A method for measurement of spin-spin couplings with sub-mHz precision using zero- to ultralow-field nuclear magnetic resonance

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A B S T R A C T

We present a method which allows for the extraction of physical quantities directly from zero- to ultralow-field nuclear magnetic resonance (ZULF NMR) data. A numerical density matrix evolution is used to simulate ZULF NMR spectra of several molecules in order to fit experimental data. The method is utilized to determine the indirect spin-spin couplings (J-couplings) in these systems, which is achieved with precision of 10^{-2}–10^{-4} Hz. The simulated and measured spectra are compared to earlier research. Agreement and improved precision are achieved for most of the J-coupling estimates. The availability of fast, flexible fitting method for ZULF NMR enables a new generation of precision-measurement experiments for spin-dependent interactions and physics beyond the Standard Model.

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1. Introduction

Nuclear magnetic resonance (NMR) has many applications, including precision measurement of physical constants, chemical detection and analysis, and bimolecular structure elucidation. In conventional NMR, large magnetic fields are used in order to enhance chemical-shift resolution and improve the sensitivity of inductive detection, as well as to increase signals due to higher polarization. Furthermore, working at high-field also serves to "truncate" second-order effects arising from nuclear spin interactions that do not commute with the Zeeman Hamiltonian. Zero- to ultralow-field (ZULF) NMR is an alternative method that does not utilize strong magnetic fields [1–5], at least not for encoding and detection. Due to the high absolute field homogeneity and the absence of some relaxation pathways such as those related to chemical-shift anisotropy, ZULF NMR frequently achieves narrow resonance linewidths on the order of tens of mHz, allowing for precise measurement of spin–spin interactions. Additionally, the absence of truncation by a large applied magnetic field means that ZULF NMR is capable of measuring spin-dependent interactions that do not commute with the Zeeman Hamiltonian [6], which is difficult in conventional NMR experiments, where such interactions do not produce splittings or frequency shifts to first order.

ZULF NMR operates in the regime where the Zeeman Hamiltonian vanishes or can be treated as a perturbation compared to the internal interactions among the nuclei of the molecule. For isotropic liquids, the direct dipole-dipole couplings are averaged due to the random motion of the molecules. The main interactions remaining are the electron-mediated indirect spin-spin coupling, J-couplings, of the form $J\mathbf{I}_1 \cdot \mathbf{I}_2$, between two nuclear spins $\mathbf{I}_1$ and $\mathbf{I}_2$. These couplings are dependent on the geometry and electronic structure of the molecule. This makes J-spectroscopy a source of information for chemical analysis and fingerprinting. Moreover, J-couplings are a source of information spin topology and torsion and bond angles. For instance, a structural analysis of several benzene derivatives is discussed in Ref. [1]. Additional information can be provided by applying small magnetic fields [7] or by reintroducing molecular alignment in, for example, stretched polymer gels [6].

Recently, J-couplings have also drawn the attention of physicists searching for anomalous spin-dependent forces [8] arising from axion-like particles [9], which are possible dark-matter candidates [10]. For example, in Ref. [8], the authors were able to set new constraints on the coupling constants between nucleons mediated by exchange of pseudoscalar (axion-like) and axial-vector bosons by comparing precision measurements and calculations of the J-coupling in hydrogen deuteride. More recent experiments have hinted that there may be a significant difference between measured and predicted values for the HD J-coupling [11]. However, while the authors of Ref. [12] also measure slight

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discrepancies between experiment and theory for the couplings in hydrogen deuteride (HD), hydrogen tritide (HT), and deuterium tritide (DT), they suggest that the effect may be associated with the absence of nonadiabatic corrections in the theory. Along with improvements to calculations, additional precise J-coupling measurements will be valuable to these efforts. Furthermore, it may be possible to search for other exotic physics mediated by new particles by fitting ZULF NMR spectra using various model Hamiltonians that include exotic interactions such as those identified in Ref. [13]. Performing such fits is required for high-precision measurement of J-couplings and/or testing model Hamiltonians. Accomplishing this task necessitates the development of fitting code that is fast enough for routine use in small-molecule ZULF NMR spectroscopy.

In this paper, we introduce a method for measurement of J-couplings that uses ZULF NMR data and provides high precision below spectral linewidths. As a proof of principle, we provide measured J-couplings for several molecules with precision comparable to or better than that currently available in the literature. This method can be readily modified to include any additional spin interactions. The zero-field data of Refs. [1–3] were reanalyzed, yielding improved (in some cases sub-mHz) precision for some of the J-couplings as discussed below.

2. ZULF NMR experiments

The experiments are discussed in Refs. [1,5]. A schematic of the zero-field NMR apparatus is shown in Fig. 1. The sample is polarized in a 2 T permanent Halbach magnet and is then pneumatically shuttled to the detection region. A ^{87}Rb alkali-vapor optical atomic magnetometer operating in the spin-exchange relaxation-free (SERF) regime [14] is used to measure the evolution of the sample's nuclear spin magnetization. The alkali vapor cell of the optical magnetometer is surrounded with two sets of three orthogonal coils: one set is used for the application of magnetic field pulses, and the other for cancellation of residual static magnetic fields.
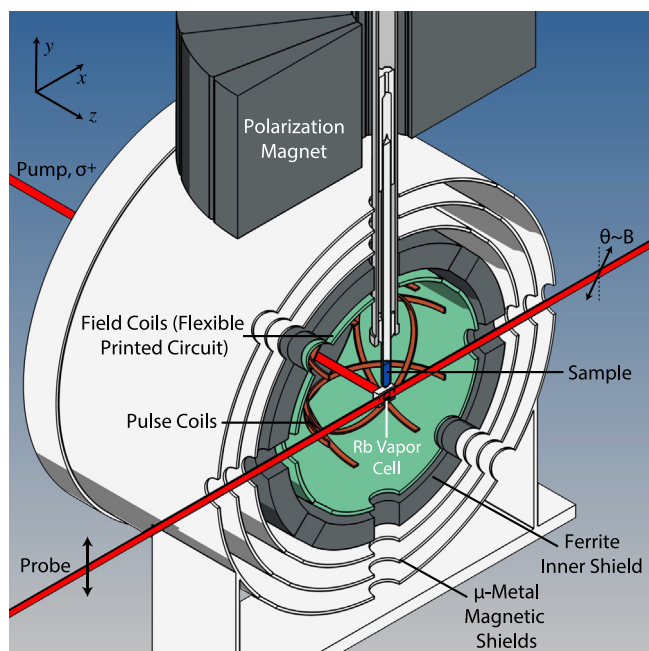
Fig. 1. Schematic of the ZULF apparatus: magnetic field in z-direction is measured by a ^{87}Rb alkali-vapor optical atomic magnetometer. Magnetic field is probed by measuring polarization rotation of a linearly polarized beam. The sample is shuttled pneumatically into the magnetically shielded detection region after being polarized.

The atoms in the cell are pumped with circularly polarized laser light tuned to the D1 transition, propagating along the +z-direction. The magnetic field is probed by optical rotation (OR) of a second frequency-detuned beam propagating along the +x direction. With this configuration, the magnetometer is sensitive to magnetic fields in the y-direction. After shuttling the sample to the detection region, a pulse (for instance, with area $B_x t = \pi/\gamma_C$, for ^{13}C-labeled molecules in x-direction, where γ_C is the gyromagnetic ratio of ^{13}C) induces coherence among nuclear spins in the molecule. The evolution of this system is then measured with the magnetometer. The signal is processed and Fourier-transformed to create the spectrum that is discussed in later sections of this work.

All samples were composed only of the neat liquid and were degassed via multiple freeze-pump-thaw cycles and then flame-sealed to prevent contamination. Sample temperature was not actively controlled, but was generally ~35–40 °C.

3. Fitting method

A density-matrix simulation was developed to model the experiment. The simulation starts by assuming a density matrix corresponding to thermal equilibrium in a magnetic field B_y

$$\rho_0 = \frac{e^{-\beta H_{pol}}}{\text{Tr}(e^{-\beta H_{pol}})}, \tag{1}$$

where $\beta = (k_B T)^{-1}$ with Boltzmann constant k_B and temperature T, and $H_{pol} = -B_y \sum_j \gamma_j I_{y,j}$ is the Zeeman Hamiltonian during the polarization step with gyromagnetic ratio γ_j of nuclear spin $\mathbf{I}_j$. For all future steps, the polarizing magnetic field B_y is removed. Then, an instantaneous magnetic field pulse (in this case a π-pulse in x-direction on the ^{13}C) is applied,

$$\rho(t = 0) = U^\dagger \rho_0 U, \tag{2}$$

with $U = \exp\left(-i/\hbar \cdot \sum_j \gamma_j I_{x,j} \cdot \pi/\gamma_C\right)$. We neglect all other interactions including J-coupling during the pulse. Finally the density matrix is evolved in $T \times f_s$ steps, where T is the measurement period, and f_s is the sample rate of the signal. The evolution is performed with the operator $e^{i/\hbar \cdot H \cdot t}$, with the Hamiltonian

$$H = \sum_{i,j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j. \tag{3}$$

Every step of the evolution is accompanied by an evaluation of the magnetization [15] of the system along the quantization axis

$$M_y(t) = \text{Tr}\left(\rho(t) \sum_i \gamma_i \mathbf{I}_{y,i}\right). \tag{4}$$

The magnetization signal is Fourier-transformed afterwards to create the simulated spectrum, which is then compared to the experimental spectrum.

The evolution of the magnetization, $M_y(t)$, is a function of the J-couplings. In order to extract the J-couplings from the experimental signals, an optimization problem is solved by iterative least-squares fitting that compares the experimental and the simulated spectra. In addition to the J-couplings, the parameters of the least-squares fit include a scaling factor A and a relaxation parameter τ, which are used to produce an ad hoc exponential decay envelope $Ae^{-t/\tau}$ that is multiplied with the signal such that the simulated signal becomes $M_y(t) \Rightarrow AM_y(t)e^{-t/\tau}$. Using a single exponential decay is justified by the fact that in the data presented here all coherences appear to decohere uniformly, although in general different parts of the density matrix may decay at different rates [16].