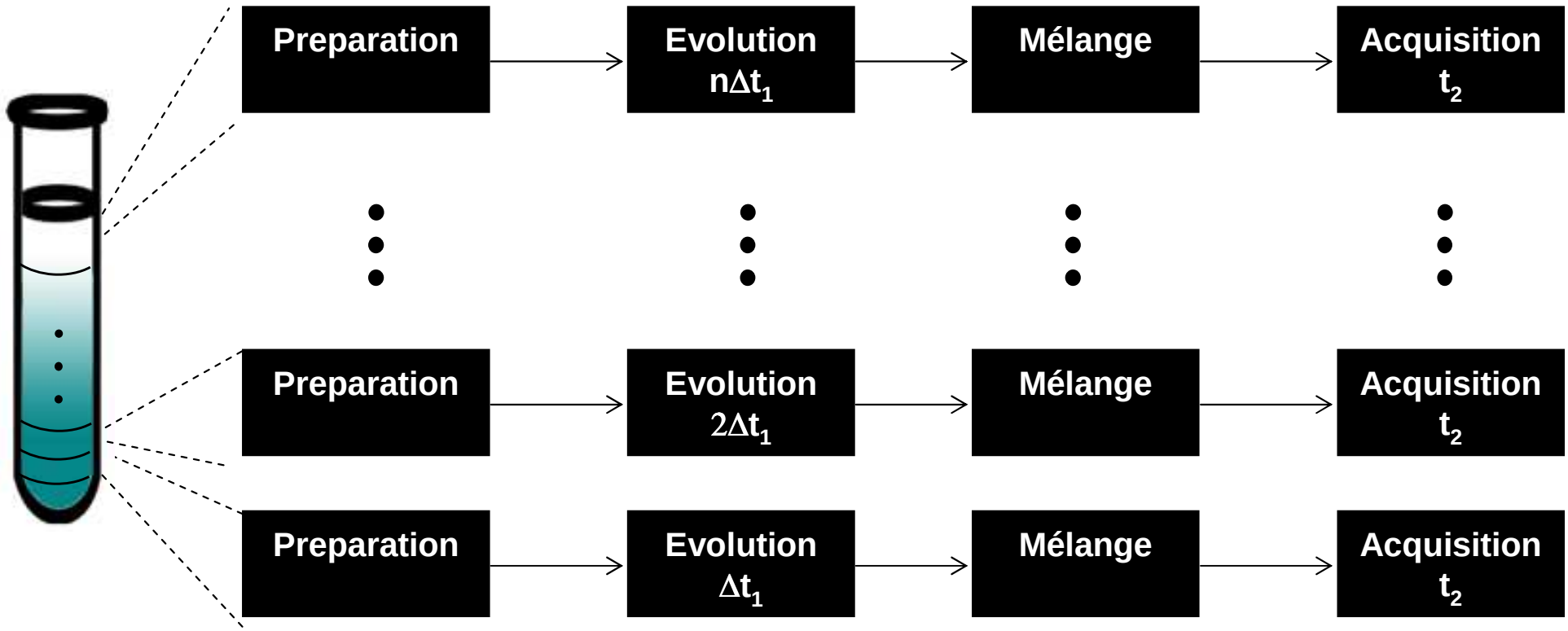
OPTIMISATION DE LA RMN 2D ULTRARAPIDE POUR L'ANALYSE STRUCTURALE DE MOLECULES ORGANIQUES

Patrick GIRAUDEAU et Serge AKOKA

CEISAM, Université de Nantes, France

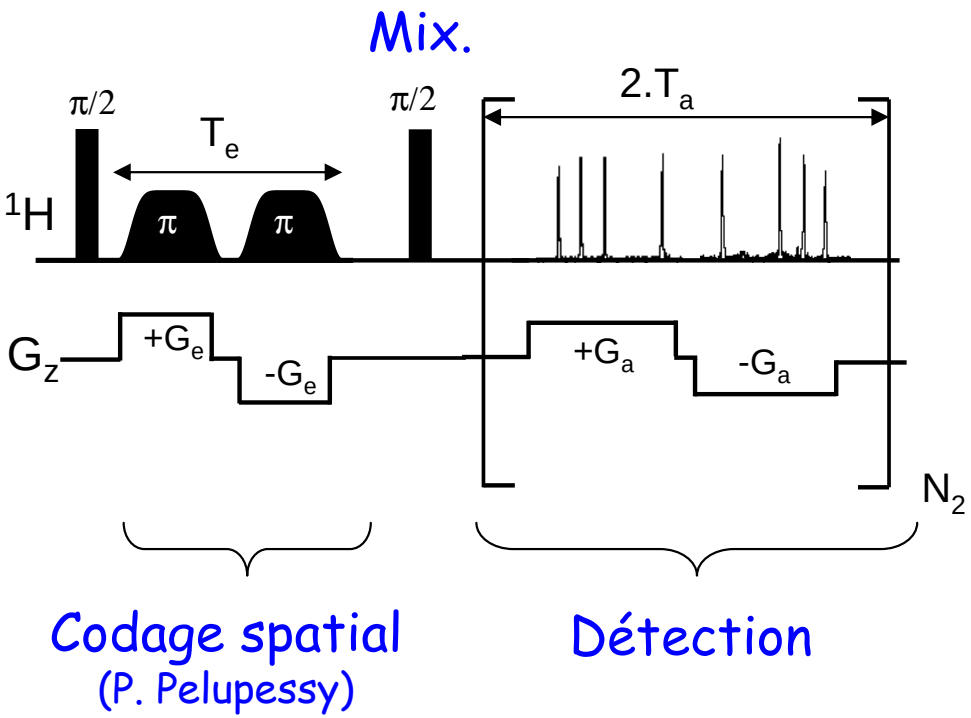
Principe

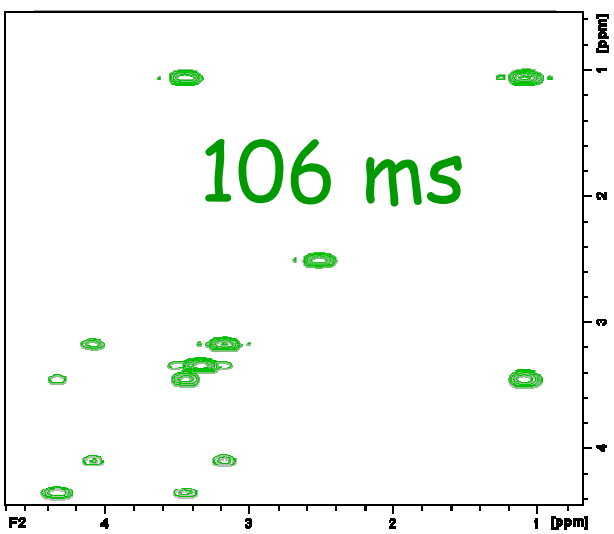


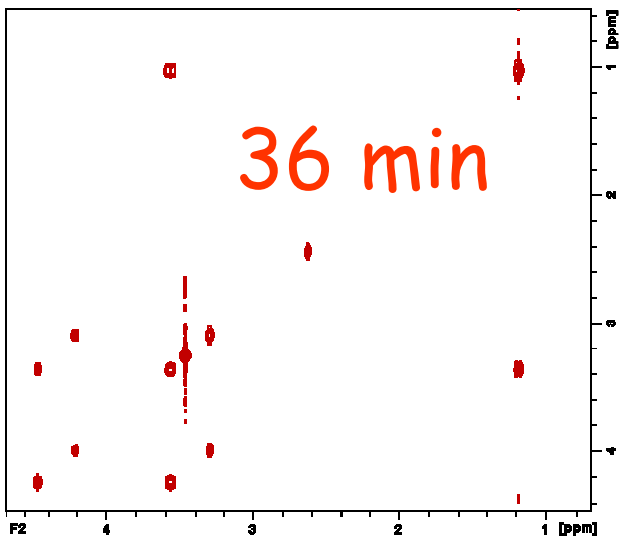
Spectre 2D en un seul scan!

L. Frydman *et al.* Proc. Natl. Acad. Sci. USA 2002, 99, 15858

Exemple – COSY Ultrarapide

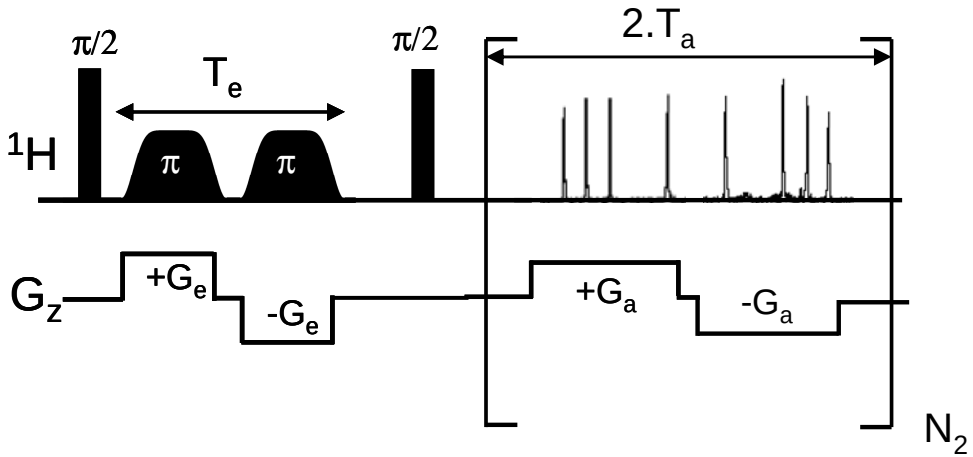






Ethanol/Methanol, 100 mM

Limites en résolution et sensibilité

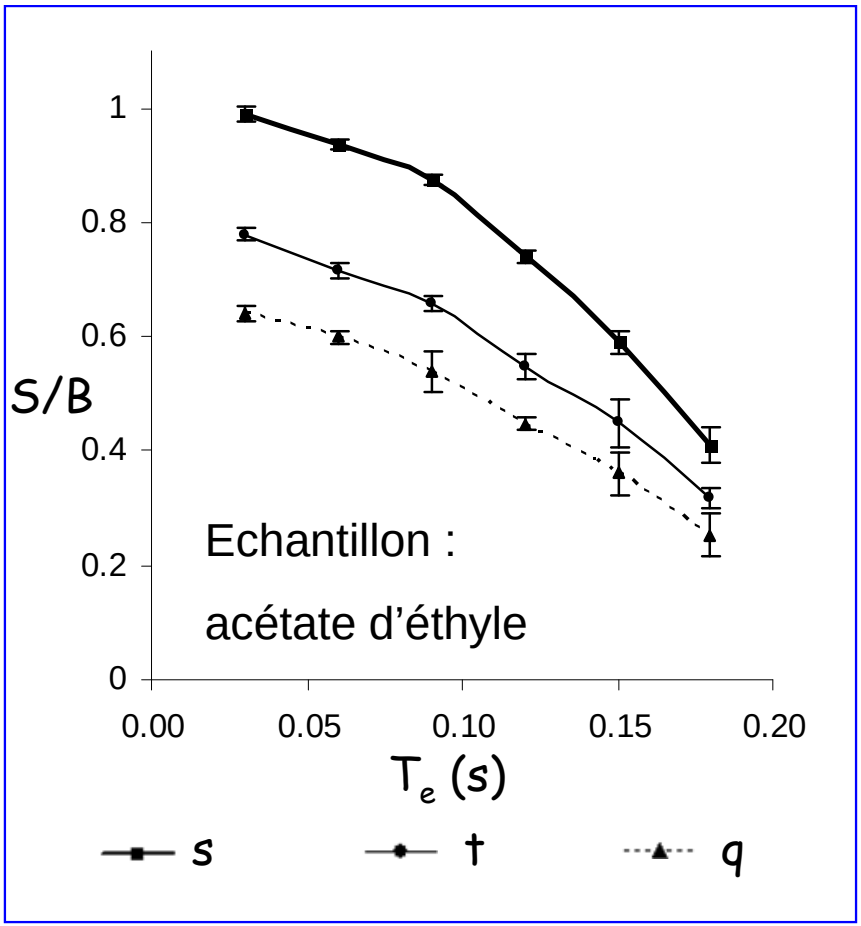


Δν: Largeur des pics dans la dimension ultrarapide

$$\Delta\nu \approx \frac{1.21}{2 \cdot T_e}$$

Solution : ↗ T_e
→ Meilleure résolution

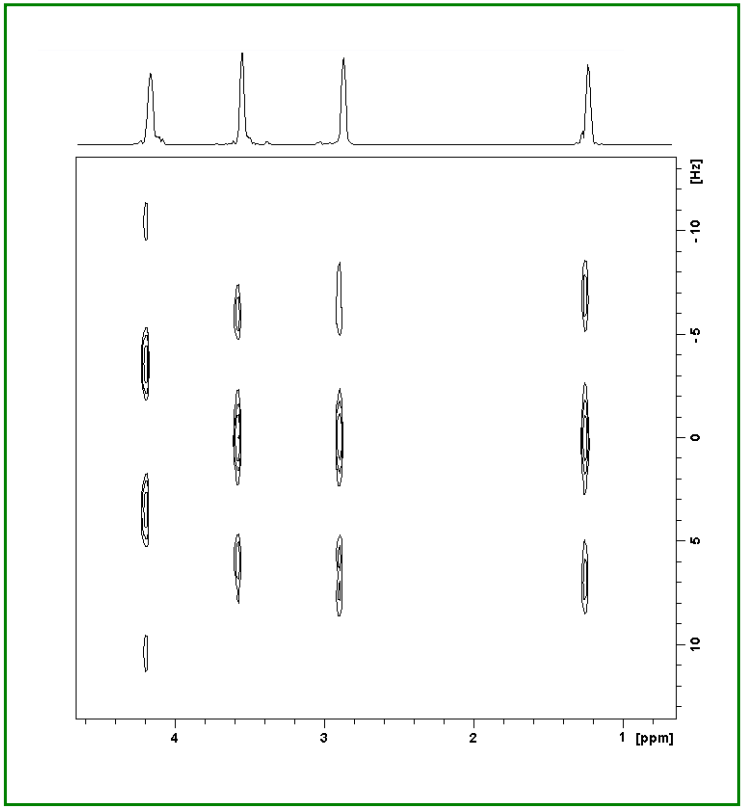
MAIS S/B ↘
(Diffusion + J-modulation)



P. Giraudeau *et al.* JMR 192 (2008)

Exemple : RMN 2D *J*-résolue ultrarapide

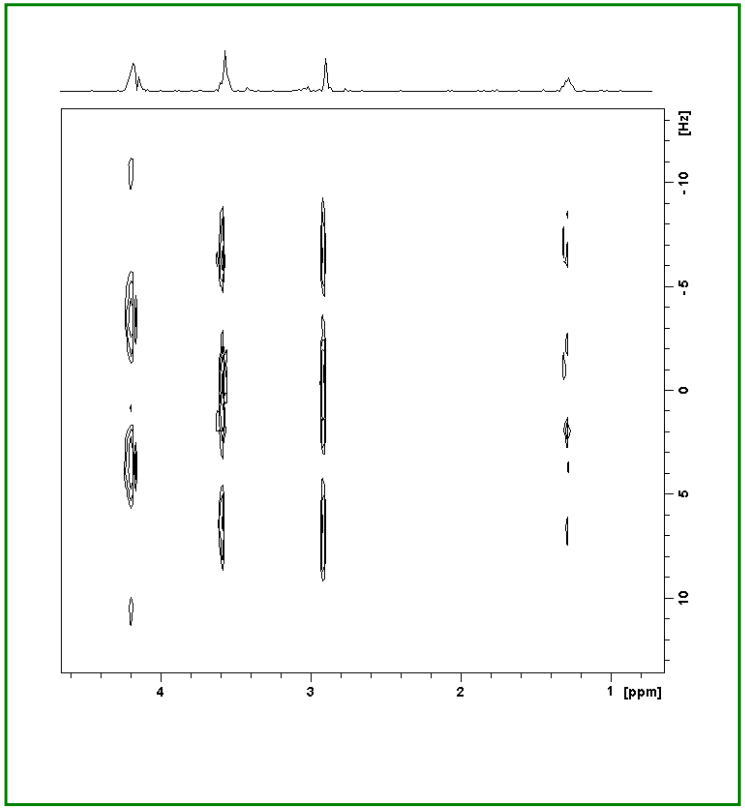
T_e = 60 ms



$\Delta\nu = 17 \pm 1$ Hz

S/B = 140 ± 15

T_e = 120 ms



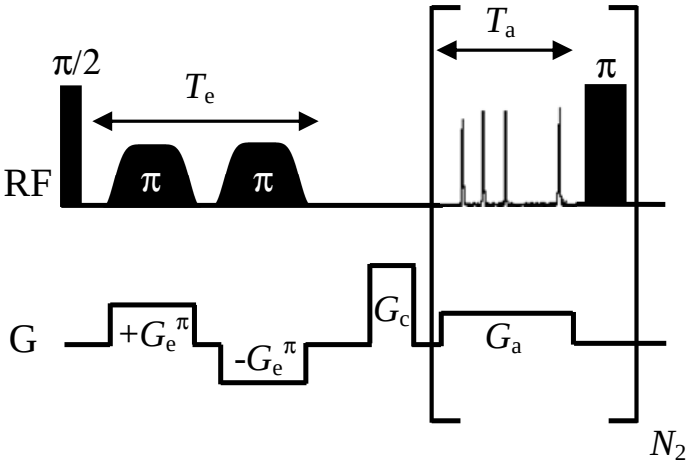
$\Delta\nu = 13 \pm 1$ Hz

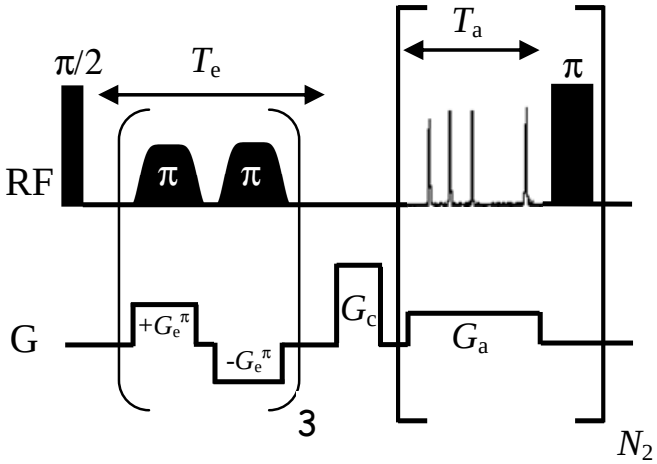
S/B = 15 ± 5

Distorsions d'intensité

P. Giraudeau *et al.* JMR 190 (2008)

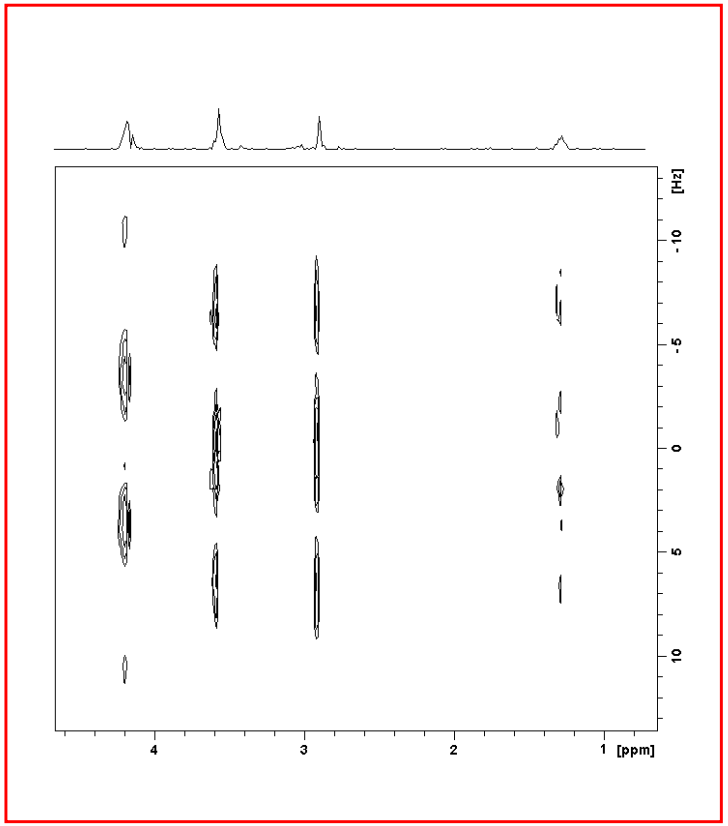
Solution : excitation multi-écho

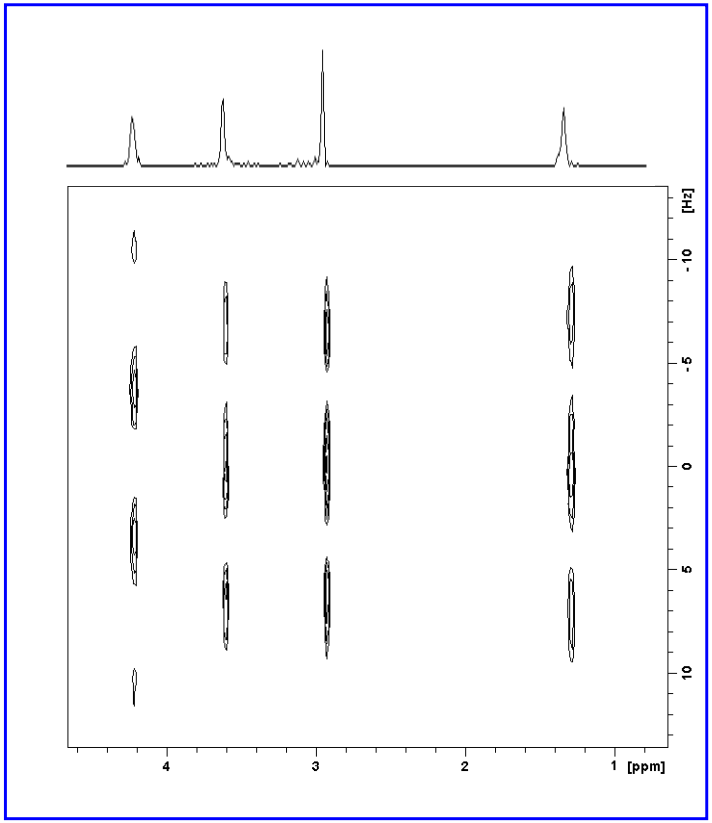




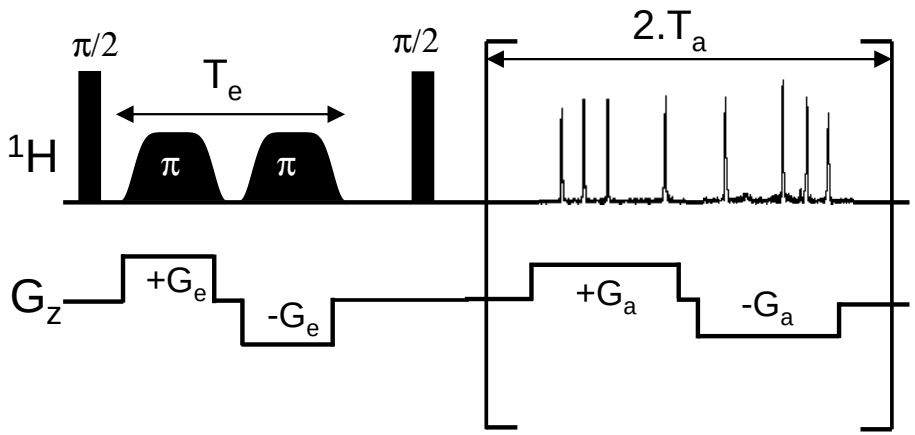
T_e = 120 ms, 2 échos

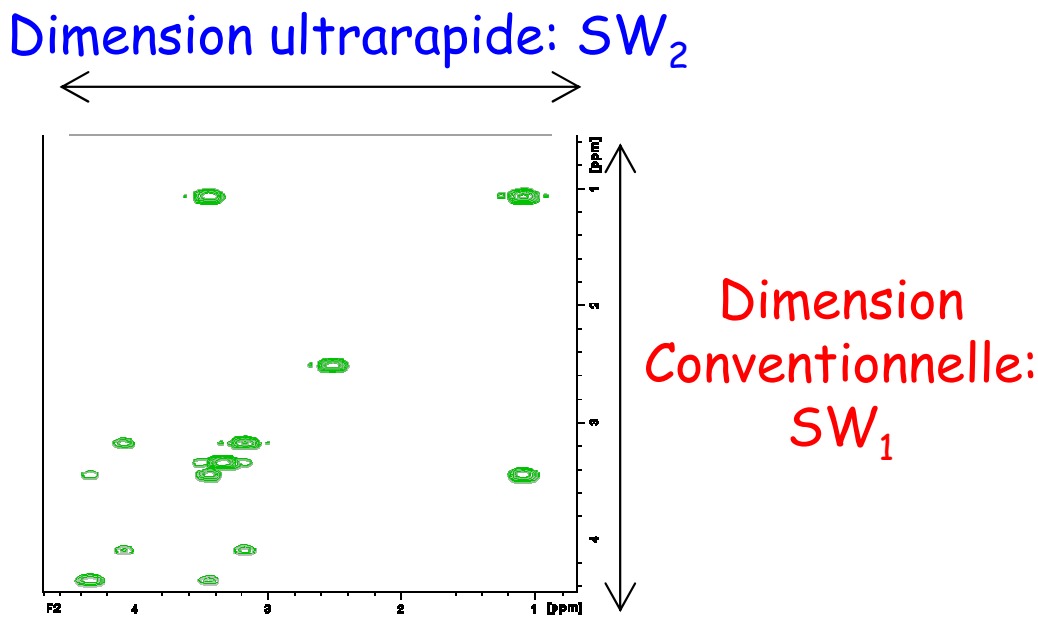
T_e = 120 ms, 6 échos





Limitations : largeur spectrale, sensibilité et résolution





Δν: Résolution (largeur des pics dans la dimension ultrarapide)

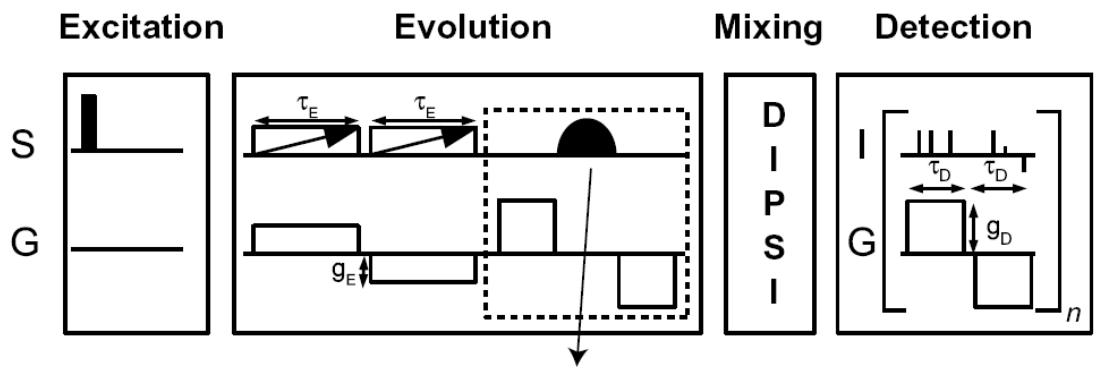
$$\gamma \cdot G_a \cdot L = \frac{2 \cdot SW_1 \cdot SW_2}{\Delta \upsilon}$$

$$S/B = \sqrt{\frac{\Delta \upsilon}{2 \cdot SW_1 \cdot SW_2}}$$

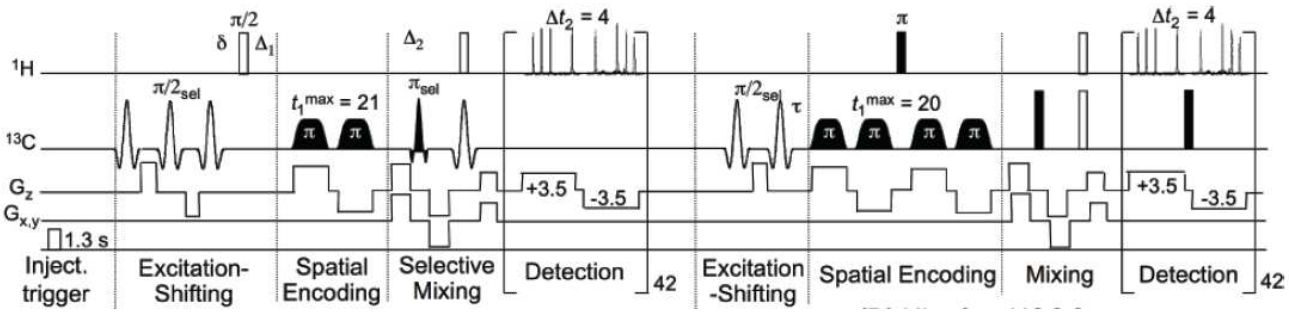
Y. Shrot *et al.* J. Chem. Phys. 2009

Pas de repliement possible dans la dimension ultrarapide ! (pas de TF)

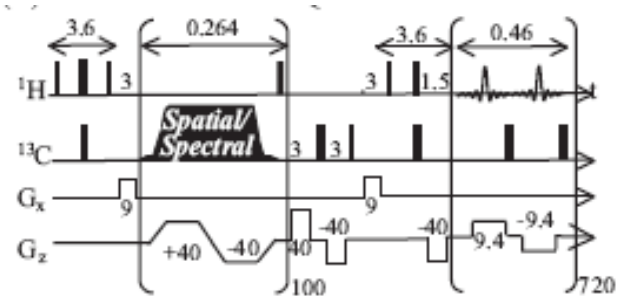
Largeurs spectrales : Solutions proposées



P. Pelupessy *et al*, JMR 2008



P. Giraudeau *et al*, JACS 2009



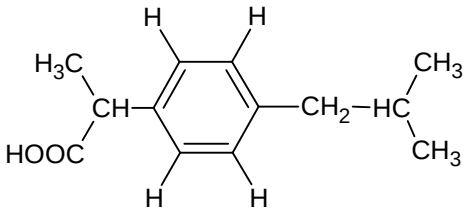
Y. Shrot *et al*, J. Chem. Phys. 2009

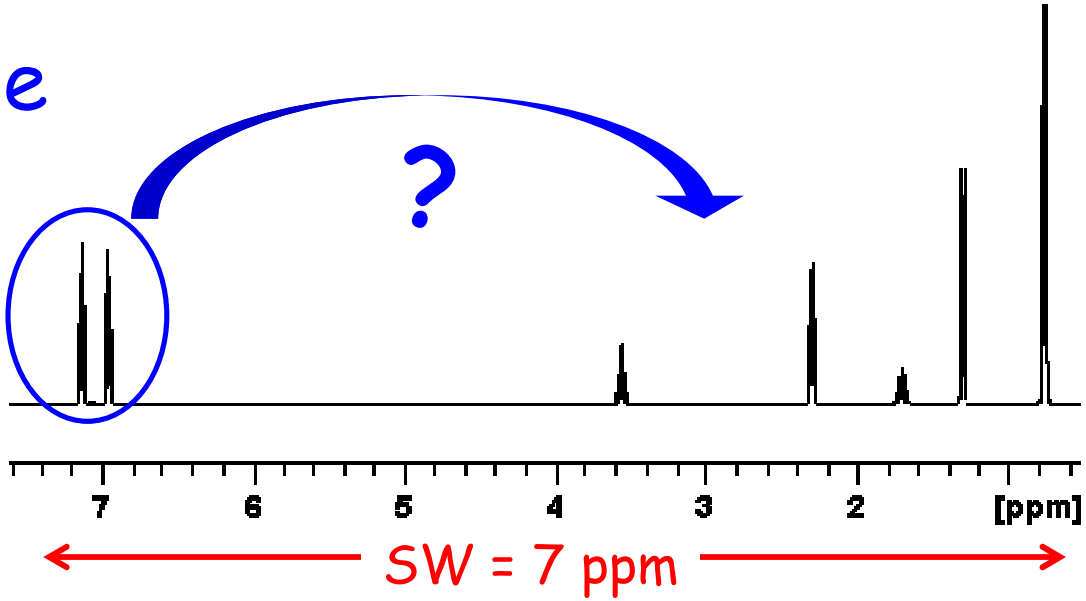
Méthodes basées sur des impulsions sélectives

Solution : “Gradient-only controled folding”

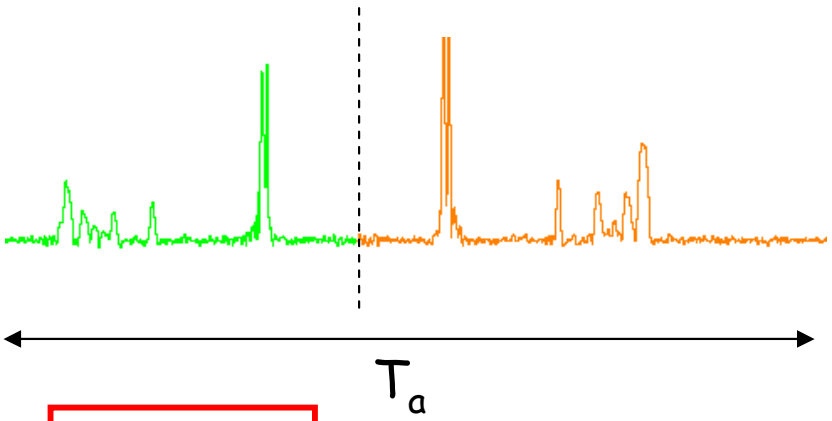
COSY-DQF ultrarapide

Ibuprofène 100 mM

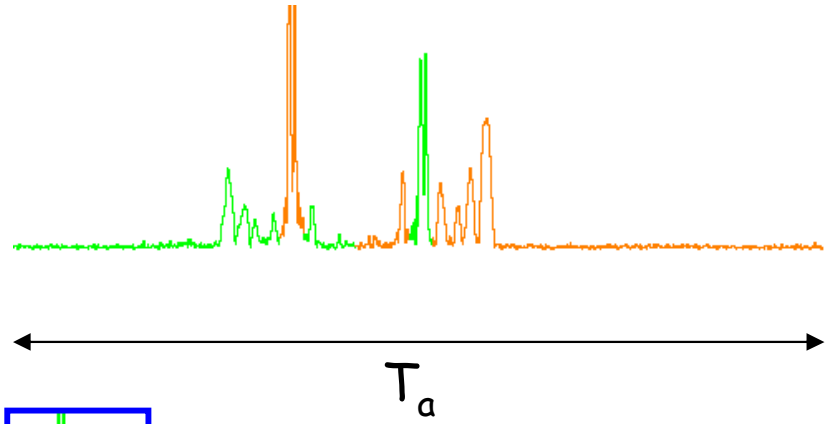


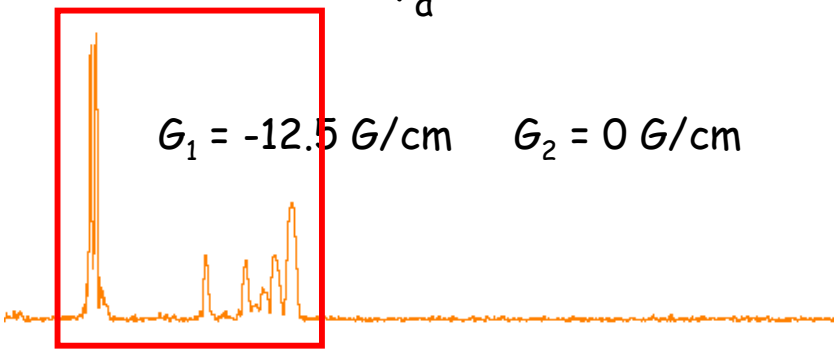


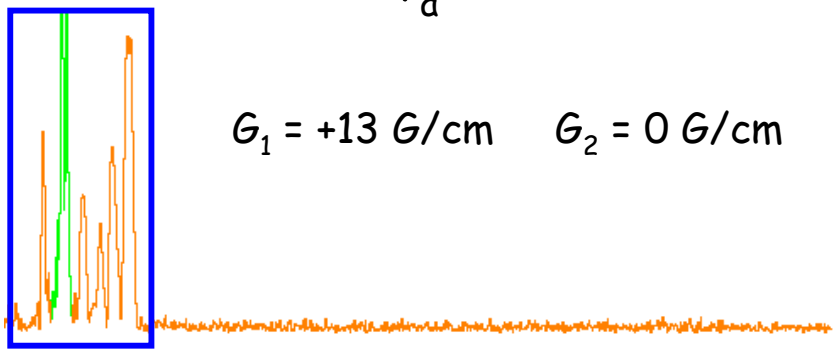
G_1 = -12.5 G/cm G_2 = -58 G/cm



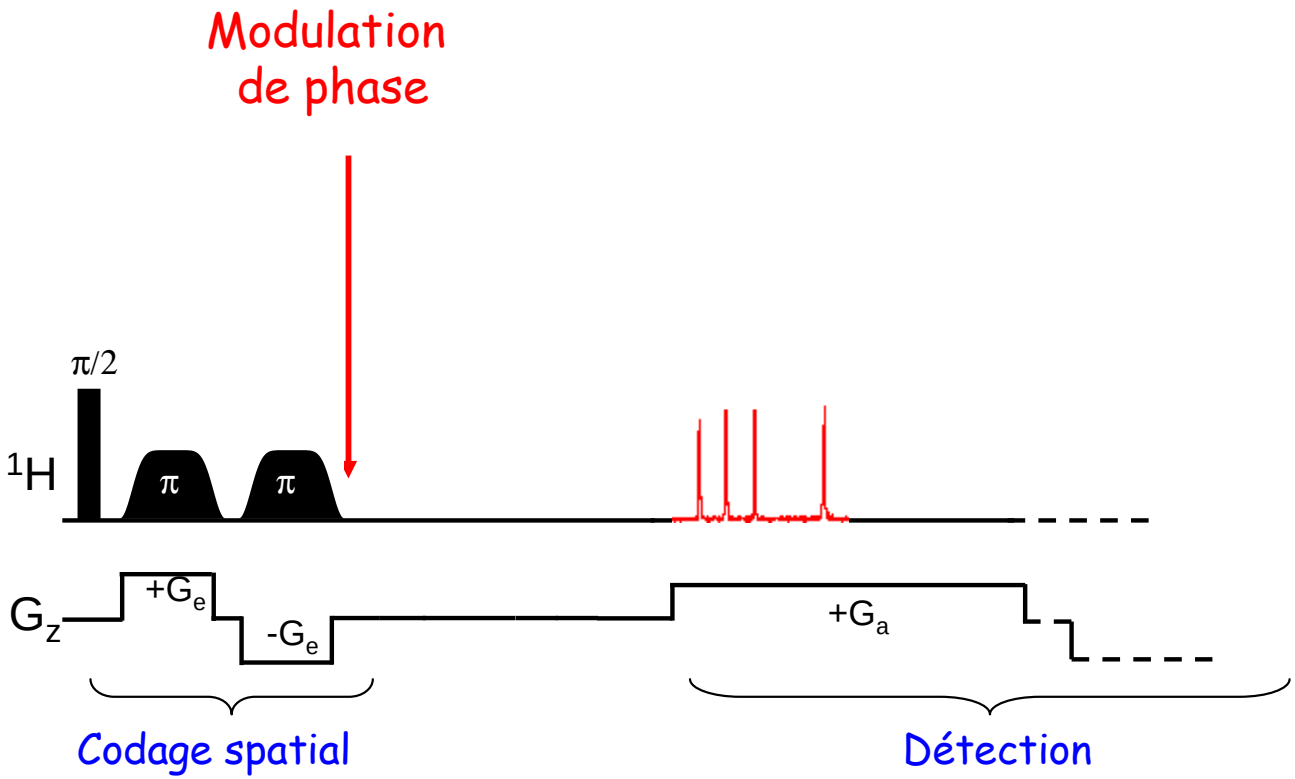
G_1 = +13 G/cm G_2 = -58 G/cm



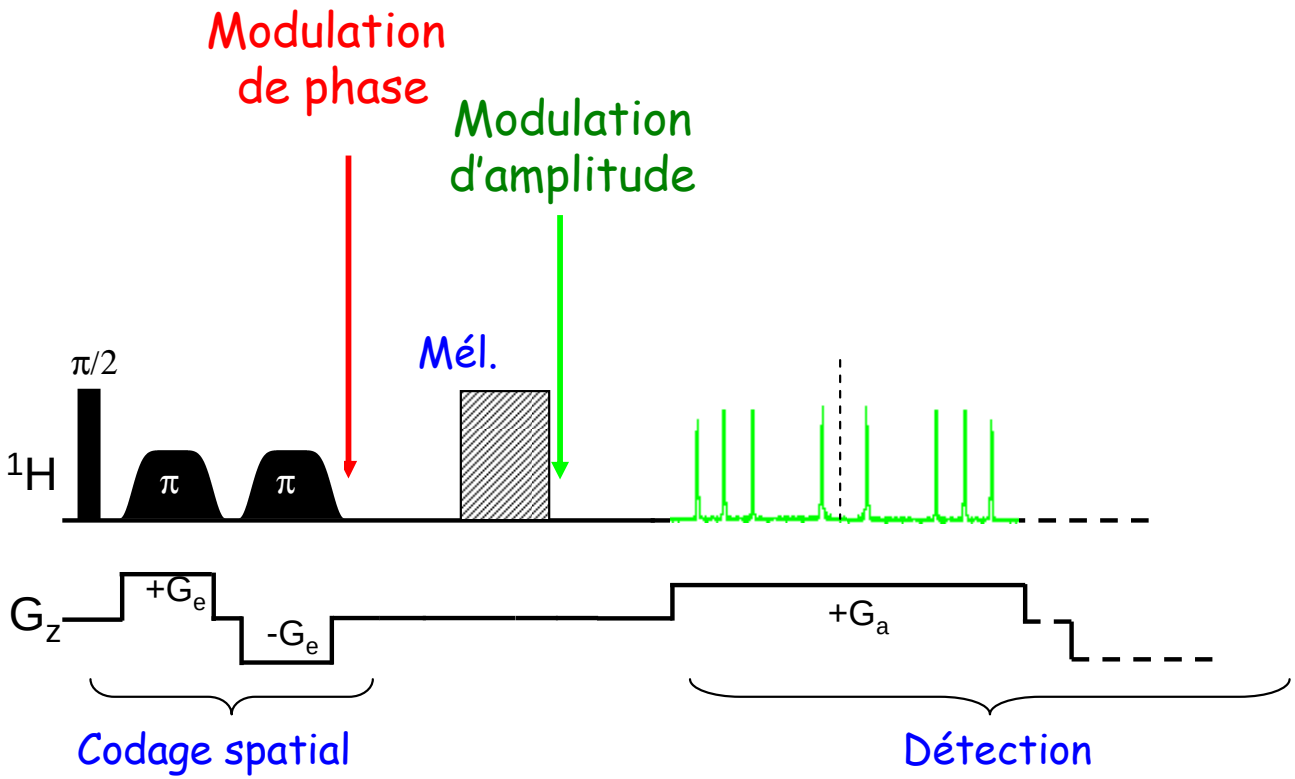




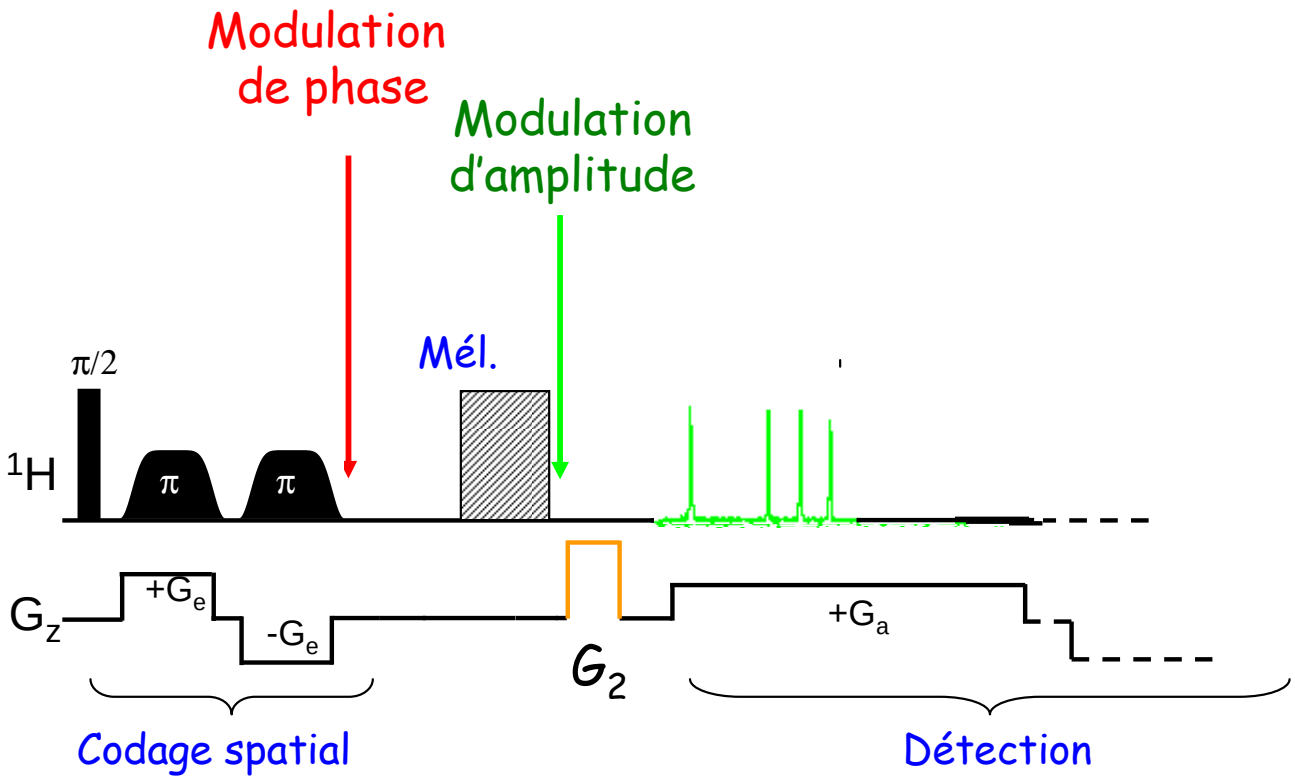
Solution : “Gradient-only controled folding”



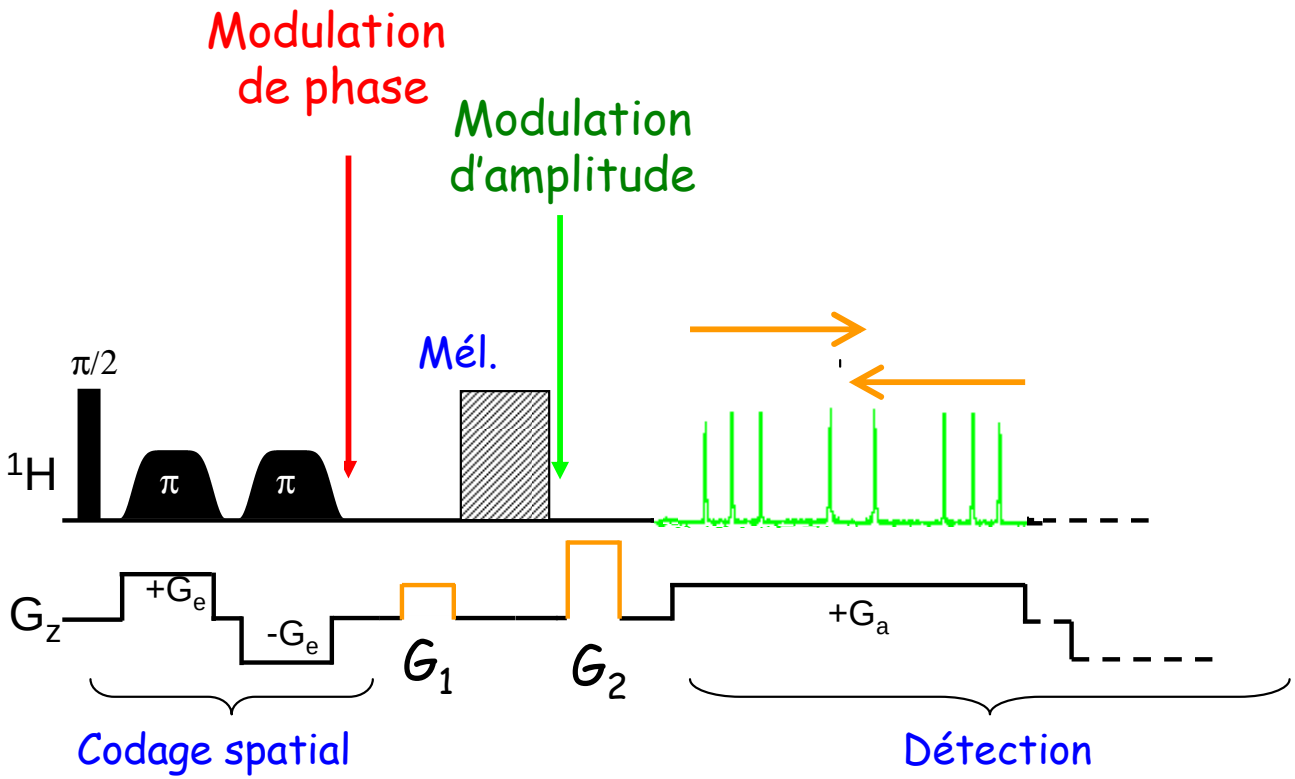
Solution : “Gradient-only controled folding”



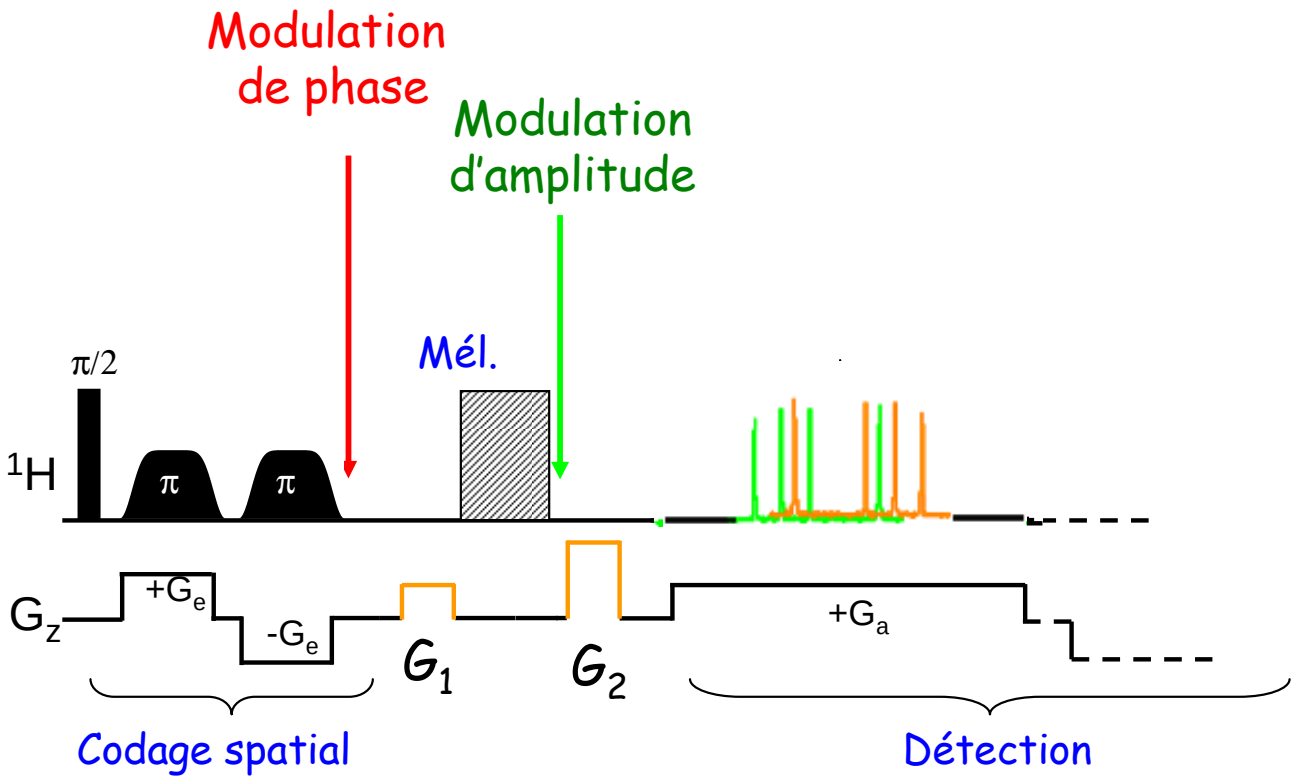
Solution : “Gradient-only controled folding”



Solution : “Gradient-only controled folding”



Solution : “Gradient-only controled folding”

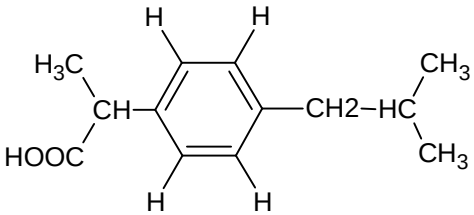


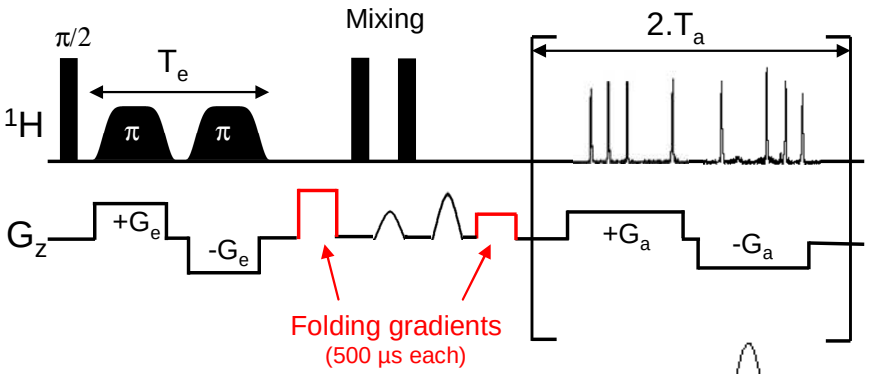
- ☑ Grandes gammes spectrales sans perte de résolution ou S/B
- ☑ Pas d'impulsions sélectives
- ☑ Facile à implémenter en routine
- ☑ Applicable à la quasi-totalité des expériences ultrarapides

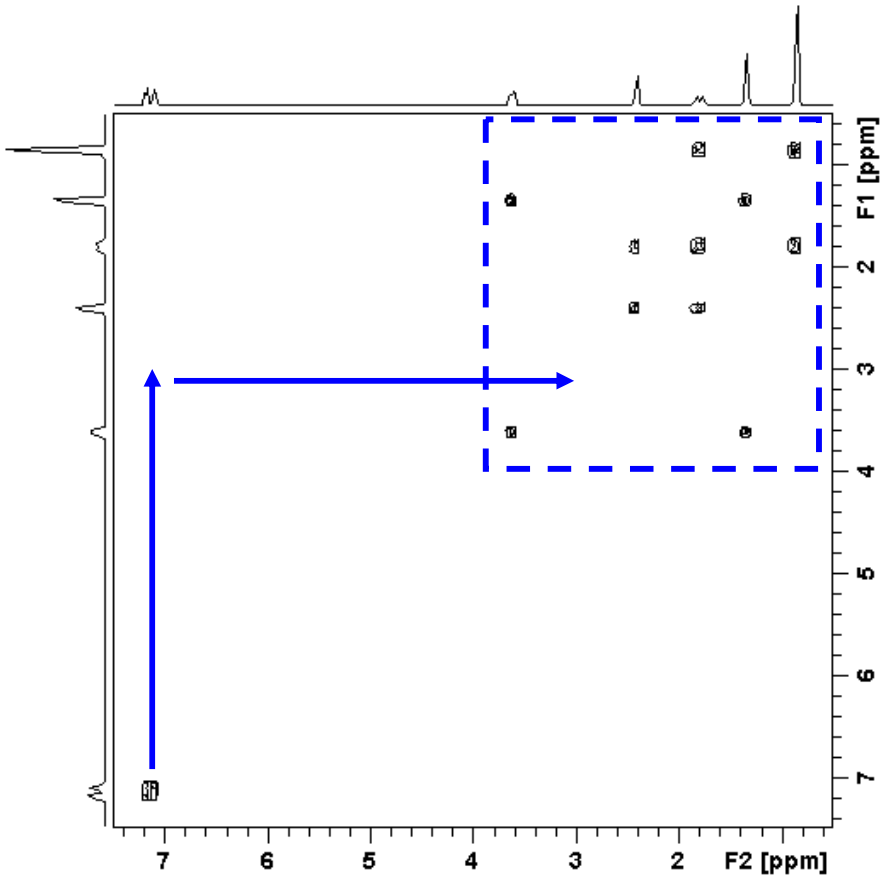
P. Giraudeau *et al.* J. Magn. Reson. (2010), sous presse

Solution : “Gradient-only controled folding”

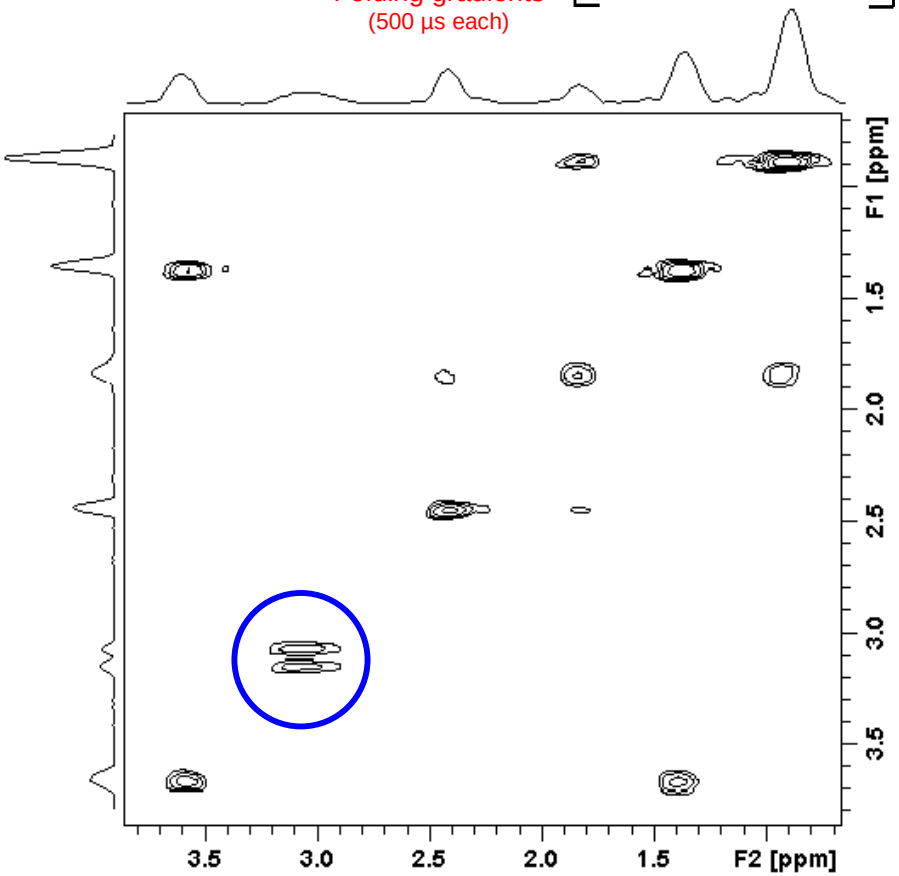
COSY-DQF ultrarapide - Ibuprofène 100 mM







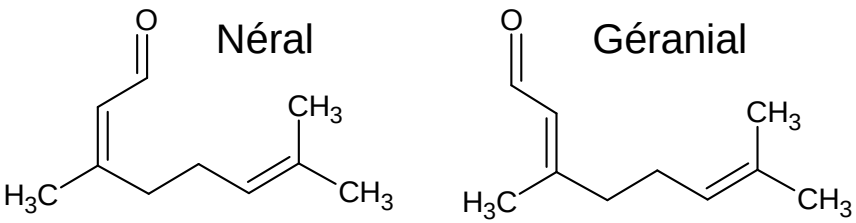
COSY-DQF Conventionnelle – 13 min

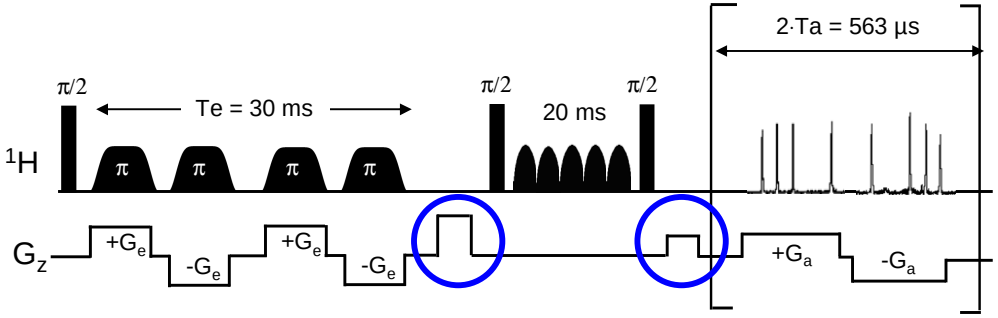


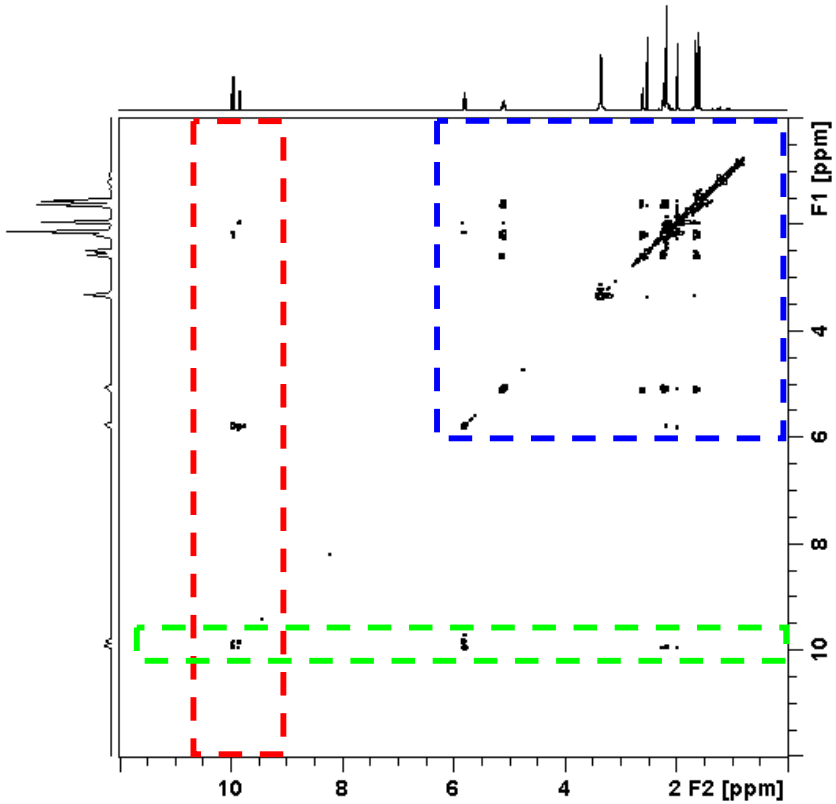
DQF-COSY Ultrarapide – 0.2 s

Application à un mélange de citrals

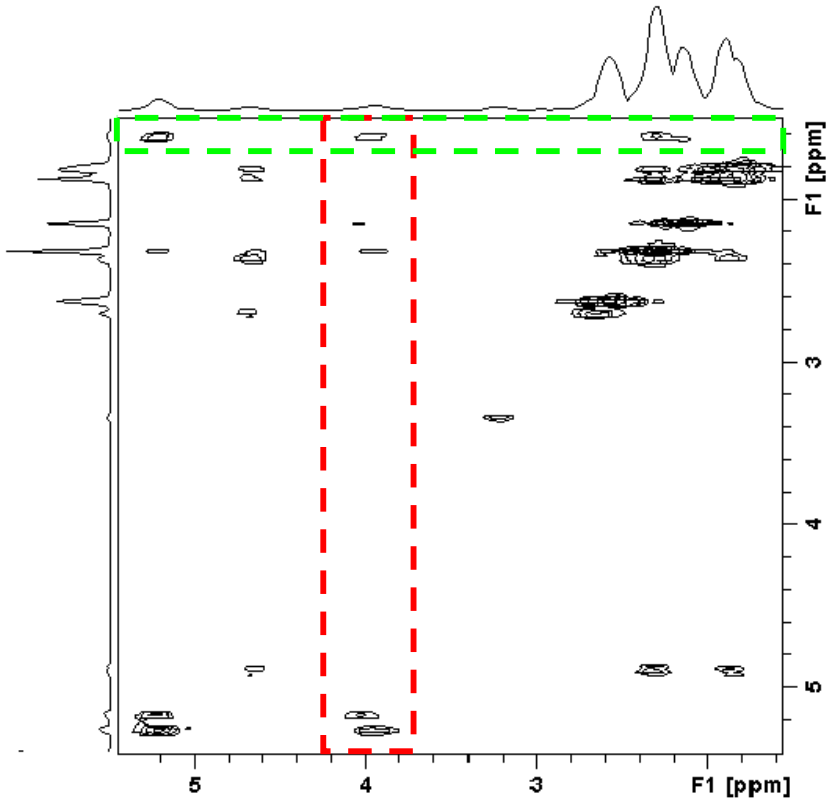
zTOCSY Ultrarapide





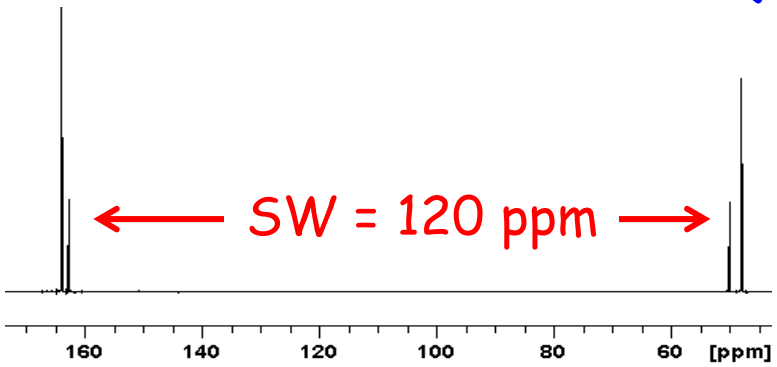


2D TOCSY Conventionnelle – 50 min

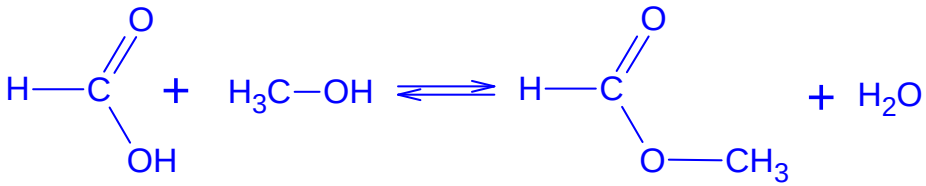


2D TOCSY Ultrarapide – 0.2 s

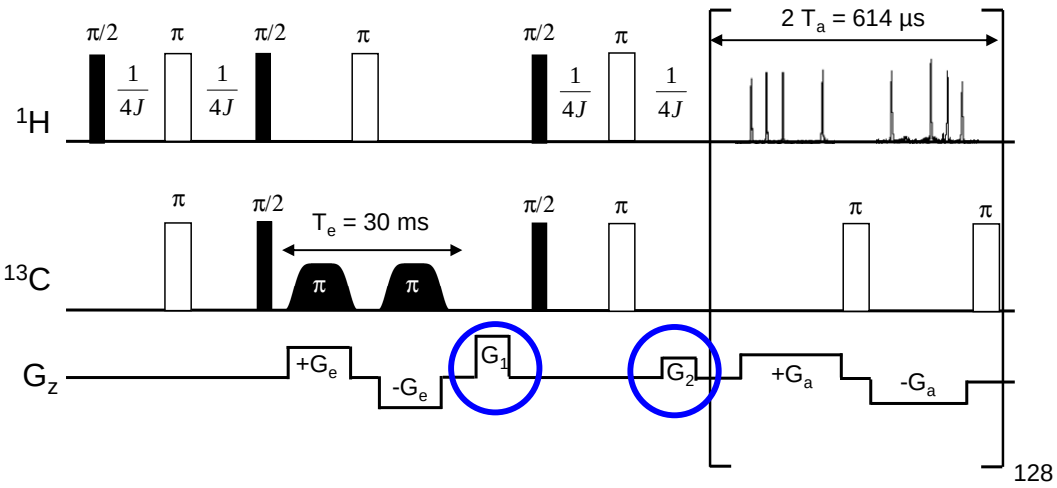
HSQC Ultrarapide

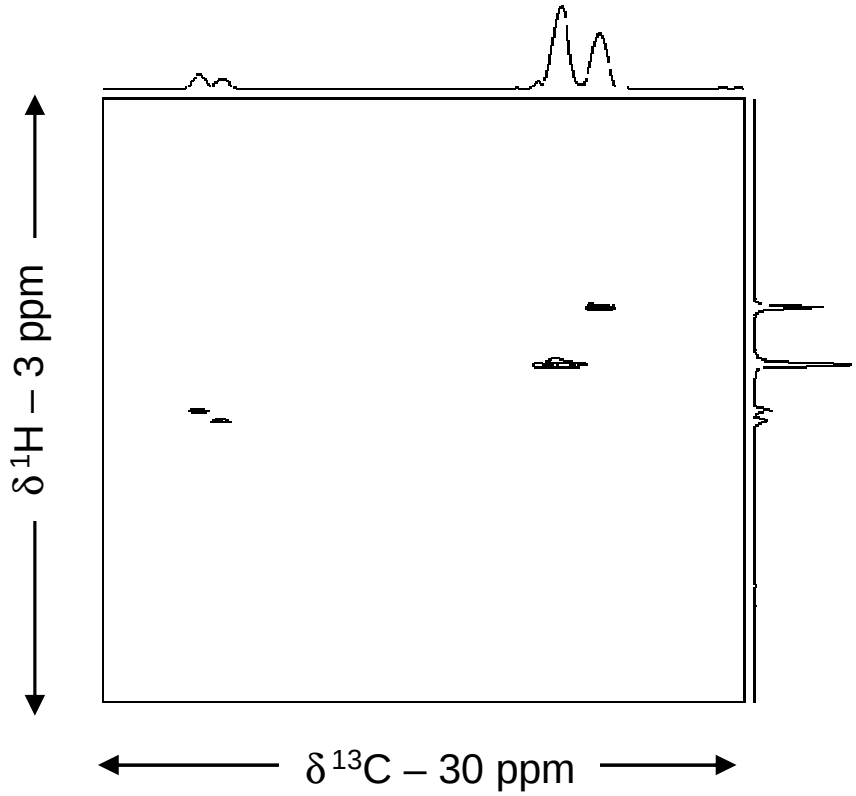


δ ^{13}C ppm



HSQC Ultrarapide repliée – 0.12 s





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Conclusion et Perspectives

Conclusion

- Méthodes ultrarapides optimisées (S/B, résolution, SW)
- Facilement implémentable en routine
- Applicable à des échantillons de complexité croissante

Perspectives

- Ajustement automatique des paramètres expérimentaux
- Reconstruction des spectres non-repliés
- Vers une utilisation en routine de la RMN 2D ultrarapide…

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