Comparison of New 2D High Resolution Experiments for Quadrupolar Nuclei Based on STMAS Concept

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INTRODUCTION

STMAS is a technique introduced in 2000 [1] using satellite transitions (usually inner ST_1), instead of Multiple Quanta coherences (3Q/5Q). Gan found in 2003 [2] a way to eliminate the CT-CT unwanted signal by using a double quantum filter (STMAS-DQF). He also expressed the concept of DQ-STMAS, where DQ coherences (instead of ST_1) are correlated with CT.

We present experimental proofs of the DQ-STMAS concept and compare its performance (sensitivity, resolution etc...) to STMAS-DQF for several reference compounds such as $RbNO_3$, $AlPO_4$ berlinite and VPI-5.

We also introduce an original t_1-split STMAS sequence specific to 3/2 spins. Instead of splitting the t_1 evolution time between MQ and CT, we split t_1 between ST_1 and DQ coherences. t_1-split STMAS performs as well as DQ-STMAS and STMAS-DQF, concerning homonuclear broadening [3] or efficiency.

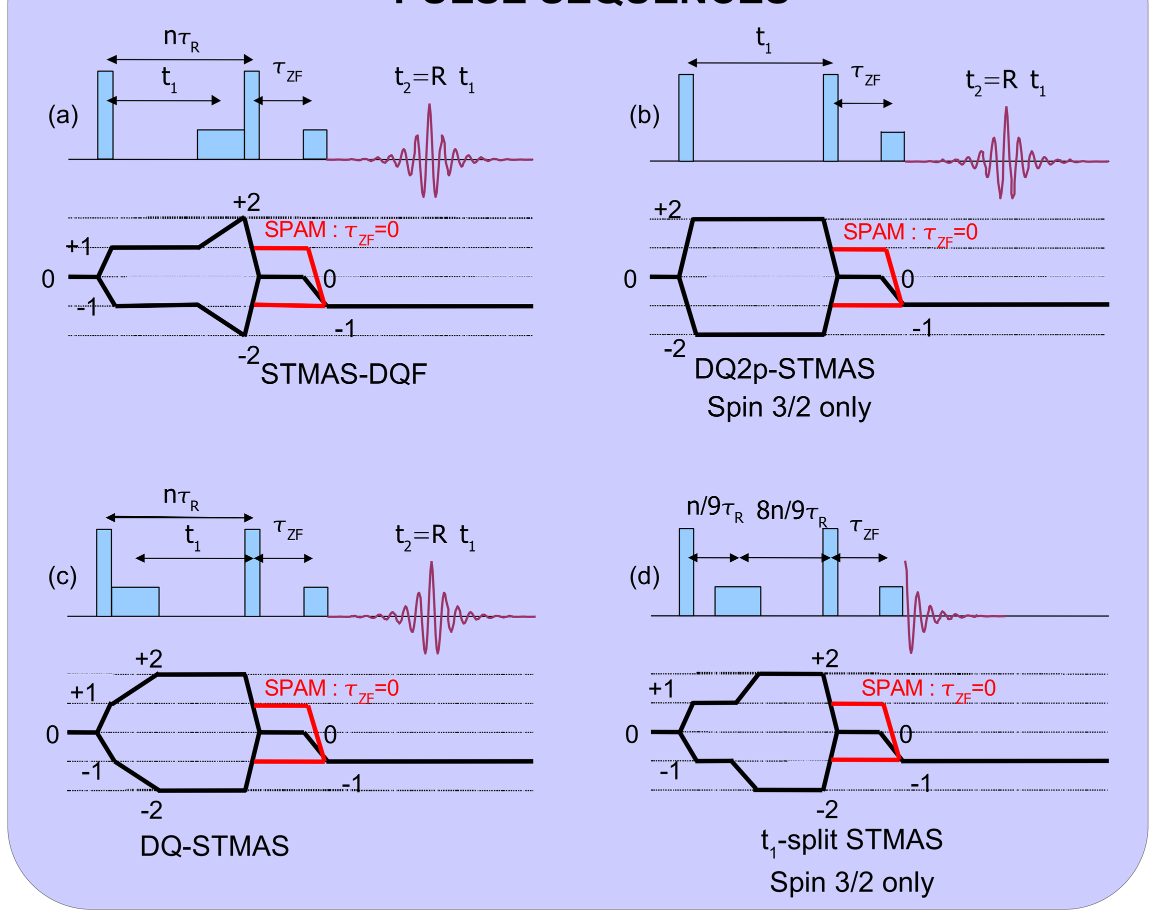
We finally show how these experiments can be combined with the SPAM technique and the sensitivity gain that can be expected.

[1] Z.H. Gan, *J. Am. Chem. Soc.* 122 **(2000)** 3242-3243.

[2] H.T. Kwak, Z.H. Gan, *J. Magn. Res.* 164 **(2003)** 369-372.

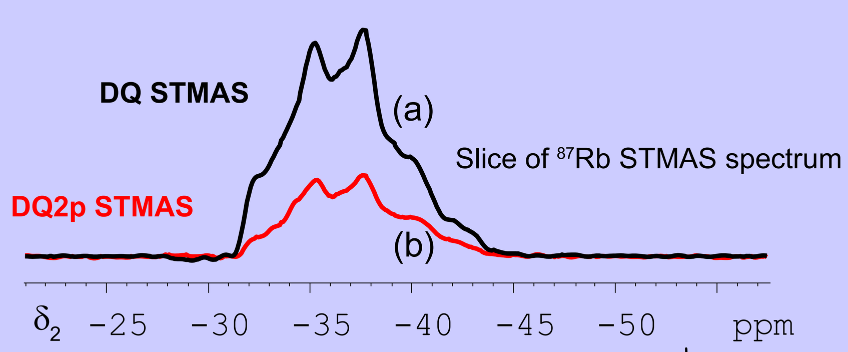
[3] J.P. Amoureux, J. Trébosc, *J. Magn. Res.* 179 (**2006**) 311-316.

PULSE SEQUENCES

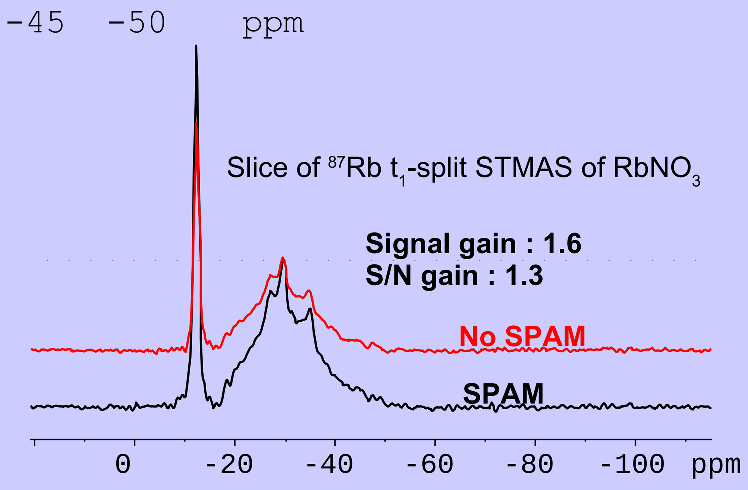


EFFICIENCY

Since they flow the same pathway, all STMAS pulse sequences, but (b), have the same efficiency. Direct excitation of DQ coherences proves to be twice less efficient than the indirect way
(note: this is not true for the reconversion pulse).



The **SPAM** technique can be applied to all STMAS sequences and produce a S/N gain of at least 1.3. This gain depends on the number of anti-echo rows that are acquired,



RESOLUTION COMPARISON

In addition to distributions (inhomogeneous broadening), in STMAS isotropic projections are affected by several parameters

- magic angle setting and spinning-speed stability,
- relaxation homogeneous effects in t_1 (T_p) and t_2 (T_{CT}),
- R ratio and p quantum level used during t_1

The magic angle has the same effect on all STMAS versions.

We have observed that T_{DQ} and T_{ST1} are often very similar. Homogeneous broadening (B) in isotropic dimension due to relaxation can be calculated with :

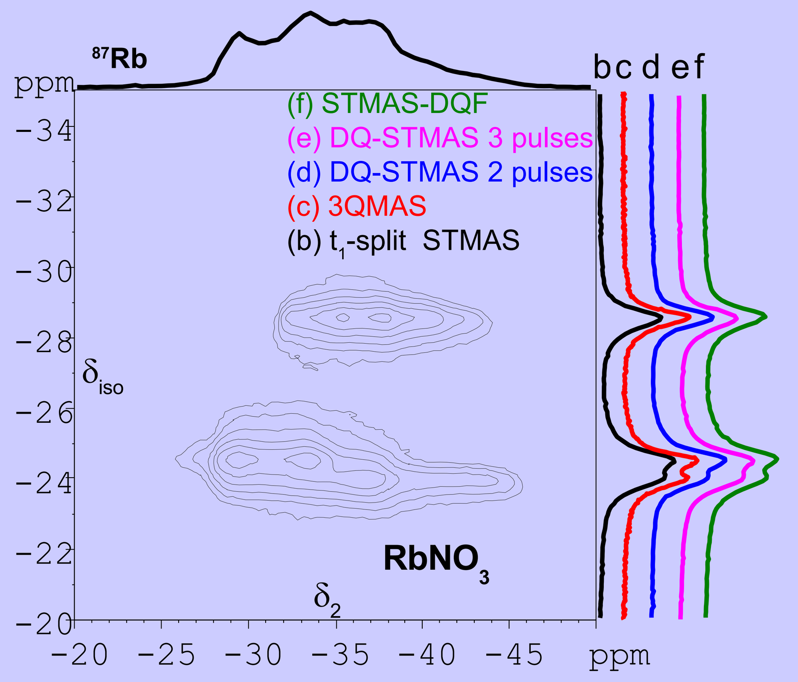
$$B=\frac{(1+R)\cdot 10^6}{\pi\,\nu_0 |R-p|\,T_{tot}} \qquad \frac{1}{T_{tot}}=\frac{R}{T_{CT}}+\frac{1}{T_p}$$

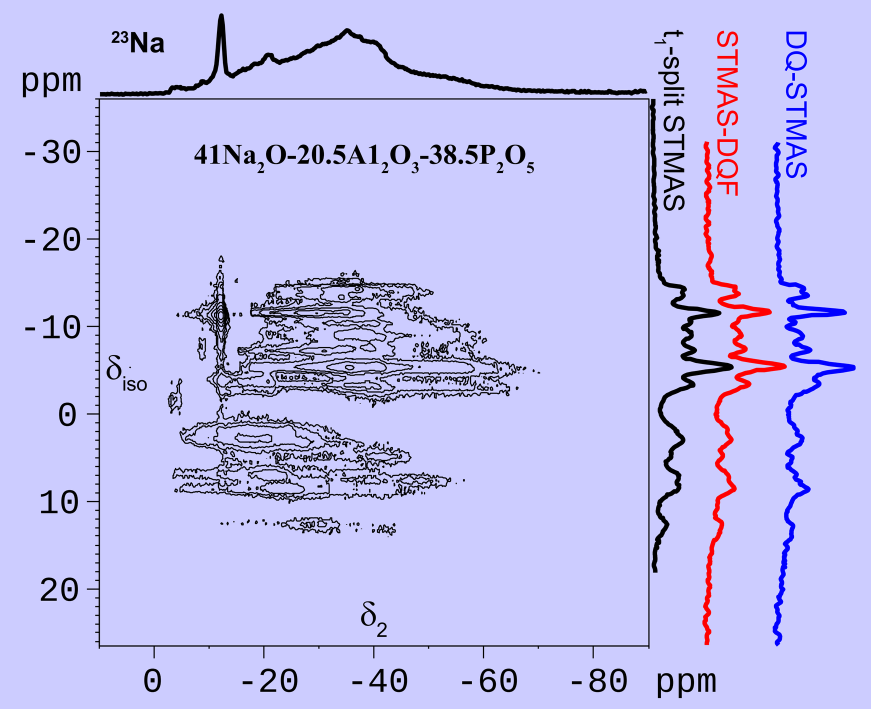
S	1D-MAS	3QMAS	5QMAS	STMAS-DQF	DQ-STMAS	t_1-split-STMAS
3/2	1	8/17		17/17	10/17	9/17
5/2	1	31/17	37/85	31/17	55/17	
7/2	1	73/17	50/85	73/17	118/17	
9/2	1	127/17	131/85	127/17	199/17	

Broadening (B), given in $10^6/\pi\nu_o T$ unit, calculated with $T_p = T_{CT}$

SPIN 3/2

In $RbNO_3$ all relation times are very large Thus all experiments have the same resolution

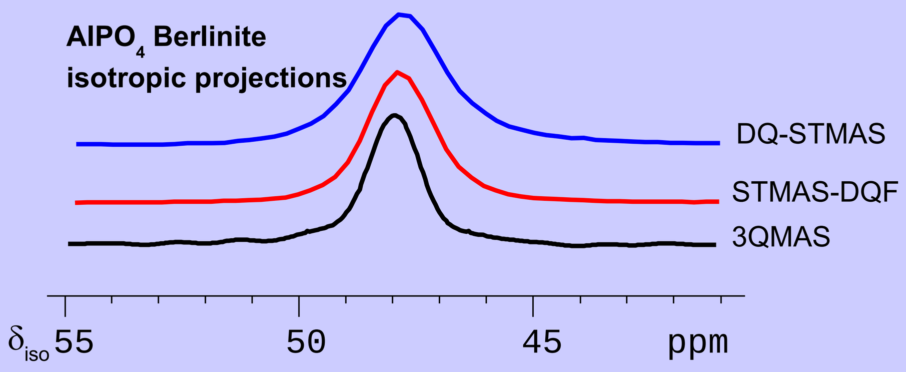




This recrystallised glass also has large T_{2s} : no difference in resolution is noticed here

Our new 800 MHz spectrometer with STMAS triple resonance probes.
Visit our web site at http://rmn800.univ-lille1.fr
(still in french sorry)

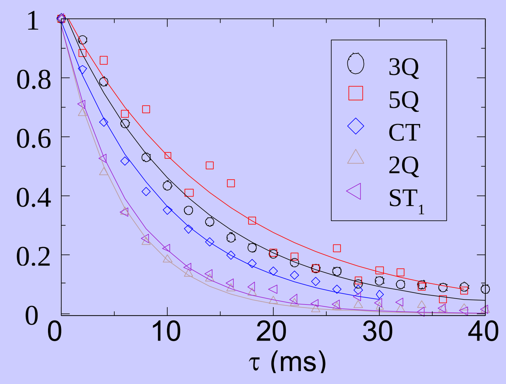
SPIN 5/2 (^{27}Al)

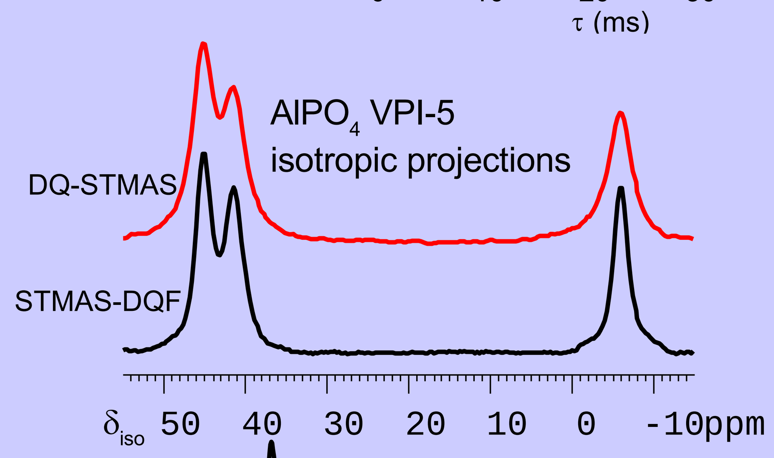


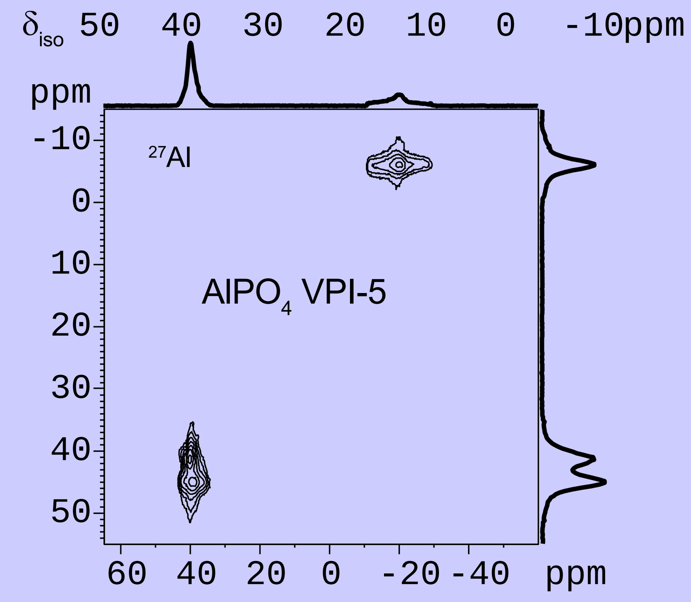
3QMAS is better resolved than STMAS-DQF due to its robustness towards magic angle and spinning speed stability, but also because ST_1 and DQ coherences have smaller T_2 than CT or 3Q coherences.

On berlinite or VPI-5, despite similar T_2 for ST_1 and DQ coherences, DQ-STMAS has unfavorable B factor (see table).

T_2 Measurements on Berlinite (**see poster P 189**)

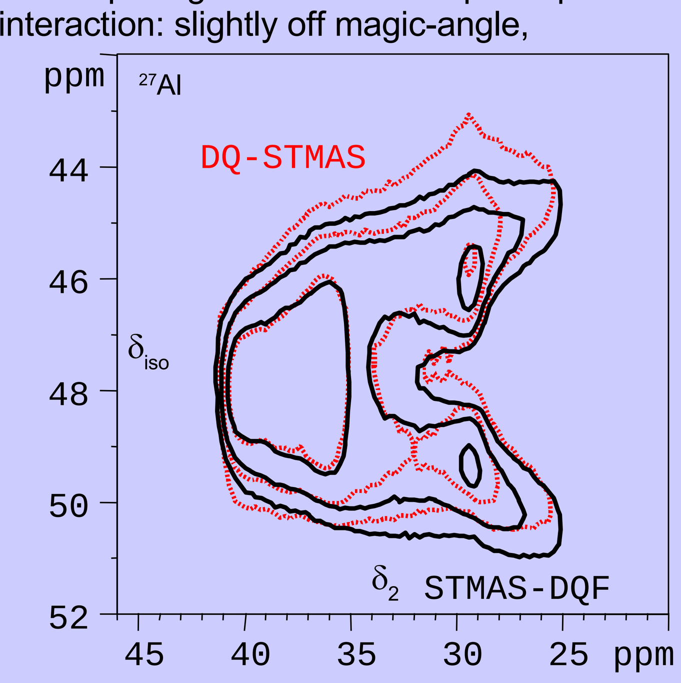






MAGIC ANGLE SETTING

DQ-STMAS or STMAS-DQF experience the same splitting due to 1st order quadrupolar interaction: slightly off magic-angle,



CONCLUSION

DQ-STMAS and STMAS-DQF have the same efficiency and constraints related to observation of satellite transition and 1st-order quadrupole interaction.
S > 3/2: due to homogeneous broadening, STMAS-DQF achieves better resolution than DQ-STMAS.
S = 3/2: DQ-STMAS has a better resolution than STMAS-DQF. In that case, t_1-split STMAS can also be a very good option (for Q-CPMG) as it balances completely echo and anti-echo in time, thus leading to very clean spectra.
SPAM concept can be applied to all these pulse sequences with a S/N gain 1.3 to 2.5, depending on the number of anti-echo registered,

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