Comment 1: Geoffrey Bodenhausen.

The paper on "Solid-State 1H Spin Polarimetry by 13CH3 Nuclear Magnetic Resonance" by Stuart J. Elliott, Quentin Stern (or should it be Quentin Chappuis, as in the Supplement?) and Sami Jannin raises all sorts of interesting questions.

The surname of our colleague has been amended in the supplement. Thank you for pointing this out to us.

When the authors write "The frequency of the dashed line corresponds to the minimum between the two peaks at high levels of 1H polarization," they discuss the two peaks phenomenologically as if they constituted a doublet. Are they implicitly referring to a doublet due to the heteronuclear dipole-dipole coupling in the Hamiltonian?

We believe that the strong HC dipolar coupling is involved in this phenomenon. We also agree that more information should be given about the origin of this asymmetry, and we will therefore add a paragraph listing the different interactions considered:

"The 13C NMR lineshape of [2-13C]sodium acetate has features which mainly originate from 13C chemical shift anisotropy (CSA) (typ. ~1.5 kHz at our magnetic field of 7.05 T) and 1H-13C dipolar couplings (typ. -22.7 kHz) that are affected by possible methyl group rotation. Since the 13C CSA is negligible with respect to the 1H-13C dipolar couplings, it is assumed that the 1H-13C dipolar couplings play the key role in the 13C NMR lineshape of [2-13C]sodium acetate."

Is this splitting only seen in methyl groups? Do these methyl groups have to rotate freely all the way down to sample temperatures near 1.2 K? Is that the case for methyl groups in acetate? Do you see similar effects in molecules such as gamma picoline that are known to have very low rotation barriers? If the methyl rotation in acetate is frozen, why are the methyl signals in acetate any different from those of other rigid chemical moieties like CH2 groups? You suggest that similar effects can be observed in molecules "such as [1- 13C]sodium formate", although there are no methyl groups in formate.

We have only seen such interesting lineshapes, *i.e.*, ones with similarly pronounced features, for [2-13C]acetate thus far. Other 13C-labelled methyl groups, such as gamma-picoline, and 13C-labelled methylene groups might also exhibit exotic spectra under our experimental *d*DNP conditions, and it is also possible that such effects could be observed in [1-13C]formate, if indeed one of the main requirements is the presence of a strong HC dipolar coupling. However, we have not yet investigated other suitable molecular candidates. To our knowledge, the observed asymmetry does not require methyl group rotation, and only a strong HC dipolar coupling. Particularly fast methyl group rotation is likely to average HC dipolar couplings and is likely to work against the phenomena observed here. As can be seen from J.-N. Dumez et al., *J. Phys. Chem. Lett.* **2017**, 8, 3549-3555, quantum rotor induced polarization (QRIP) phenomena are observed for the methyl group of acetate, which suggests that these groups rotate to some extent at low temperatures in DNP juice.

Can you explain your observation "where the [proton] polarization is higher, the peak intensities become more equal"? Can you explain why "[proton] polarizations (...) were observed to decrease linearly with increasing 13C peak asymmetries"? As you wrote, this behaviour is opposite to what was observed by Mammoli et al. and by Aghelnejad et al. It seems that polarisation and asymmetry should increase together.

The phenomenon at hand is related to the influence which the 1H polarization has on the 13C lineshape. When the 1H polarization is low a single peak is observed in the 13C NMR spectrum, which indicates a high asymmetry according to the definition given in our manuscript. In the opposite case, *i.e.,* when the 1H polarization is high two peaks are observed in the 13C NMR spectrum, which indicates a low asymmetry. Looking at the 13C NMR spectra acquired at the CP contacts in our experiment, at which point the 1H polarization has reached a constant value whilst the 13C NMR signal continues to grow, it is observed that there is minimal distortion to the 13C lineshape, indicating that it is the 1H polarization which is mostly responsible for this phenomenon. It is indeed an interesting observation, and one which goes against the rest of the literature surrounding this field. We felt that it was worth reporting, even though this phenomenon is not completely understood yet. There may also be other ways to interpret the data, but our current approach is intentionally one of the most simplistic ways we have found so far.

What do you expect to see in the presence of "solid-state methyl group AE population imbalances at low temperatures"?

We were simply suggesting that if a fully deuterated DNP solvent was to be used, we may be able to see changes in the 1H spectra of [2-13C]acetate as a function of the microwave irradiation period, and hence 1H polarization, which might reveal information about the build-up of AE population imbalances. The manuscript will be amended to make this point clearer.

For practitioners of DNP, it would be nice to know more details about how you determined the "power of ca. 80 ***P****μw = 125 mW at the output of the microwave source and ca.* ***P****μw = 30 mW reaching the DNP cavity (evaluated by monitoring the helium bath pressure.)" Is the first number given by the manufacturer of the microwave source? How did you convert pressure changes into mW? How do you calibrate this empirical relationship?*

125 mW is given by *VDI* (our microwave source provider). 30 mW was determined by comparison with the heating from a resistor in the bath and calibrating how much the bath pressure increases vs. power. In practice, the measurement was performed as follows:

- The variable temperature insert (VTI) was filled with liquid helium and pumped down to 0.65 mbar, corresponding to 1.2 K.
- The change of pressure when turning on a resistive heater or the microwave source for 120 s was monitored. The pressure plateaus after approximatively 60 s.
- The pressure difference between the base pressure and that under the effect of the resistive heater or the microwave irradiation ΔP is calculated.

All measurements were performed ensuring that the liquid helium level in the VTI was not varying more than a few centimetres: the microwave cavity was immersed under 5-10 cm of liquid helium. The measurements performed using the resistive heater with power P_{heater} are used to plot a calibration curve P_{heater} vs. ΔP with slope a. The deposited microwave power in the cavity is then obtained by computing $P_{\text{microwave}} = a\Delta P$. This information will be added to experiments section of the main text.

The statement "the 1H and 13C [transverse] relaxation time constants in the presence of an rf-field are extended by orders of magnitude" seems a bit exaggerated. Bornet et al. have shown experimentally that T_1rho can be extended by a factor 5 or so when the microwaves are switched on.

Thank you for pointing this out to us. We will make this amendment to the manuscript.