Two-dimensional ^{1}H DQ CRAMPS NMR: Very-High Resolution Identification of Proton-Proton Proximities

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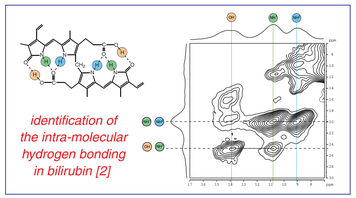
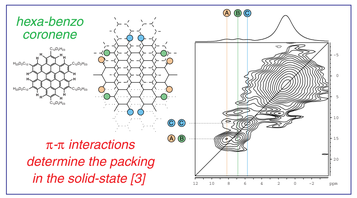
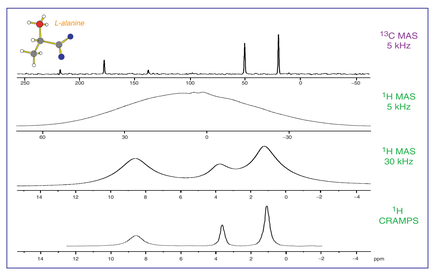
Introduction

The information about *proton-proton proximities* provided by ^{1}H-^{1}H *double-quantum* (DQ) magic-angle spinning (MAS) spectra has provided much insight into the *hydrogen-bonding* and aromatic π-π *interactions* controlling the solid-state structures adopted by various materials [1].

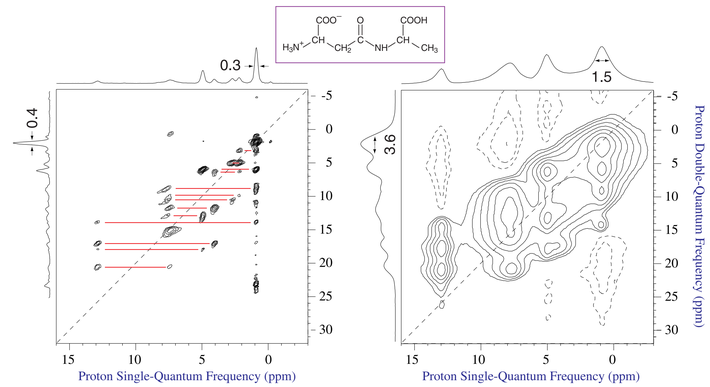




Considerable resolution enhancement in ^{1}H spectra as compared to fast MAS alone can be obtained by combining MAS with the application of carefully synchronized multiple-pulse sequences (e.g., PMLG [4] or DUMBO [5]) in the so-called CRAMPS approach [6].



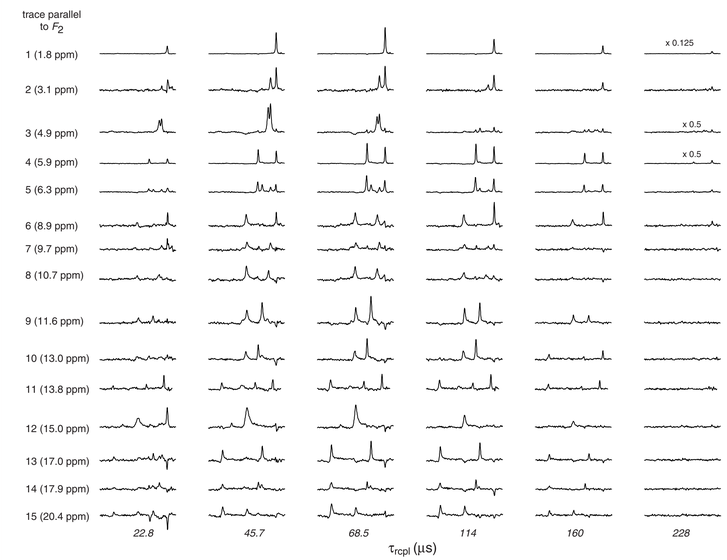
^{1}H-^{1}H DQ CRAMPS (12.5 kHz) versus ^{1}H-^{1}H DQ MAS (30 kHz)



ν_1 = 87 kHz (POST-C7), 100 kHz (DUMBO)
τ_{rcpl} = 68.6 µs (3 basic POST-C7 elements)
Δt_1(States) = 96 µs (3 eDUMBO-1_{22} cycles)
320 t_1 slices, 16 transients co-added,
recycle delay = 2 s (expt. time = 170 mins)
In t_2, acq window = 5 µs,
DUMBO-1 block = 96 µs, max. t_2 = 16.4 ms
scaling factor:
0.58 (eDUMBO-1_{22}), 0.50 (DUMBO-1)

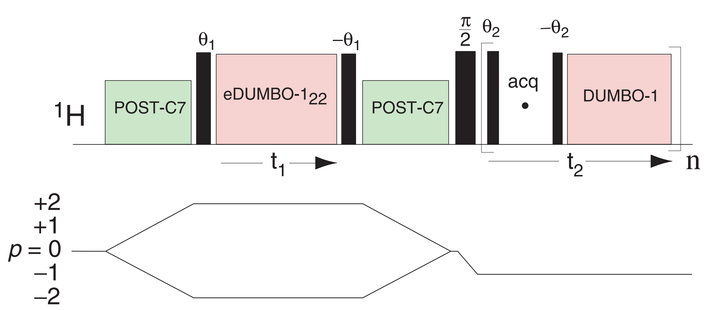
ν_1 = 100 kHz
τ_{rcpl} = 33.3 µs (1 τ_R, BABA)
Δt_1(States) = 33.3 µs
48 t_1 slices, 16 transients co-added,
recycle delay = 1.5 s

The Dependence upon the DQ Recoupling Time



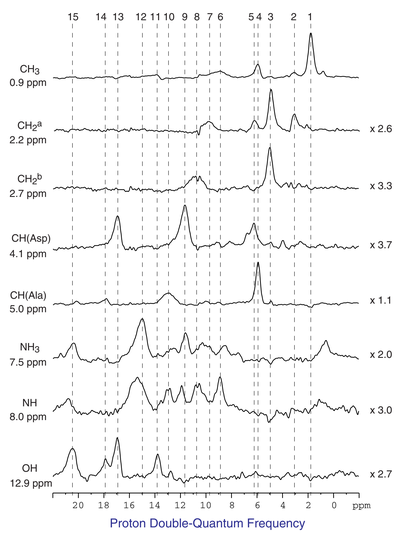
^{1}H-^{1}H Double-Quantum CRAMPS NMR Spectroscopy

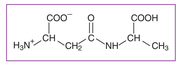
The incorporation of windowless and windowed homonuclear decoupling in the indirect (t_1) and direct (t_2) dimensions, respectively, of a two-dimensional ^{1}H DQ CRAMPS experiment has much potential to offer enhanced resolution [7,8].



Experiments were performed on a Bruker Avance 500 MHz spectrometer using a single-channel CRAMPS probe supporting a 2.5 mm rotor containing ~10 mg of sample.

Identification of Proton-Proton Proximities





DQ peaks corresponding to proton-proton proximities (under 350 pm) [9]

		sum of SQ freqs (ppm)	DQ freq (ppm)
1.	CH_3-CH_3	0.9+0.9	1.8
2.	CH_3-CH_2^a	0.9+2.2	3.1
3.	CH_2^a-CH_2^b	2.2+2.7	4.9
4.	CH_3-CH(Ala)	0.9+5.0	5.9
5.	CH_2^a-CH(Asp)	2.2+4.1	6.3
6.	CH_3-NH	0.9+8.0	8.9
7.	CH_2^a-NH_3	2.2+7.5	9.7
8.	CH_2^b-NH	2.7+8.0	10.7
9.	CH(Asp)-NH_3	4.1+7.5	11.6
10.	CH(Ala)-NH	5.0+8.0	13.0
11.	CH_3-OH	0.9+12.9	13.8
12.	NH_3-NH_3	7.5+7.5	15.0
13.	CH(Asp)-OH	4.1+12.9	17.0
14.	CH(Ala)-OH	5.0+12.9	17.9
15.	NH_3-OH	7.5+12.9	20.4
16.	CH_3-CH_2^b	0.9+2.7	3.6
17.	CH_2^b-CH(Asp)	2.7+4.1	6.8
18.	CH_3-NH_3	0.9+7.5	8.4
19.	CH_2^a-NH	2.2+8.0	10.2
20.	CH_2^b-NH_3	2.7+7.5	10.2
21.	CH(Ala)-NH_3	5.0+7.5	12.5
22.	NH_3-NH	7.5+8.0	15.5

NB: DQ peaks 16 to 22 are visible as shoulders of the 15 more intense labelled peaks
intermolecular proximities are in orange

Conclusions

For a model medium-sized molecule, the ^{1}H DQ CRAMPS experiment yields high-quality high-resolution spectra as compared to the reference fast MAS technique.

This yields access to the crowded alkyl region of DQ spectra, which was inexploitable with the standard MAS technique.

In the example given here we observed all 22 of the short range inter- and intramolecular contacts expected from the crystal structure.

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