

Interactive comment on “Surprising absence of strong homonuclear coupling at low magnetic field explored by two-field NMR spectroscopy” by Ivan V. Zhukov et al.

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Referee Report for the manuscript: “Surprising absence of strong homonuclear coupling at low magnetic field explored by two-field NMR spectroscopy” from I.V. Zhukov, A. S. Kiryutin, Z. Wang, M. Zachrdly, A. V. Yurkovskaya, K.L. Ivanov, F. Ferrage

1. General Comments:

This paper describes theoretically and experimentally the phenomenon that the ^{13}C polarization transfer efficiency between various labeled ^{13}C nuclei in an amino acid after a field cycling experiment (from 14.1 T to 0.3 T and back) is reduced significantly in

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the absence of ^1H decoupling. This is due to hetero-nuclear ^1H - ^{13}C J-coupling, which alters the strong coupling condition between different ^{13}C sites. If proton decoupling is performed at low field (0.33 T), the ^1H - ^{13}C J coupling is switched off and efficient ^{13}C polarization transfer takes place between homo-nuclear strongly J-coupled ^{13}C sites, where the chemical shift difference is smaller than the homo-nuclear J-coupling. This work is a nice contribution to the field of biomolecular NMR methodologies. There are, however, a number of issues that need to be resolved before I can recommend this article for publication in JMR.

2. Individual scientific comments and questions:

(a) A small confusion arises due to Figure 1, where the ^{13}C spectrum from L-leucine measured at 100.62 MHz is shown. Later in Figure 5 the ^{13}C spectra is presented at 150.9 MHz. The reader will ask why the ^{13}C NMR spectrum has not been measured at 150.9 MHz ?

(b) In section B in line 99 an unprecise statement is made “First, a non-equilibrium state is generated at B_{HF} by applying a selective pulse”. Please specify here that a selective 180° pulse is applied to $C^{\delta 2}$, leading to a non-equilibrium state, i.e. to a population inversion (refer here to Figure 2).

(c) There is an error in the signs in Equation (1), either all signs in the Zeeman terms ($-\omega_1 I_z - \omega_2 I_z - \omega_3 S_z$) are negative or all are positive, but mixed signs cannot be true. Furthermore Equation (1) and (10) are inconsistent with Equation (2), where all signs before I_z and S_z are negative.

(d) The exact form of ω_1 , ω_2 and ω_3 should be stated in line 139, i.e. $\omega_1 = \gamma_{\text{C}}(1+\delta^2) B_{\text{HF}}$, $\omega_2 = \gamma_{\text{C}}(1+\delta^2) B_{\text{HF}}$ and $\omega_3 = \gamma_{\text{H}} B_{\text{HF}}$.

(e) The experimental results in Figures 5B and 6B are in good agreement with the theoretical expectation only in the first 10 ms. Especially in Figure 6B the experimental data does not show the oscillating features as suggested by the theory. An explanation

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for this deviation would be very helpful.

3. Technical corrections, typing errors and references:

(a) In Figure 1 each panel should be labelled with (A), (B). . . (E), where (A) should be the molecule, (B) the overall ^{13}C spectrum, (C) C' - spectrum, and so on.

(b) Caption in Figure 3 (line 156) should be (A) and (B) instead of (a) and (b). Similar in Figure 3,4,5,6 with labels (A) and (B) instead of A and B. Please be consistent with (A), (B), .. between captions and figures.

(c) I plotted the paper in black and white. Some indices, for example the “alpha, beta” symbols in Figs. 4 (A,B) can be hardly identified. The same problem in Figs.5,6 with C^{gam} , C^{delt1} , and C^{delt2} .

(d) A reference studying the polarization transfer from para-hydrogen onto ^{13}C in a HA-HB- ^{13}C three spin system is: P. Türschmann, J. Colell, T. Theis, B. Blümich and S. Appelt, PCCP (2014), (DOI: 10.1039/c4cp01807a). Some aspects described there are related to the present manuscript and might be suitable as a reference.

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