Reviewer 3:

On the whole, the study is very interesting and the following remarks are meant to be part of a final ironing process. … The paper is certainly worthwhile publishing, and I enjoy reading it; however, it can do with a lot of clarifications to improve readability.

We thank the reviewer for the positive assessment of our work and for helpful suggestions on how to improve our manuscript. The point by point response to the reviewer's comments is below.

The authors claim that 13.8 watts of MW were applied at the sample. Where was that measured, and how was that measured? This should be included in the experimental. Was it measured in front of the sample or in the sample? What exactly means 'at' in this case?

The MW power was measured at the waveguide entrance. We have revised the corresponding sentence of the Experimental section to: "The microwave (MW) frequency was 395.18 GHz and the MW irradiation generated by a second-harmonic gyrotron, which delivered 13.8 W of power, as measured at the waveguide entrance."

The spectra shown in Fig. 1 were all recorded with a recycle delay of 10 s. The authors should briefly state why they choose to do the experiment in this way and not using appropriately chosen multiples of T1 which is very different for the samples, and which would lead to optimal signal-to-noise-ratios for the fast relaxing ones. More importantly, they should discuss the implications of choosing the same delay for all samples appropriately. Enhancements are given in the top row of Fig. 1a, and I wonder whether there is a typo somewhere. Since so different radical concentrations are used I would expect different depolarization effects, by the way. One sentence discussing their possible contributions and in general the change with radical concentration would be good.

The authors should also indicate the scaling factors between the displays of spectra in the top and bottom rows in Fig. 1. They cannot be the same, otherwise the statement that in all three cases E=76 is likely not correct.

Thanks for alerting us to a typo and a mistake in Figure 1. On the bottom left panel, the traces for CP spectra of samples with 22.8 and 28.2 mM AMUPol were displayed with incorrect normalization. We have corrected this mistake as well as the typo in the signal enhancement values in the revised manuscript.

As to the choice of recycle delay, we have added the following explanation/justification to Results and Discussion:

"In conventional NMR, where a single variable (T_1) governs longitudinal spin relaxation, the recycle delay is generally simply chosen to maximize signal-to-noise ratio per unit time (e.g., $1.3*T_1$). The situation in DNP-NMR is significantly more complex: here, the recycle delay represents not only the longitudinal relaxation period but also the polarization buildup time period, since microwaves are always on throughout the experiment. If multiple DNP mechanisms are involved, each may have a different polarization buildup time constant (T_B), further varying by site on the molecule. The relationship between the experimental recycle delay and T_B governs the relative contributions of the various mechanisms. As a result, the DNP buildup profiles provide unique insight into the complex interplay of DNP effects."

It should always clearly be stated which pulse sequences were used; names are not enough. Fig. 3 is good to have, but where is the SCREAM sequence, where are the CORD sequences (yes, they are easy), which sequence is used for which spectra in Fig. 1, 2 and 4, etc. For the outside reader it is very difficult to understand what TB, TB+ and TB- refers to, there is nothing like this in the pulse sequences of Fig. 3 and there is also no description in the experimental. Furthermore, the letters in the pulse sequences of Fig. 3 are far too small, especially those for the DANTE delay. It requires quite some magnification to see that it is Tr. Elderly persons who need to print the manuscript will not see anything.

SCREAM is not an NMR sequence but rather a DNP mechanism, which is explained in the text. The SCREAM-DNP effect is clearly seen in the 1-pulse (direct polarization experiments). In regard to the SCREAM sequence, the reviewer appears to be referring to a difference experiment introduced by Corzilius and co-workers, where a spectrum acquired by DP (a combination of direct and indirect transfer pathways) was subtracted from the DP spectrum with saturation pulses applied to suppress the indirect transfers, hence yielding pure spectrum from the indirect pathway due to the methyl group dynamics. The purpose of the current study was to discern the competing transfer pathways, and therefore there was no need for such a difference experiment: the SCREAM

pathway is clearly seen in a DP experiment, Figure 4a (trace IV).

We have compiled all pulse sequences used in this work into a separate figure (Figure 1 of the revised manuscript) and indicated clearly in the figure captions to Fig. 2-6 which sequence was used for which experiment. We increased the font size in Figure 2 of the revised manuscript, so that the individual letters can be seen clearly.

Fig. 4 reports CP-CORD spectra whereas this name does not appear in Fig. 3 nor in the experimental part of the paper. There is no reference where I would expect it. Again, its needs to be stated to which pulse sequence Fig. 4 correlates to, and what the numbers mean above the spectra. By the way, they are very misleading, they could be mistaken for the CORD mixing time by an unexperienced reader. Better write RD= and define somewhere in the paper or in the legend.

There are no CP-CORD spectra anywhere in Figure 3; none of the spectra presented in Figure 3 of the original submission used CORD or any other C-C mixing periods. We added a reference to the CORD paper in the Experimental section. We have placed all pulse sequences in Figure 1 of the revised manuscript, including CP-CORD and DP-CORD sequences, as discussed above.

It is very instructive to see spectra recorded with 4.3 mM Amupol only, it is an important point of the paper, but it is always tricky to compare contour plots. To me it is obvious that spectra are different yet comparing one or two selected cross sections would be probably wise.

Thank you for this suggestion. We have added several selected 1D traces from the 2D spectra to the figure so that the differences are clear.

In the conclusion section it is said that 4.3 mM Amupol yielded the highest DNP signal enhancements. In stark contrast, Fig. 1 announces exactly the same enhancement for all three concentrations. Furthermore, the statement needs probably some seasoning, since there was no T1-optimized relaxation delay employed, and the S/N would be better with appropriate choices for the samples with higher Amupol concentrations. On the other hand, the better resolution in the spectra for the sample 4.3 mM Amupol does its job, too. Resolution is good, yes. To me it looks like similar T1 effects lead to the appearance of narrow signals in those direct polarization experiments recorded with longer relaxation delays. Maybe this should also be discussed appropriately.

The same enhancement factors was a typo, which we have now corrected. As mentioned in previous comments, finding a T_1-optimized relaxation delay for DNP spectra is not quite as straightforward as it might be in conventional NMR: each DNP mechanism must be considered and weighted. For HIV-1 CA tubular assemblies discussed in this work, we find that the optimal balance between sensitivity and resolution is achieved for 4.3 mM AMUPol concentration and recycle delay of 10 s.