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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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We are glad that you like the manuscript and we thank you for your constructive comments. Here below a point-by-point answer:

-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.

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It is correct that the recovery is not monoexponential. However, the “calculated rates” were indeed obtained from a monoexponential fit of the magnetization curves. We will clarify this point immediately after the first paragraph of the Results and discussion section, by stating that “although for some nuclei the magnetization recovery curves deviate from monoexponential functions as expected (see below), the relaxation rates were calculated for simplicity as the rate constants of the monoexponential time-dependences of the magnetization curves”.

-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 T_1” effect) and not simply the contribution of nucleus dipole-nucleus dipole interactions to relaxation (a “non-selective T1” effect).

Both indicated effects are effective when a non-selective pulse is applied, as done in our simulations. Most of the deviations is due to the different contributions from nucleus dipole-nucleus dipole interactions caused by the hyperfine coupling, but also cross relaxation effects are present. This can be checked by comparing the calculated rates from selective and non-selective experiments (see Figure below). This will be clarified in the text.

-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)?

Although this effect may slightly contribute to the experimental observations by Hansen and Led, we do not expect sizable contributions in that case. In fact, whereas the effects that we calculate are sizable at 13 Å or farther from the metal, the deviations were observed by Hansen and Led at less than 10 Å from the metal.

-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 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.

We will clarify that we call Solomon equation the widely used equation provided by Solomon for paramagnetic solutions (Solomon, 1955), although in the same work Solomon also provided the coupled equations which include cross-relaxation terms and should be taken into account for treating the case of nucleus dipole-nucleus dipole interacting spins. We prefer not to refer to the Bloembergen-Solomon equation because it includes contributions from Fermi-contact relaxation, which are not considered in this work.

-I wonder if calculating the evolution of the magnetization would be easier with the use of the Homogeneous Master Equation (Levitt and di Bari 1992).

This could be possible, but we have preferred a more “classical” approach, to better control all steps in the implementation of the model.

-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?

Contributions from outer-sphere relaxation are not considered in this work because of the large distance of the water molecules from the paramagnetic center, and thus not included into the model. This will be clarified in the text.

- 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.

The relaxation rates at 1 T (solid lines) and 3 T (dashed lines) are calculated from the Solomon relaxation rates R_1M of the exchangeable protons in the absence of any cross-relaxation terms, according to the relationship R_1bulk=R_1dia+ f(R_1Mˆ(-1)+τ_M)ˆ(-1). This will be clarified in the text.

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

We will contact the authors of CORMA and, if allowed, we will make available a version of the code as soon as completed with a user-friendly interface.

Minor:

-On lines 32-34, the question of non-monoexponential evolution of polarizationin 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).

We agree to cite these more general references.

-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.

OK

-Including chemical exchange in the CORMA approach has been done in the past, for instance by Jayalakshmi and Rama Krishna (JMR 2002).

This work will be cited. Thank you for pointing it out.

-Many symbols are not defined in the main text. I may have missed some but could not find the definition of rho_i, k_i, sigma_ij, g_e, mu_B, B_0, gamma_i, tau_e, Delta_1, and tau_nu.

All symbols will be defined in the revised version of the manuscript.

-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.

OK

Thank you for all your valuable comments.

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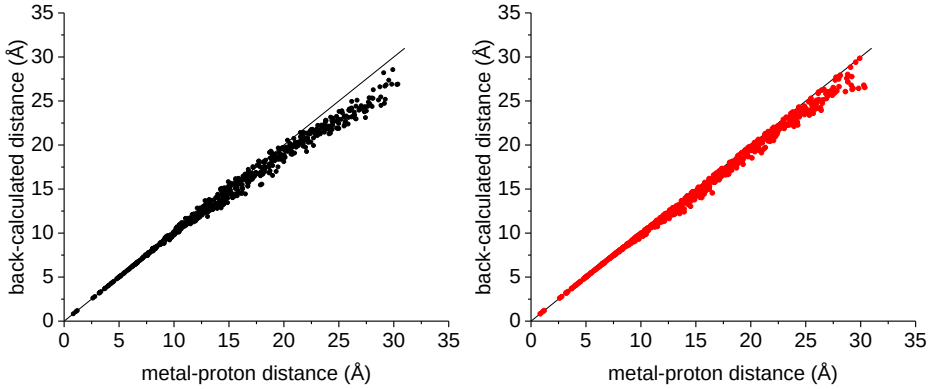

Figure 1. Agreement between metal-proton distances in Cu^{2+}-plastocyanin as measured in the PDB 2GIM structure and back-calculated from the predicted R_1 at 500 MHz: left panel, the relaxation rates are predicted by simulating a non-selective experiment (same plot shown in Figure 1 of the manuscript), right panel, the relaxation rates are predicted by simulating a selective experiment.

Fig. 1.

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