High sensitivity and quantitative ^{13}C measurements using "Q-POMMIE"

Product used : Nuclear Magnetic Resonance (NMR)

POMMIE (**P**hase **O**scillations to **M**axi**MI**ze **E**diting) is a ^{13}C experiment that, like the more familiar DEPT experiment, utilizes polarization transfer to enhance the intensities of the ^{13}C signals. However, unlike DEPT, POMMIE edits the spectrum by varying pulse phase rather than adjusting pulse flip angle.

Fig. 1 shows the pulse program of Q-POMMIE (Quantitative-POMMIE)[1]. It improves quantitative performance by varying Δ and pulse phase to average the efficiency of polarization transfer (Fig. 1). The spectrum pattern of Q-POMMIE is identical to DEPT45.

Quantitative NMR measurements require sufficiently long repetition times to allow the (near complete) recovery of magnetization between scans. For the standard $^{13}C\{^1H\}$ inverse gated decoupling method, the minimum acceptable repetition time is dictated by the ^{13}C T_1s, which can be very long (up to several minutes). On the other hand, the minimum repetition time of the Q-POMMIE method is dictated by the usually much shorter ^1H T_1s. This means that Q-POMMIE can yield quantitative ^{13}C spectra in less time and with higher sensitivity than via the $^{13}C\{^1H\}$ inverse gated decoupling method.

Fig. 2 shows a comparison of $^{13}C\{^1H\}$ inverse gated decoupling and Q-POMMIE spectra of 10% Cinnamic acid cis-3-hexenylester in $CDCl_3$. Although quaternary carbons are not observable in the Q-POMMIE spectrum, protonated carbon signals are recorded with significantly higher sensitivity, thereby allowing more accurate quantitation. Tab. 1 shows the comparison of the peak integrals obtained from each spectrum. While the CH integrals are significantly underrepresented in DEPT45, those obtained using Q-POMMIE are very close to those obtained via the $^{13}C\{^1H\}$ inverse gated decoupling method.

Features of Q-POMMIE (Comparison with $^{13}C\{^1H\}$ inverse gated decoupling)

- Higher sensitivity
- Quaternary carbons are not observed
- Quantitative condition is dictated by ^1H T_1s not ^{13}C T_1s
- Requires large minimum number of scans (96 × n)

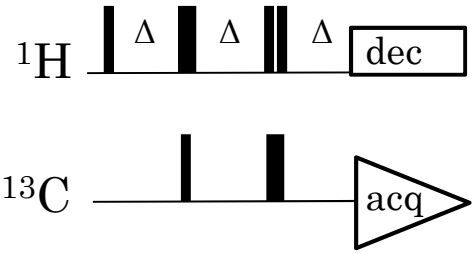

Fig. 1: Pulse program of Q-POMMIE

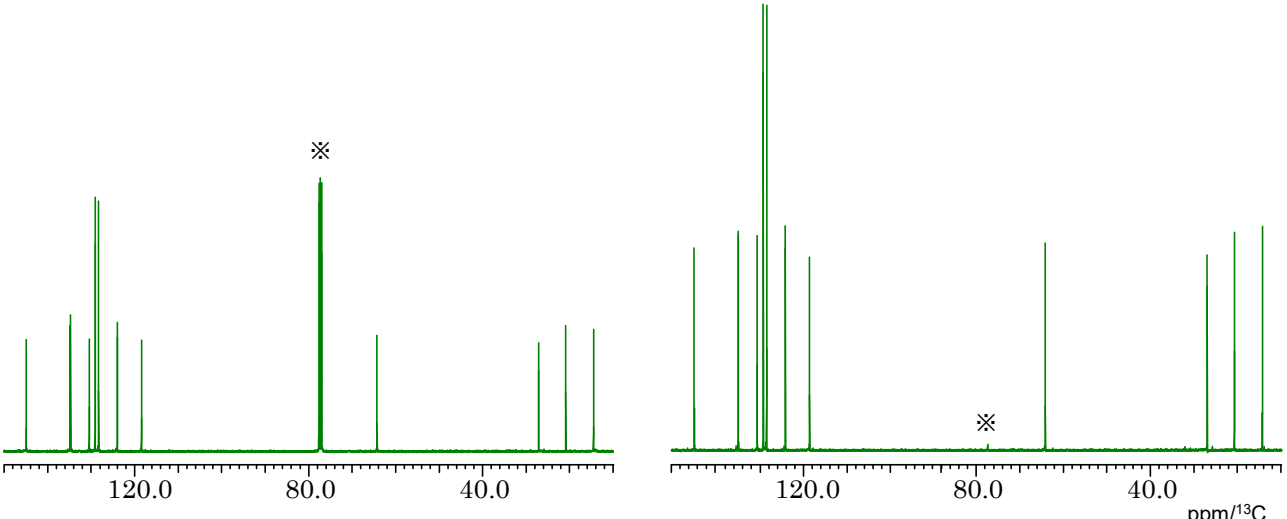

Fig. 2: a) $^{13}C\{^1H\}$ inverse gated decoupling **b) : Q-POMMIE**

Sample: 10% CAHE/$CDCl_3$
Instrument: JNM-ECZ400S & ROYALprobe™HFX
Number of scans: 384
Pulse repetition time: 46 s

Reference

1) *Anal. Chem.* 2008, 80, 8293-8298.

Tab. 1: Integral values of protonated ^{13}C signals shown in Fig. 2

Exp / δ(ppm)	$^{13}C\{^1H\}$ inverse gated decoupling	Q-POMMIE	DEPT45
14.3 (CH_3)	1.00	1.00	1.00
20.7 (CH_2)	0.98	0.97	0.92
26.9 (CH_2)	0.89	0.94	0.94
64.2 (CH_2)	0.99	1.07	1.07
118.3 (CH)	0.95	0.97	0.69
123.9 (CH)	0.91	0.92	0.67
128.1 (CH)*2	1.85	1.87	1.44
129.0 (CH)*2	1.96	1.92	1.45
130.3 (CH)	0.95	0.99	0.67
134.5 (CH)	0.87	0.85	0.64
144.8 (CH)	0.95	0.96	0.66

Practical Example: UV Initiator

As an illustration of the utility of the Q-POMMIE experiment, Fig. 3 shows a comparison of spectra recorded on a sample of a UV initiator. The ^{13}C spectrum of this sample contains a signal at 77.2 ppm which is completely obscured by the solvent signal, so its integral cannot be determined via $^{13}C\{^1H\}$ inverse gated decoupling (Fig. 3a). On the other hand, the solvent signal is not visible in the Q-POMMIE spectrum, allowing this signal to be cleanly observed and hence integrated (Fig. 3b).

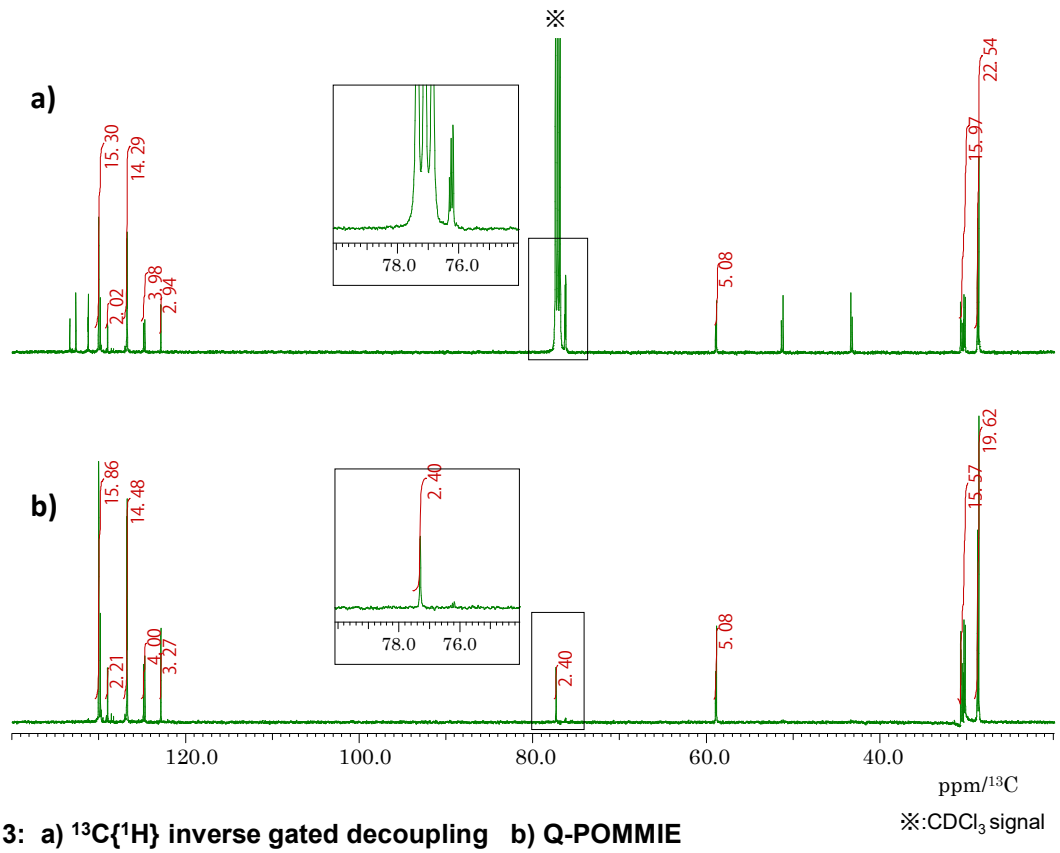

Fig. 3: a) $^{13}C\{^1H\}$ inverse gated decoupling b) Q-POMMIE

Sample preparation: 10 mg sample/$CDCl_3$
Instrument: JNM-ECZ500R & 5mm SuperCOOL probe
Scans: 960
Pulse repetition time: 20 s

Sample courtesy of Mr. Yuuji Itoh (TOYO INK SC HOLDINGS CO., LTD)

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