

We thank the Reviewers for their overall positive impression of the revised article. While Reviewer 3 recommended the publication of the article as is, Reviewer 2 suggested a major revision. The reason for a major revision was that our mathematical description involved modulations along I_z , while physically, these B_1 modulations should only affect the signal when along I_y (when the spin-lock is along x). Mathematically, there is no difference in the result if the B_1 modulation is along y or z . However, we agree that still we should have highlighted that, physically, B_1 modulation on y contributes, while modulation on z does not. Due to the solenoidal symmetry, no change to the distribution of these modulations is needed, and a relatively minor change in the text addresses this issue. We added the missing part that connects B_1 modulation in the y -direction (with the I_y operator) to Eqn. (S1) in the SI, where B_1 modulation is with the I_z operator. This general description is useful since we also discuss B_0 modulations, for which both I_z and I_y modulations are relevant.

We also moved the equations to the main text as suggested by the Reviewer.

Additionally, to improve the presentation quality of the article, we have added the following figure to the SI, which visualizes of the inhomogeneity factor and B_0 or B_1 modulations as a 2D color map. We added the following to the SI:

“Figure S8 shows the weighting factors (the color map) according to the range of input inhomogeneity factor values (y-axis) and B_0 modulation amplitude values (x-axis, A) and B_1 modulation amplitude values (x-axis, B). For B_0 modulation (A), the amplitude with the highest value of 200 Hz has the largest weighting factor (red), while for B_1 modulation (B), the opposite is true – the amplitude with 0 value has the largest weighting factor on the total signal. This approximates the expectation that a B_0 field inhomogeneity (e.g. in the y direction) would more strongly affect the sample at the rotor wall, where there is more sample volume. On the other hand, the B_1 field inhomogeneity may be less linear, and affect only a small annulus of sample near the coil. Changes to the distribution mainly affect the location of the first minimum in the SL intensity (see Figure S6 and Figures 4 and 5 in the main text).

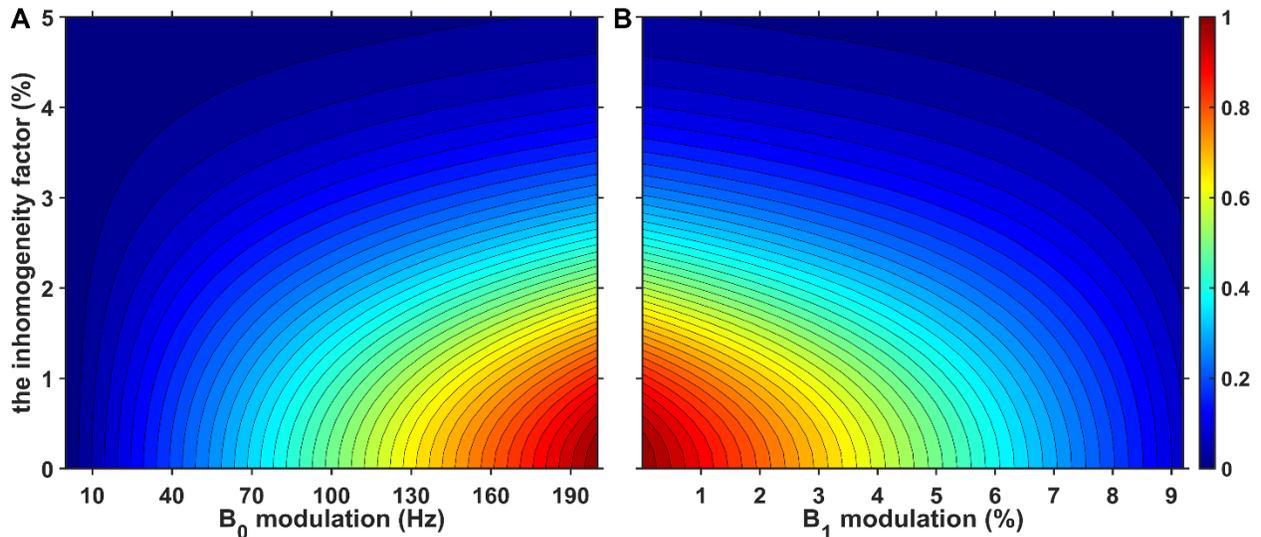


Figure S8 The weighting factor maps are plotted as a function of the inhomogeneity factor (y-axis, in %) and B_0 (A) or B_1 (B) amplitude modulations (x-axis). (A) The amplitudes values range between [0:200] (Hz). (B) The amplitude values range between [0:9.14] (%) with respect to the applied v_{SL} value. In both color maps, the inhomogeneity factor ranges between [0:5] (%) with respect to the applied v_{SL} value.”

Below is a point-by-point response (in blue) to the second Reviewer’s comments (in black).

Referee #2: Zdeněk Tošner

(1) The presentation of the pseudo rotary-resonance relaxation dispersion improved with respect to the original submission last year. Including measurements on water sample excludes any doubts this effect is real. Arguments based on average Hamiltonian theory are strong, if assumptions were correct.

I have a fundamental problem with the explanation that the phenomenon is caused by variations of B_1 field along z-direction. Typically, rf fields are thought of as perpendicular to the B_0 field, that is within the xy plane. In MAS configuration, yes, the coil is tilted at the magic angle and significant rf field is produced along z-axis. BUT!!! This component oscillates at Larmor frequency (it is not affected by transformation into rotating frame) and thus averages out promptly, orders of magnitude faster than MAS.

Thanks for pointing this out. We have modified the presentation to make clear that only for B_0 , a z-modulation survives the secular approximation, while for the B_1 case it does not.

(2) Surprisingly, the importance of z-component modulations is not mentioned in the main text while it is the key component of simulations and theory treatment. It is only vaguely stated on page 10, lines 12-13, “orthogonal to the applied rf field spinlock”. Blessed statement! It is not the z-component, it is the y-component, the other orthogonal. Changing direction of Hamiltonian H_t in equation S1 to I_y does not influence the conclusions...

We agree with the Reviewer, that changing direction of Hamiltonian H_t in equation S1 from I_z to I_y does not influence the conclusions, and also that the I_y component is the relevant component in relation to B_1 modulations. If H_t depends on the I_y operator, we can rotate the total Hamiltonian, H_{total} , by $\frac{\pi}{2}$ around the \hat{x} axis and obtain the same Hamiltonian as in Eqn. (S1), where it depends on the I_z operator. Since the initial and final operators commute with this rotation, Eqn. (S2) remains exactly the same. Therefore, the Average Hamiltonian Theory (AHT) analysis¹ is identical in both cases, whether H_t depends on the I_y or I_z operator.

To clarify, we have modified Eqn. (S1) to make it more general and moved it to the main text, as suggested by the Reviewer.

The added text reads:

“To understand the origin of the pseudo-RRD effect, we start with the simplest case, investigating the behavior of an on-resonance spin (I) during the rf-field spin-lock. The simulated SL-signal is defined as follows:

$$S_{SL}(t_{SL}) = \text{Tr} \left\{ I_x \hat{T} e^{-i \int_0^{t_{SL}} dt H_{total}} I_x \hat{T} e^{i \int_0^{t_{SL}} dt H_{total}} \right\}, \quad \text{Eqn. (1)}$$

where \hat{T} is a Dyson operator and H_{total} is a total Hamiltonian. We consider the effects of B_0 and B_1 modulations or dipolar interaction. For all three sources, H_{total} can be defined as follows:

$$H_{total} = H_{SL} + H_t = \omega_{SL} I_x + \quad \text{Eqn. (2)}$$

$$2\pi \sum_n a_n \cos(n\omega_R t + \phi_n) [I_z \cos\varphi + I_y \sin\varphi] \widehat{O}p,$$

where $\omega_{SL} = 2\pi\nu_{SL}$ and H_{SL} is an ideal spin-lock Hamiltonian. Here, $\widehat{O}p = 1$ for a single spin with B_0 ($\varphi \geq 0$) or B_1 ($\varphi = \pi/2$) modulations, or $\widehat{O}p = 2S_z$ with $\varphi = 0$ for a two-spin system (dipolar interaction). While for dipolar interaction, n is 1 or 2,^{2,3} for B_0 and B_1 modulations, n may take any integer value.⁴ This is because these modulations are not purely sinusoidal; there are contributions from overtone frequencies. In the experimental SL profiles (Figures 2 and 3), two rotary-resonance conditions are clearly observed. Therefore, in the following discussion, $n = 1, 2$ will be considered for all three cases. Note also that for the cosine modulated terms of Eqn. 2, only I_y (and not I_z) survives the rotating frame transformation and secular approximation for the case of B_1 modulation. Both terms are relevant for B_0 modulations. For the dipolar interaction, a_k inversely depend on the distance between the pair of spins and the orientation:^{2,3} $a_1 = \frac{\nu_D}{\sqrt{2}} \sin(2\beta)$ and $a_2 = -\frac{\nu_D}{2} \sin^2(\beta)$; $\nu_D = \nu_{D,IS} = -\frac{\mu_0}{8\pi^2} \frac{\hbar\gamma_I\gamma_S}{r_{IS}^3}$ and (β) is the Euler angle with respect to the rotor frame. (Mehring, 1983) For B_0 and B_1 modulations, a_k values do not exhibit any orientation dependence. It is worth noting that for B_1 modulations, a_k values change with the strength of the applied rf-field lock value (ν_{SL}).

If φ does not vary with time, Eqn. (2) can be simplified by rotation of H_{total} by an φ angle around the \hat{x} using the operator $e^{-i\varphi I_x}$. Such a rotation removes any dependence on φ , since the initial and the final operators in Eqn. (1) commute with $e^{i\varphi I_x}$. The modified Eqn. (2) is written as follows:

$$H_{total} = e^{-i\varphi I_x} H'_{total} e^{i\varphi I_x} = H_{SL} + H_t = \omega_{SL} I_x + 2\pi \sum_n a_n \cos(n\omega_R t + \phi_n) I_z \widehat{O}p. \quad \text{Eqn. (3)}$$

Thus, while B_0 modulation may occur anywhere in the yz -plane, the theoretical treatment remains exactly the same as for z modulation. Mathematically, this is also true for B_1 modulation, while physically, these modulations are only relevant when in the transverse plane.”

(3) Average Hamiltonian treatment is a convincing proof of the phenomenon and should be moved to the main text. At least Equation S1 highlighting variations along z -direction for B_0 , and along y -direction for B_1 . And the result, like Eq. S10, but with better explanation what is the frequency of signal amplitude modulations and what is a time (in Eq. S10, N_{SL} supplements the time axis, but it depends on MAS frequency and thus is confusing). It should be clear that the frequency of signal amplitude modulations does not depend on MAS in case of B_0 variations, but it does depend on MAS in case of B_1 variations (it is clear from simulations in the figure S4 but it is possible to write a formula as well)

We now clarify that the z -direction (and y) is relevant for B_0 and the y -direction is relevant for B_1 . We added the sentence regarding dependence of the frequency of signal amplitude modulations for B_0 and B_1 :

“In the case of B_0 modulation, adjustments to the shimming coil are expected to have a profound effect, but oscillations in signal amplitude are expected to be independent of the applied B_1 field. By contrast, for B_1 modulation, changes in the strength of the applied spin-lock have a major effect, since the oscillation frequency of signal amplitude is expected to depend on B_1 .”

(4) I suggest major revisions. It must be highlighted and evident from the first reading of the abstract and the paper which component of rf field is causing the phenomenon.

While mathematically there is no difference if B_1 modulation occurs along I_y or I_z or both at the same time, physically, only I_y is relevant (when the spinlock is on x).

(5) Just a note to the author's response to Reviewer #1, point 2, regarding rf-field inhomogeneity profile. The figure included in the response documents common misunderstanding in the community. The nutation profile is NOT symmetric, and it has an important tail towards lower frequencies which is easily overlooked in data suffering from truncation artifacts like those shown in the figure. Best analytical function to fit nutation profiles is not a gaussian but the power law suggested by Gupta et al. 2015. Gaussian captures most abundant features though...

We added the following sentences to the main text:

"A more quantitative assessment would call for calculation of the exact values and shapes of B_1 fields for a particular coil, as well as better characterization of B_0 distribution.⁴⁻¹⁴ Note that the magnitudes within these distributions are reasonable, considering the published calculations for solenoidal coils.^{7,15,16}"

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