

Interactive comment on “Revisiting paramagnetic relaxation enhancements in slowly rotating systems: how long is the long range?” by Giovanni Bellomo et al.

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This manuscript describes a theoretical investigation of the effect of nucleus-nucleus dipole-dipole interactions on longitudinal relaxation rates measured in a protein, as well as the same effect combined with chemical exchange of protons on the longitudinal relaxation of water protons in solutions of a paramagnetic complex, as encountered with contrast agents for MRI. The authors use the CORMA approach to include all dipole-dipole interactions between all nuclei in the molecule, including all relaxation pathways (but neglecting all cross-correlated cross-relaxation pathways). The authors show that nucleus-nucleus interactions cannot be neglected when the electron-nucleus

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distance is larger than 15 Å. In the case of a paramagnetic complex, the authors show that chemical exchange of protons in the complex or weakly bound to the complex, can lead to enhancements of the longitudinal relaxation rate of water. Particularly when the complex tumbles slowly and when the exchange of magnetization is fast (a few ms or faster) This is a very interesting manuscript. The work is convincing and nicely presented. The mention of the late Jens Led in the acknowledgements is very nice given how closely related this work is to several studies from the Led group over the years. I list below a series of mostly technical points that should be addressed to further improve the manuscript and make it more accessible.

-It is not fully clear from the main text what the authors mean by “calculated rates”. The authors use the adapted CORMA approach, they compute the evolution of the magnetization from Eq. 4. After this, one has to check Fig. S2 (not the main text) to find a fit of recovery to obtain the “calculated rate”? If so, are the recovery monoexponential? There seem to be some deviations in Figure S2.

-In the discussion of Figure 1, the authors should make it more clear whether the effect discussed is due to cross-relaxation with faster relaxing protons (a “selective T₁” effect) and not simply the contribution of nucleus dipole-nucleus dipole interactions to relaxation (a “non-selective T₁” effect).

-In the light of the discussion between the authors and Gottfried Otting on a decrease of paramagnetic relaxation enhancements at intermediate distances, could this effect explain part of the surprising observations made by Flemming Hansen and Jens Led in their beautiful investigation of the blue copper site in Plastocyanin (JACS 2004)?

-The authors rightfully refer the contribution to relaxation from interactions with electrons to the seminal work of Solomon by mentioning the “Solomon Equation”. However, I find this expression possibly confusing, especially in the context of this investigation. The legacy of Ionel Solomon reached beyond the expression of relaxation in paramagnetic systems and it is widely accepted in NMR that the Solomon EquationS describe

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the evolution of magnetization in the presence of dipolar cross-relaxation, which is also perfectly relevant to this study. I believe that the authors should mention these Solomon Equations (introduced in the same Phys. Rev. 1955 article). It would be fantastic if the authors could take this opportunity to clarify the Solomon Equation vs. Solomon Equations issue, possibly by referring to the former as the Bloombergen-Solomon Equation as some do in the literature.

-I wonder if calculating the evolution of the magnetization would be easier with the use of the Homogeneous Master Equation (Levitt and di Bari 1922).

-On lines 128-129, the authors mention that, in the absence of exchange, the bulk water relaxation rate is not altered by the interaction with the electron magnetic dipole. Is it true or is it an approximation since outer-sphere relaxation mechanisms are not the topic of this investigation?

- I am not sure I understand exactly how the relaxation rates of the bulk calculated from the Solomon equation represented by dashed and solid lines in Figure 3 were calculated, what was included in each calculation.

-In the spirit of Magnetic Resonance, it would be preferable that the authors publish the simulation code used in their study.

Minor: -On lines 32-34, the question of non-monoexponential evolution of polarization in the presence of cross-relaxation could fill out volumes. The reference to the work of Banci and Luchinat is perfectly relevant here but could be accompanied by a general reference to nuclear Overhauser effects (e.g. the already cited Solomon article or the textbook by Neuhaus and Williamson). -Similarly, the “Furthermore” on line 33 could be replaced by “Indeed” or any other suggestion by the authors since cross-relaxation is the cause of non-monoexponentiality. -Including chemical exchange in the CORMA approach has been done in the past, for instance by Jayalakshmi and Rama Krishna (JMR 2002). -Many symbols are not defined in the main text. I may have missed some but could not find the definition of ρ_i , k_i , σ_{ij} , g_e , μ_B ,

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B_0, gamma_i, tau_e, Delta_1, and tau_nu. -Unless this is a format requirement of Magnetic Resonance, I would suggest the authors use a first page with article title and authors list in the supplementary information document.

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