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Pseudo Rotary Resonance Relaxation Dispersion Effects in Isotropic Samples
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In this manuscript, the authors report the experimental observation of rapid signal loss during a spinlock pulse in MAS NMR experiments of isotropic samples when irradiating at a rotary resonance condition (nu_1 = n · nu_R, with n = 1, 2). This phenomenon is well-known for solid samples, where irradiating at one of the rotary resonance conditions recouples the chemical-shift anisotropy as well as the anisotropic heteronuclear dipolar coupling which leads to coherent broadening and, therefore, signal decay. Moreover, irradiating at the rotary resonance conditions leads to a sampling of the spectral-density function at zero and can, thus, lead to enhanced rotating-frame relaxation (T1rho, incoherent broadening) in dynamic systems. In this work, however, the authors report enhanced signal decay in MAS experiments of polybutadiene rubber and polyethylene glycol solution samples that exhibit liquid-like spectra and are, thus, considered isotropic. They attribute the observed signal decay at the rotary resonance conditions to the MAS modulation of the applied rf field due to the spatial inhomogeneity of the rf field. Numerical simulations of spinlock experiments that are performed using a relatively basic model of the spatial rf-field distribution generated by a solenoid coil appear to support this explanation.

Although the work reports a potentially relevant phenomenon, there are notable issues that need to be addressed. My major concern is that the simulation results presented in the paper are not reproducible based on the description provided in the SI. The conclusions drawn by the authors about the enhanced signal decay originating from the MAS modulation of the applied rf field solely based on the simulation results that are presented therefore appear to be unsubstantiated. Additionally, the model employed for the spatial distribution of the RF field generated by a solenoid coil in a typical MAS NMR probe is overly simplistic and may overestimate the magnitude of phase errors arising from the radial rf-field inhomogeneity. This raises questions about the validity of the authors' interpretation of their simulation results. To enable a proper assessment of the manuscript and determine whether it can be recommended for publication, it is essential that the authors provide additional information regarding their numerical simulations and address the specific concerns outlined below.

1) Numerical simulations

The description of the numerical simulations provided in the SI suggests that the authors performed simulations for a single-spin-1/2 system by numerical integration of the Liouville-von Neumann equation. Based on Eq. (S2), both the initial density operator as well as the detection operator correspond to Ix (x magnetization). For simulations taking the spatial rf-field inhomogeneity into account, the Hamiltonian of the system corresponds to a spinlock along the x-axis (Eq. (S3C)) and an orthogonal component along the y-axis that is modulated by the MAS frequency (Eq. (S3B)). This will generate an effective field whose orientation and magnitude will be modulated by the MAS frequency and about which the magnetization will nutate. Due to spatial inhomogeneity of the rf field, the orientation and magnitude of this effective field will vary across the sample space. The authors model the spatial rf-field distribution using distribution functions f_B1 (that models the amplitude distribution along the rotor axis) and f_nu1 (that models the magnitude of the modulated component along the y-axis) and compute the total signal as the weighted average of these distributions (Eq. (S2)). Unfortunately, the functional forms of these distribution functions are not provided (which they should be) and can only be approximated based on Fig. S1. Since no other spin-spin or spin-field interactions are mentioned, it must be assumed that no other interactions are taken into account, which would be in line with an isotropic sample of an isolated nucleus. Moreover, the authors explicitly say that no relaxation is taken into account in the simulations and the effect therefore has to be coherent in nature. However, computing the signal based on this information (which is computationally inexpensive for a single-spin system) does not lead to the same results presented by the authors in Fig. 3 in the main text. I would therefore ask the authors to provide additional information on how the simulations were performed.

2) Model for the rf inhomogeneity

In my opinion, the model used for the spatial distribution of the rf-field in a solenoid coil is not appropriate due to the following issues:

- The authors assume an amplitude deviation from the nominal spinlock amplitude of only 0-5% (Eq. (S3C)). However, both simulated (e.g. Tosner et. al. 2017) and measured (e.g. Gupta et. al. 2015) rf-field distributions of common MAS NMR probes suggest that the field drops to approximately 50% at the edges of the sample space. Since there is no mention of spatial sample restriction to the central part of the rotor, the chosen amplitude distribution is not appropriate.
- For a maximum deviation of the spinlock amplitude of 5% the signal weighting function given in Fig. S1C is not appropriate. According to the reciprocity theorem (e.g. Hoult 1976), the induced signal is directly related to the B1 field of the receiving coil at a given position in the sample space. A deviation from the nominal field by 5% should therefore not lead to a weighing of the signal with a factor of close to zero as is shown in Fig. S1C.
- The orthogonal component (Eq. (S3B)) occurs due to the MAS modulation of the phase of the rf irradiation which is known to be strongest at the edges of the sample space (e.g. Tosner 2017). Since the spinlock amplitude is also significantly lower than the nominal spinlock amplitude in these parts of the sample, the rotary resonance condition is no longer fulfilled in these parts of the sample and the coil sensitivity is significantly lower. However, the model implemented by the authors uses the same magnitude of the modulation for all values of f_B1.

Since simulated realistic rf-field distributions can be found in the literature (Tosner et. al. 2017), I would suggest that the authors perform their simulations using such a distribution instead of this crude model that appears to overestimate the magnitude of the phase errors due to the rf-field inhomogeneity.

3) Isotropic sample

The experimental results presented in the paper stem from measurements of a polybutadiene rubber sample as well as a polyethylene glycol sample. Although these sample exhibit “liquid-like” spectra, they both correspond to large polymer systems, where partial alignment might lead to residual anisotropic dipolar interactions that will be recoupled for irradiation at a rotary resonance condition. The comparison of experimental spectra of the rubber sample with and without MAS (Fig. S4A) shows that the static spectrum is significantly broader than the one under MAS. This line broadening can either be attributed to residual anisotropic interactions or susceptibility effects and raises the question if either of the two are re-introduced by irradiating at the rotary resonance condition which would lead to signal decay.

The authors attribute the observed signal decay solely to the modulation of the rf-field due to the rf inhomogeneity, based on numerical simulations of a single-spin system. This raises the question why the authors didn't choose to demonstrate the effect using a truly isotropic system (such as, for example, the residual H2O line in D2O) that would correspond more closely to what is simulated.

4) Additional Remarks:
   - The different positions of the minima of the signal intensity in the experimental and simulation results is never discussed.
   - I think the authors should put more emphasis on distinguishing coherent from incoherent effects that lead to signal decay. Since the experimental data clearly shows an oscillating behavior and no stochastic processes (e.g. molecular motion) are taken into account in the numerical simulations that are used to explain the observed phenomenon, the underlying mechanism has to be coherent. However, the abstract of the paper suggests "maxima in relaxation rates" (p. 1, l. 15) and "enhanced transverse relaxation" (p.1, l.10), which makes it sound like the observed signal decay is due to incoherent line broadening.
   - In the experimental data, it is not clear what the "signal intensity" is that is plotted. Is this the integrated intensity or the maximum peak intensity?
   - In the text and the figure legends the spinlock amplitude is referred to as nu_SL whereas in the axis of the figure it is denoted by nu_RF. The nomenclature should be consistent to avoid confusion.
   - The discussion of other reports of the effects of the MAS modulation of the rf field due to the spatial inhomogeneity is rather minimalistic. The authors may want to include the seminal works by Tekely and Goldman for example.
     - Goldman, M. and Tekely, P.: Effect of radial RF field on MAS spec tra, CR Acad. Sci. II C, 4, 795–800, 2001.
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