \pm 0.356 \text{ s}^{-1} \] and \[ \gamma_2 = 1/T_2^{2H} = 6.761 \pm 0.286 \text{ s}^{-1} \] for spin 1 and spin 2, respectively.

G. Decay of multiple-quantum coherences

The zero (double)-quantum coherences relaxation rates were experimentally measured by first preparing either the \( \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle) \) or the \( \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle) \) from the thermal state, followed by a delay and then rotating the magnetization of the the first spin by a \( \pi \) rf pulse and finally, a measurement of the magnetization of the second spin. The resulting magnetization decay of the second spin was fitted to the noise model to obtain an estimate of the multiple-quantum relaxation rates.

When the initial state is \( \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle) \) i.e. a zero-quantum coherence, the parameters \( \alpha_i, \beta_i \) in Eqn. 12 are given in terms of the decay rates of the \( \gamma \) of the uncorrelated and correlated PD channels and decay rates \( \Gamma \) of the independent GAD channels by:

\[
\begin{align*}
\alpha_1 &= \frac{1}{4} \left(1 - e^{-t(\Gamma_1 + \Gamma_2)}\right) \\
\alpha_2 &= \frac{1}{4} \left(1 + e^{-t(\Gamma_1 + \Gamma_2)}\right) \\
\alpha_3 &= \frac{1}{4} \left(1 + e^{-t(\Gamma_1 + \Gamma_2)}\right) \\
\alpha_4 &= \frac{1}{4} \left(1 - e^{-t(\Gamma_1 + \Gamma_2)}\right) \\
\beta_1 &= \beta_2 = \beta_3 = 0 \\
\beta_4 &= \frac{1}{2} \left(e^{-t(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)}\right) \\
\beta_5 &= \beta_6 = 0
\end{align*}
\]

When the initial state is \( \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle) \) i.e a double-quantum coherence, the parameters \( \alpha_i, \beta_i \) in Eqn. 12 are given by:

\[
\begin{align*}
\alpha_1 &= \frac{1}{4} \left(1 + e^{-t(\Gamma_1 + \Gamma_2)}\right) \\
\alpha_2 &= \frac{1}{4} \left(1 - e^{-t(\Gamma_1 + \Gamma_2)}\right) \\
\alpha_3 &= \frac{1}{4} \left(1 - e^{-t(\Gamma_1 + \Gamma_2)}\right) \\
\alpha_4 &= \frac{1}{4} \left(1 + e^{-t(\Gamma_1 + \Gamma_2)}\right) \\
\beta_1 &= \beta_2 = \beta_3 = 0 \\
\beta_4 &= \frac{1}{2} \left(e^{-t(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)}\right) \\
\beta_5 &= \beta_6 = 0
\end{align*}
\]

The decay of zero- and double-quantum coherences with time is shown in Figs. 6-8(c)-(d), for the two-spin homonuclear systems of BTC acid, cytosine and coumarin.
FIG. 7. Decay of signal intensity with time of the (a) single-quantum coherence of spin 1, (b) single-quantum coherence of spin 2, (c) zero-quantum coherence and (d) double-quantum coherence of the cytosine molecule.

FIG. 8. Decay of signal intensity with time of the (a) single-quantum coherence of spin 1, (b) single-quantum coherence of spin 2, (c) zero-quantum coherence and (d) double-quantum coherence of the coumarin molecule.

coumarin, respectively. The experimentally measured values of zero-quantum coherence decay rates in these systems was obtained to be $0.430 \pm 0.062 \text{ s}^{-1}$, $0.189 \pm 0.004 \text{ s}^{-1}$, and $4.247 \pm 0.267 \text{ s}^{-1}$ for the two-spin systems of BTC acid, cytosine, and coumarin, respectively. The experimentally measured values of double-quantum coherence decay rates in these systems was obtained to be $12.182 \pm 1.289 \text{ s}^{-1}$, $6.975 \pm 0.465 \text{ s}^{-1}$, and $21.594 \pm 0.897 \text{ s}^{-1}$, for the two-spin systems of BTC acid, cytosine, and coumarin, respectively. The correlated phase damping rate $\gamma_3$ obtained from fitting the experimental data to a noise model which incorporates independent and correlated phase damping as well generalized amplitude damping, is given in Table III G. The plots displayed in Figures 6-8 show clear evidence of non-exponential behavior, with systematic variations above and below the best fit exponential. This implies that the Markovian model of noise we assumed may not fully capture the noise processes active in these systems.

For systems of heteronuclear coupled spin-1/2 nuclei, it was previously shown that the intrinsic NMR noise acting on the spins can be modeled completely by considering uncorrelated phase damping channels acting independently on both spins [39]. Our results indicate that this does not hold true for homonuclear systems of coupled spin-1/2 nuclei, where the spins are physically proximate and have identical gyromagnetic ratios. In such cases, the true picture of noise that emerges is a “correlated” one, wherein a new phase damping channel acts on both spins together, in addition to the independent channels acting on each spin separately. Furthermore, this correlated phase damping channel contributes differentially to the relaxation rates of the multiple-quantum coherences inherent in the system. This noise model hence provides a plausible explanation for why the double-quantum coherences in homonuclear spin systems decay much faster than the zero-quantum coherences. On the other hand, heteronuclear spin systems do not exhibit such effects, indicating that such systems do not have appreciable correlated phase noise.

IV. CONCLUSION

We used a previously designed model by Childs et al. [39] for intrinsic NMR noise in homonuclear two-spin systems as arising from a correlated phase damping channel acting on both the spins and a generalized amplitude damping channel acting independently on each spin. Our results suggest that the major contribution to spin relaxation in coupled homonuclear two-spin systems comes from correlated phase damping noise. The theoretical model used to describe multiple quantum relaxation in homonuclear two-spin systems is in good agreement with our experimental data. We conjecture that the correlated phase damping behavior exhibited by the multiple quantum coherences has its origins in contributions from dipolar auto-correlated relaxation as well as from
“remote” cross-correlated interference terms between two different CSA relaxation mechanisms that are present in such systems. Our results have potential applications to NMR relaxation dispersion experiments in large proteins and to recent quantum information processing studies which utilize out-of-time-order (OTOC) correlators, where multiple-quantum coherences play a key role. The more general theories of master equations which are used to describe decoherence processes in open quantum systems can provide deeper insights into the mechanisms which govern the relaxation of NMR multi spin relaxation. The validity of the correlated phase damping noise model is by no means limited to the two-spin case, but can be extended to higher-order multiple quanta as well as to larger networks of magnetically equivalent homonuclear spins.

ACKNOWLEDGMENTS

All experiments were performed on a Bruker Avance-III 600 MHz FT-NMR spectrometer at the NMR Research Facility at IISER Mohali.

[1] A. Streltsov, G. Adesso, and M. B. Plenio, Rev. Mod. Phys. 89, 041003 (2017).
[2] R. R. Ernst, G. Bodenhausen, and A. Wokaun, Principles of NMR in One and Two Dimensions (Clarendon Press, 1990).
[3] J. Tang and A. Pines, J. Chem. Phys. 72, 3290 (1980).
[4] M. Schlosshauer, Rev. Mod. Phys. 76, 1267 (2005).
[5] J. Cavanagh, W. Fairbrother, A. Palmer, and N. Skelton, Protein NMR Spectroscopy: Principles and Practice (Elsevier Science, 1995).
[6] G. Pileio, Prog. Nucl. Magn. Reson. Spect. 98-99, 1 (2017).
[7] D. Khurana and T. Mahesh, Journal of Magnetic Resonance 284, 8 (2017).
[8] D. Pires, I. A. Silva, E. R. deAzevedo, D. O. Soares-Pinto, and J. G. Filgueiras, Phys. Rev. A 98, 032101 (2018).
[9] Z. Tosner, T. Vosegaard, C. Kehlet, N. Khaneja, S. J. Glaser, and N. C. Nielsen, J. Magn. Reson. 197, 120 (2009).
[10] A. M. Souza, G. A. Ivrarez, and D. Suter, Phil. Trans. Roy. Soc. A: Mathe., Phys. Engg. Sci. 370, 4748 (2012).
[11] H. Singh, Arvind, and K. Dorai, Phys. Rev. A 90, 052329 (2014).
[12] S. Pal, S. Moitra, V. S. Anjusha, A. Kumar, and T. S. Mahesh, Pramana-J. Phys. 82, 26 (2017).
[13] D. Das, R. Sengupta, and Arvind, Pramana-J. Phys. 88, 82 (2017).
[14] K. Hashimoto, K. Murata, and R. Yoshii, J. High Energ. Phys. 138, 1 (2017).
[15] M. Niknam, L. F. Santos, and D. G. Cory, Phys. Rev. Research 2, 013200 (2020).
[16] J. Li, R. Fan, H. Wang, B. Ye, B. Zeng, H. Zhai, X. Peng, and J. Du, Phys. Rev. X 7, 031011 (2017).
[17] D. Khurana, V. R. Krithika, and T. S. Mahesh, arXiv e-prints , arXiv:1906.02692 (2019), arXiv:1906.02692 [quant-ph].
[18] N. I. Gershenzon, K. Kobzar, B. Luy, S. J. Glaser, and T. E. Skinner, J. Magn. Reson. 188, 330 (2007).
[19] N. Khaneja, T. Reiss, B. Luy, and S. J. Glaser, J. Magn. Reson. 162, 311 (2003).
[20] N. Khaneja and S. Glaser, in 42nd IEEE International Conference on Decision and Control (IEEE Cat. No.03CH37475), Vol. 1 (2003) pp. 422-427 Vol.1.
[21] D. Stefanatos, N. Khaneja, and S. J. Glaser, Phys. Rev. A 69, 022319 (2004).
[22] N. Khaneja, B. Luy, and S. Glaser, Proc. Natl. Acad. Sci. USA 100, 13162 (2003).
[23] G. Long, G. Feng, and P. Sprenger, Quantum Engineering 1, e27 (2019).
[24] K. Li, Quantum Engineering 2, e28 (2019).
[25] I. Chakraborty, A. Chakrabarti, and R. Bhattacharyya, Phys. Chem. Chem. Phys. 17, 32384 (2015).
[26] D. Khurana, G. Unnikrishnan, and T. S. Mahesh, Phys. Rev. A 94, 062334 (2016).
[27] A. Redfield, in Advances in Magnetic Resonance, Advances in Magnetic and Optical Resonance, Vol. 1, edited by J. S. Waugh (Academic Press, 1965) pp. 1 – 32.
[28] A. Kumar, R. C. R. Grace, and P. Madhu, Prog. Nucl. Magn. Reson. Spectr. 37, 191 (2000).
[29] D. Canet, ed., Cross-relaxation and Cross-correlation Parameters in NMR, New Developments in NMR (The Royal Society of Chemistry, 2018) pp. P001–324.
[30] J. Jeener, A. Vlassenbroek, and P. Broekaert, J. Chem. Phys. 103, 1309 (1995).
[31] M. Goldman, J. Magn. Reson. 149, 160 (2001).
[32] D. Abergel and A. G. Palmer, J. Phys. Chem. B 109, 4837 (2005).
[33] G. Lindblad, Communications in Mathematical Physics 48, 119 (1976).
[34] D. O. Soares-Pinto, M. H. Y. Moussa, J. Maziero, E. R. deAzevedo, T. J. Bonagamba, R. M. Serra, and L. C. Céleri, Phys. Rev. A 83, 062336 (2011).
[35] N. Boulant, T. F. Havel, M. A. Pravia, and D. G. Cory, Phys. Rev. A 67, 042322 (2003).
[36] T. Xin, S.-J. Wei, J. S. Pedernales, E. Solano, and G.-L. Long, Phys. Rev. A 96, 062303 (2017).
[37] T. Yuwen, A. Sekhar, A. J. Baldwin, P. Vallurupalli, and E. Solano, Phys. Rev. A 103, New Developments in NMR (The Royal Society of Chemistry, 2018) pp. P001–324.
[38] Y. Toyama, M. Osawa, M. Yokogawa, and I. Shimada, J. Am. Chem. Soc. 138, 2302 (2016), pMID: 26855064.
[39] A. M. Childs, I. L. Chuang, and D. W. Leung, Phys. Rev. A 64, 012314 (2001).
[40] P. Kumar and A. Kumar, J. Magn. Reson. A 119, 29 (1996).
[41] M. A. Nielsen and I. L. Chuang, Quantum Computation and Quantum Information (Cambridge University Press, Cambridge UK, 2000).
[42] C. Macchiavello and M. F. Sacchi, Phys. Rev. A 94, 052333 (2016).
[43] C. Addis, G. Karpat, C. Macchiavello, and S. Maniscalco, Phys. Rev. A 94, 032121 (2016).
[44] E. Jung, M.-R. Hwang, Y. H. Ju, M.-S. Kim, S.-K. Yoo, H. Kim, D. Park, J.-W. Son, S. Tamyar, and S.-K. Cha, Phys. Rev. A 78, 012312 (2008).
[45] S. Dafer, K. Wódkiewicz, J. D. Cresser, and J. K. McIver, Phys. Rev. A 70, 010304 (2004).
[46] A. Rivas, A. D. K. Plato, S. F. Huelga, and M. B. Plenio, New. J. Phys. 12, 113032 (2010).
[47] V. Gorini, A. Kossakowski, and E. C. G. Sudarshan, J. Math. Phys. 17, 821 (1976).
[48] F. M. Paula, I. A. Silva, J. D. Montealegre, A. M. Souza, E. R. deAzevedo, R. S. Sarthour, A. Saguia, I. S. Oliveira, D. O. Soares-Pinto, G. Adesso, and M. S. Sarandy, Phys. Rev. Lett. 111, 250401 (2013).
[49] R. Auccaise, L. C. Céleri, D. O. Soares-Pinto, E. R. deAzevedo, J. Maziero, A. M. Souza, T. J. Bonagamba, R. S. Sarthour, I. S. Oliveira, and R. M. Serra, Phys. Rev. Lett. 107, 140403 (2011).
[50] H. Singh, Arvind, and K. Dorai, EPL 118, 50001 (2017).
[51] I. A. Silva, A. M. Souza, T. R. Bromley, M. Cianciaruso, R. Marx, R. S. Sarthour, I. S. Oliveira, R. L. Franco, S. J. Glaser, E. R. deAzevedo, D. O. Soares-Pinto, and G. Adesso, Phys. Rev. Lett. 117, 160402 (2016).
[52] T. Xin, L. Hao, S.-Y. Hou, G.-R. Feng, and G.-L. Long, Sci. China-Phys. Mech. Astron. 62, 960312 (2019).
[53] J. W. Wen, X. C. Qiu, X. Y. Kong, X. Y. Chen, F. Yang, and G. L. Long, Sci. China-Phys. Mech. Astron. 63, 230321 (2020).
[54] A. Ghosh and A. Kumar, J. Magn. Reson. 173, 125 (2005).
[55] R. Auccaise, J. Teles, R. Sarthour, T. Bonagamba, I. Oliveira, and E. deAzevedo, J. Magn. Reson. 192, 17 (2008).
[56] D. Cory, M. Price, and T. Havel, Physica D 120, 82 (1998).
[57] G. L. Long, H. Y. Yan, and Y. Sun, J. Opt. B: Quantum Semiclass. Opt. 3, 376 (2001).
[58] G. M. Leskowitz and L. J. Mueller, Phys. Rev. A 69, 052302 (2004).
[59] H. Singh, Arvind, and K. Dorai, Phys. Lett. A 380, 3051 (2016).
[60] R. Jozsa, J. Mod. Opt. 41, 2315 (1994).
[61] A. Uhlmann, Rep. Math. Phys. 9, 273 (1976).