Chemical Communications

Electronic Supplementary Information

Detection of quadrupolar nuclei by ultrafast 2D-NMR: exploring the case of deuterated analytes aligned in chiral oriented solvents

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- Comment on the sensitivity considerations.

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Figure S1. Conventional ^{2}H-{^{1}H} δ-resolved 2D map of **1** dissolved in PBLG/CHCl$_3$ and recorded at 303 K.

Figure S2. Conventional δ-resolved 2D map of **1** manipulated to be formally identical to the ADUF 2D map.

Figure S3. ^{2}H-{^{1}H} 1D spectrum of **2** dissolved in PBLG/CHCl$_3$ and recorded at 303 K.

Figure S4. Conventional ^{2}H-{^{1}H} δ-resolved 2D maps of **2** without or with carbon-13 decoupling in F_1 and F_2 dimensions.

FURTHER COMMENTS

i) Comment on the QUOSY 2D experiments.

From the spectral viewpoint, it can be remarked that the ADUF 2D maps are formally identical to two conventional QUOSY experiments: i) the δ-resolved 2D experiments after reversing of F_2 spectral dimension (by Topspin software) followed by a 90° clockwise rotation of the map; ii) the tilted Q-COSY 2D experiments. In the former, the ^{2}H quadrupolar interaction is refocused during the t_1 dimension (quadrupolar echo) while for the latter, the quadrupolar doublets are simply removed by the tilt processing.

ii) Comment on the sensitivity considerations.

Signal-to-noise ratio (SNR) measurements were performed for sample **1,** so that potential users of this methodology can figure out what would be the sensitivity of the method on their own system:

-t he SNR measured on the deuterium signals on $C_{5,}$ for the ADUF spectrum of Fig. 2, is equal to **150** in a single scan.

- the SNR for the same signals on the 1D ^{2}H spectrum is 2450 when 8 scans are added. It would be equal to **870** in a single scan.

These results show that there is a sensitivity loss by a factor *ca*. 6 between the 1D and the ADUF 2D spectra. This is a well-known limitation of UF experiments, arising from many factors (J-modulation, translational diffusion, but above all the large receiver bandwidths that need to be applied due to the acquisition in the presence of gradients).

Sample **1** was prepared with 100 mg of solute. Assuming a limit of detection for a SNR of 10, this means that with our hardware (700 MHz with cryoprobe) we should be able to go down to 15 mg of ^{2}H labeled compound detectable in a single-scan experiment. In addition, UF experiments can be averaged, leading to a sensitivity increase of a factor $NS^{1/2}$, NS being the number of scans. Assuming, for instance, that experiments are repeated every 3 seconds for 10 minutes (a duration above which conventional 2D NMR would probably become more interesting), we would be able to detect as low as 1 mg of labeled compound in 10 minutes.

Obviously, detecting natural abundance ^{2}H with the ADUF method is not possible, yet. However promising perspectives in this direction could arise from the combination of UF 2D NMR with hyperpolarization techniques capable of boosting the nuclear polarization by orders of magnitude.

FURTHER FIGURES

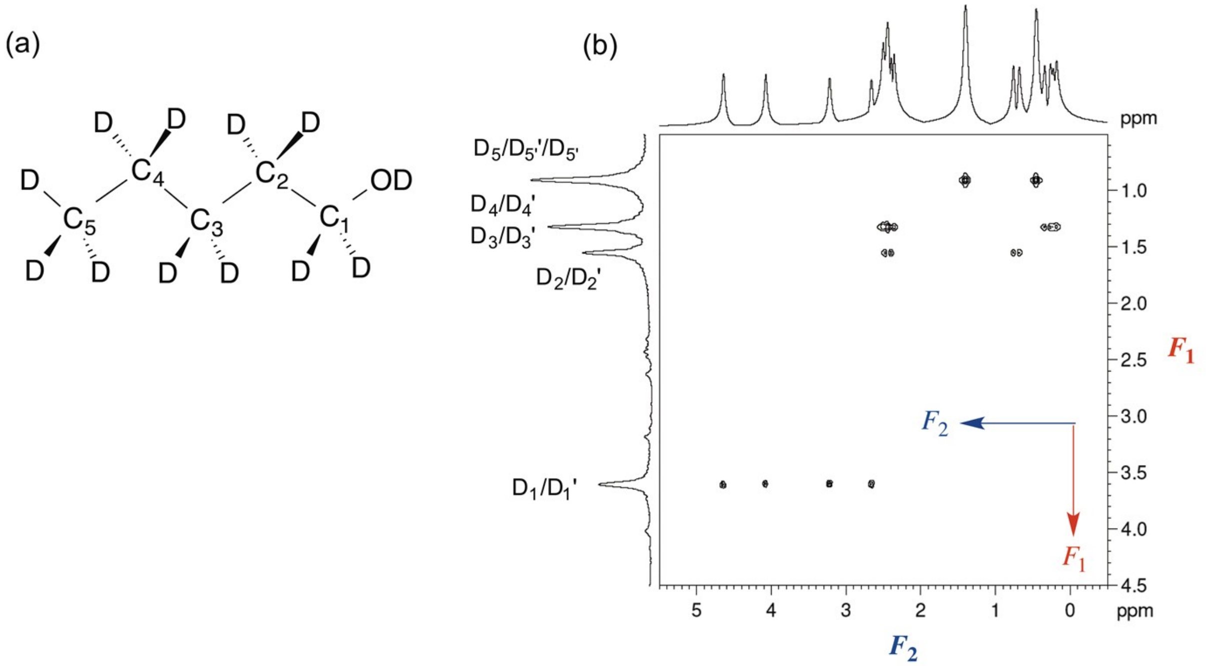

Figure S1. (a) Structure of pentan-1-ol-d$_{12}$. (b) Conventional 107.4 MHz ^{2}H-{^{1}H} δ-resolved 2D map of **1** dissolved in PBLG/CHCl$_3$ and recorded at 303 K in 19 min. The 2D spectrum was recorded using a matrix of 1400 (t_2) × 128 (t_1) data points and 8 scans for each t_1 increment. Proton nuclei are decoupled during the experiment to remove residual HD couplings. Zero-filling to 2k × 2k data point was applied. A Lorentzian filtering (LB = 1.5 Hz) was applied in both spectral dimensions. On the F_1 and F_2 axes are shown the spectral 2D projections. Note the significant broadening of lines due to the magnitude mode processing of the data.

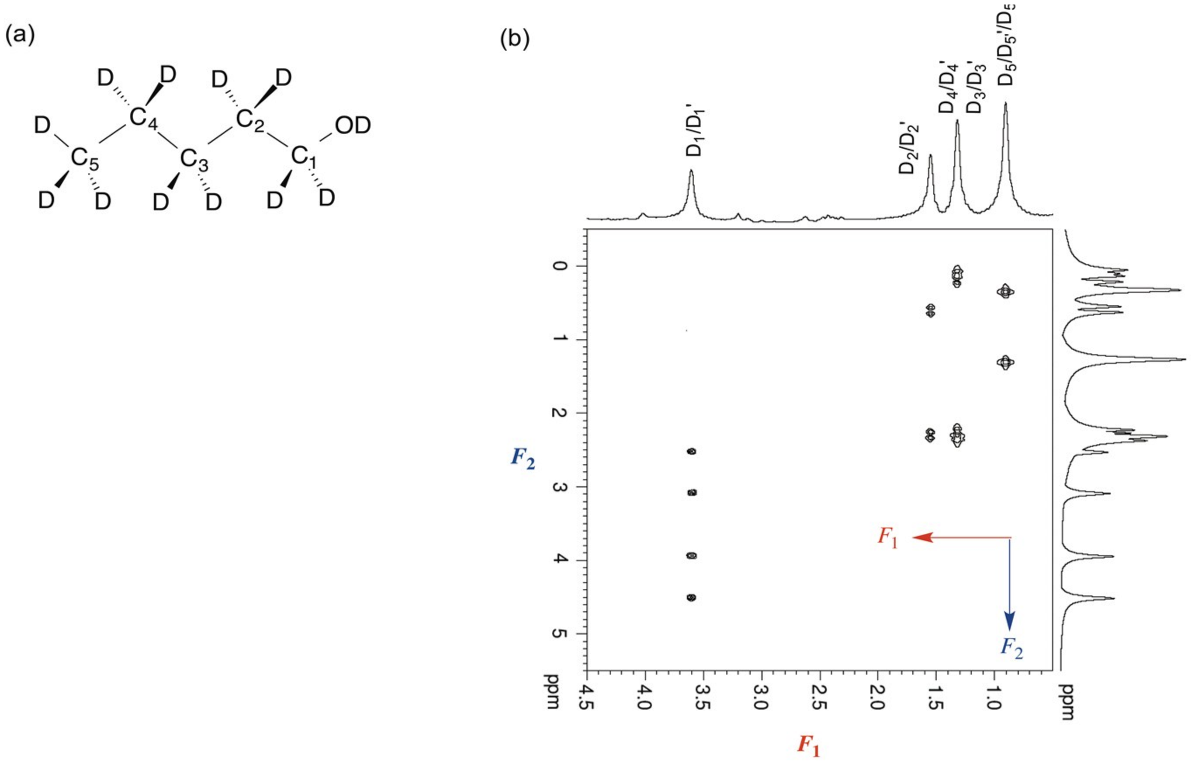

Figure S2. (a) Structure of 1-pentanol-d$_{12}$. (b) Conventional δ-resolved 2D map (same data as **Figure S1**) after reversing the F_2 spectral dimension (by the topspin software) followed by a 90° clockwise rotation of the map. Under this presentation, the map obtained is identical to that shown in **Figure 1** of the article and associated to the ADUF 2D experiment.

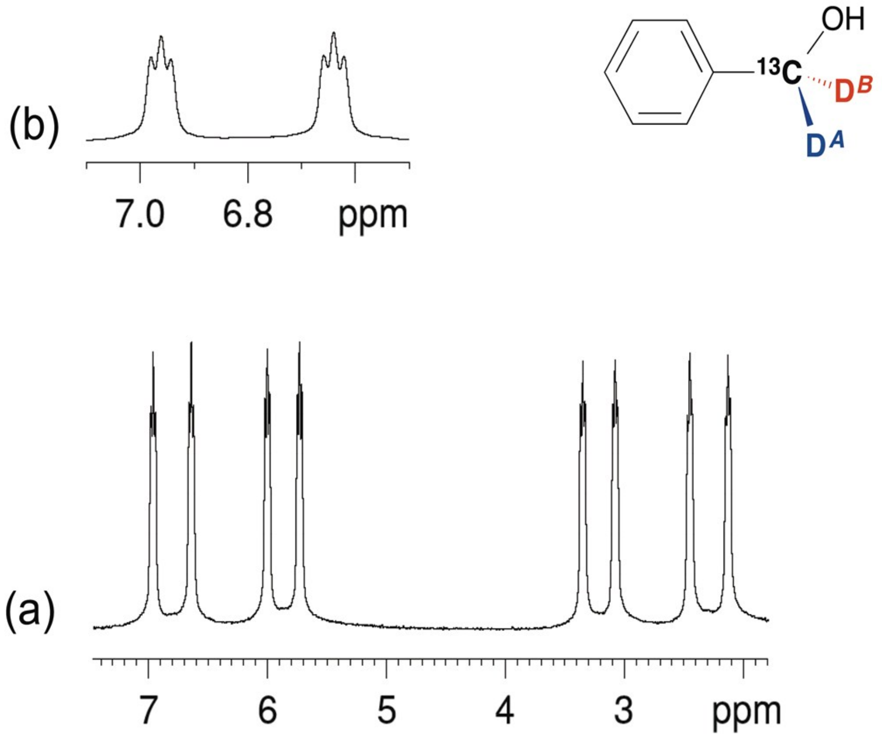

Figure S3. 107.4 MHz ^{2}H-{^{1}H} 1D spectrum of **2** dissolved in PBLG/$CHCl_3$ and recorded by adding 8 scans at 303 K. The further sub-spectral patterns observed on each component of quadrupolar doublets originate from the intramethylene geminal DD (dipolar and scalar) coupling.

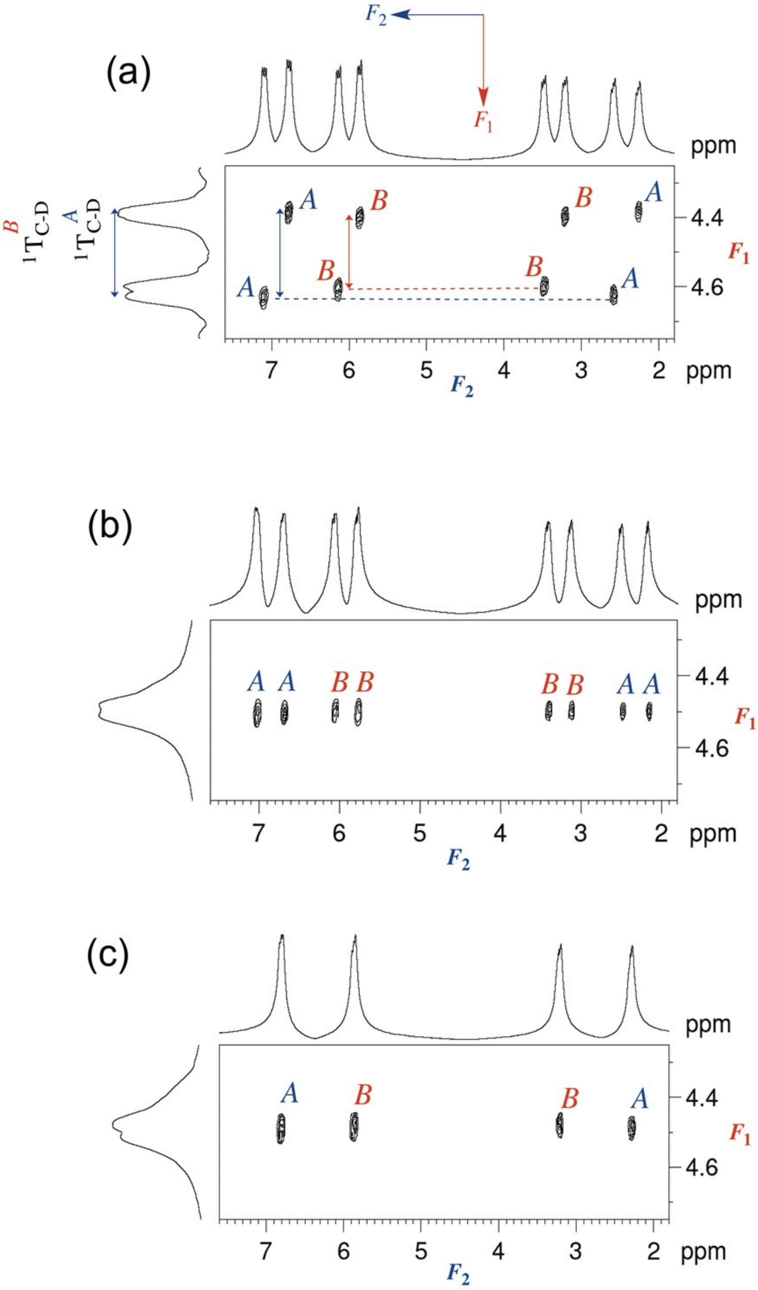

Figure S4. Conventional 107.4 MHz ^{2}H-{^{1}H} δ-resolved 2D maps of **2** without carbon-13 decoupling (a), with carbon-13 decoupling in F_1 dimension (b) and with carbon-13 decoupling in F_1 and F_2 dimensions. The 2D spectra were recorded using a matrix of 1400 (t_2) × 128 (t_1) data points and 8 scans for each t_1 increment, leading to an experimental time of 19 min. Proton nuclei are decoupled during the 2D experiment to remove possible long-range residual HD couplings. Zero-filling to 2k × 2k data point was applied. A Lorentzian filtering (LB = 1.5 Hz) was applied in both spectral dimensions. On the F_1 and F_2 axes are shown the spectral 2D projections. Note the significant broadening of lines due to the magnitude mode processing of the data (compared to 1D spectrum of **Figure S3**). On map (a), the spectral resolution in F_1 dimension allows to separate the dipolar doublets despite the magnitude mode displaying.