

スペクトル編集

J変調スピンエコー (SFT, APT)

Refocused HSQC

DEPT/DEPTQ/PENDANT

refocused HSQCによる編集

CH_n系のrefocused (full INEPT) HSQC

$$^{13}\text{Cの信号強度} \propto (\gamma_{\text{H}}/\gamma_{\text{C}})^{5/2} n \sin \pi^1 J_{\text{CH}} t \cos^{n-1} \pi^1 J_{\text{CH}} t$$

信号強度は¹Hの数にほぼ比例する。

¹³Cの信号が最大になる時間は¹Hの数に依存する。

n=1では t=1/2J で最大値 1×γ_H/γ_C

n=2では t=1/4J で最大値 2×γ_H/γ_C

n=3では t={cos⁻¹√(2/3)}/(πJ) で最大値 (2/√3)×γ_H/γ_C

t=1/2Jのとき

$$\text{CH} \propto 1$$

$$\text{CH}_2 \propto 0$$

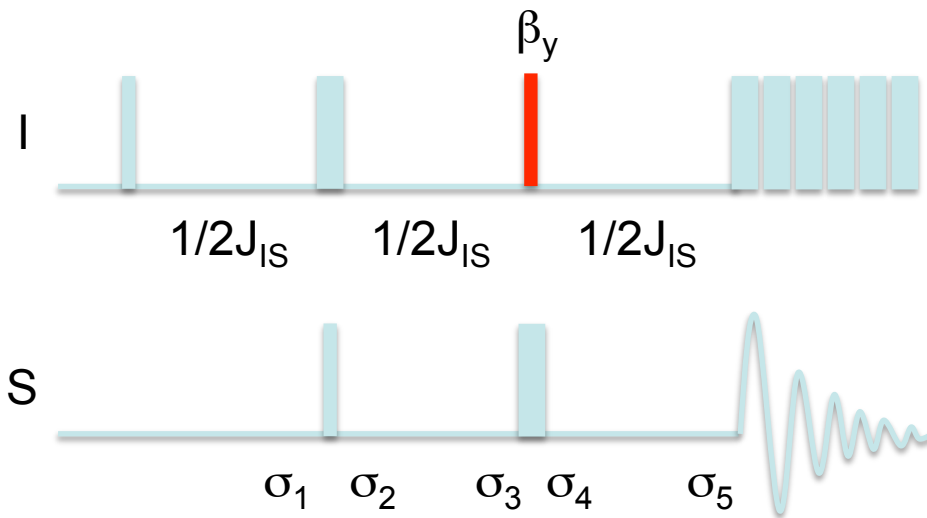
$$\text{CH}_3 \propto 0$$

$$\text{CH} \propto \sin \pi J t$$

$$\text{CH}_2 \propto 2 \sin \pi J t \cos \pi J t$$

$$\text{CH}_3 \propto 3 \sin \pi J t \cos^2 \pi J t$$

DEPTによる編集



$\beta = 45^\circ$ DEPT-45

$$\text{CH} \propto 1/\sqrt{2} \approx 0.71$$

$$\text{CH}_2 \propto 2 \times 1/\sqrt{2} \times 1/\sqrt{2} = 1$$

$$\text{CH}_3 \propto 3 \times 1/\sqrt{2} \times (1/\sqrt{2})^2 \approx 1.06$$

$\beta = 90^\circ$ DEPT-90

$$\text{CH} \propto 1$$

$$\text{CH}_2 \propto 2 \times 1 \times 0 = 0$$

$$\text{CH}_3 \propto 3 \times 1 \times 0 = 0$$

$$\text{CH} \propto \sin\beta$$

$$\text{CH}_2 \propto 2 \sin\beta \cos\beta$$

$$\text{CH}_3 \propto 3 \sin\beta \cos^2\beta$$

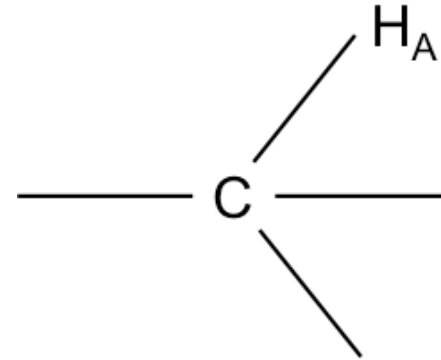
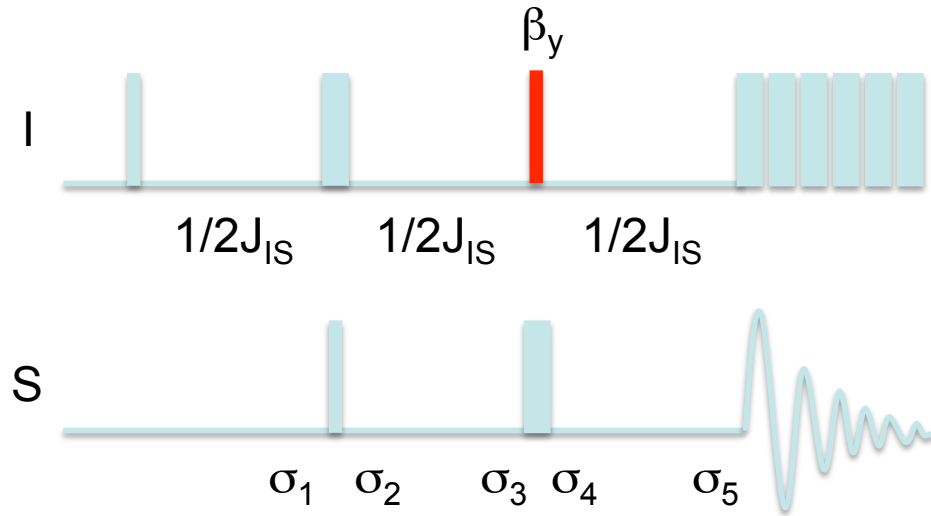
$\beta = 135^\circ$ DEPT-135

$$\text{CH} \propto 1/\sqrt{2} \approx 0.71$$

$$\text{CH}_2 \propto 2 \times 1/\sqrt{2} \times (-1/\sqrt{2}) = -1$$

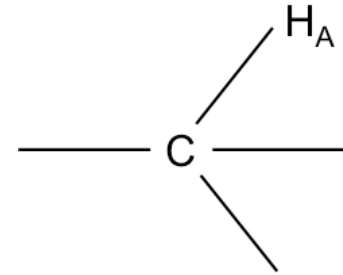
$$\text{CH}_3 \propto 3 \times 1/\sqrt{2} \times (-1/\sqrt{2})^2 \approx 1.06$$

CHのDEPT



- Q1. ISスピン系において、 σ_1 でのプロダクトオペレータを表示せよ。
- Q2. ISスピン系において、 σ_2 でのプロダクトオペレータを表示せよ。
- Q3. ISスピン系において、 σ_3 でのプロダクトオペレータを表示せよ。
- Q4. ISスピン系において、 σ_4 でのプロダクトオペレータを表示せよ。
- Q5. ISスピン系において、 σ_5 でのプロダクトオペレータを表示せよ。

CH \emptyset DEPT

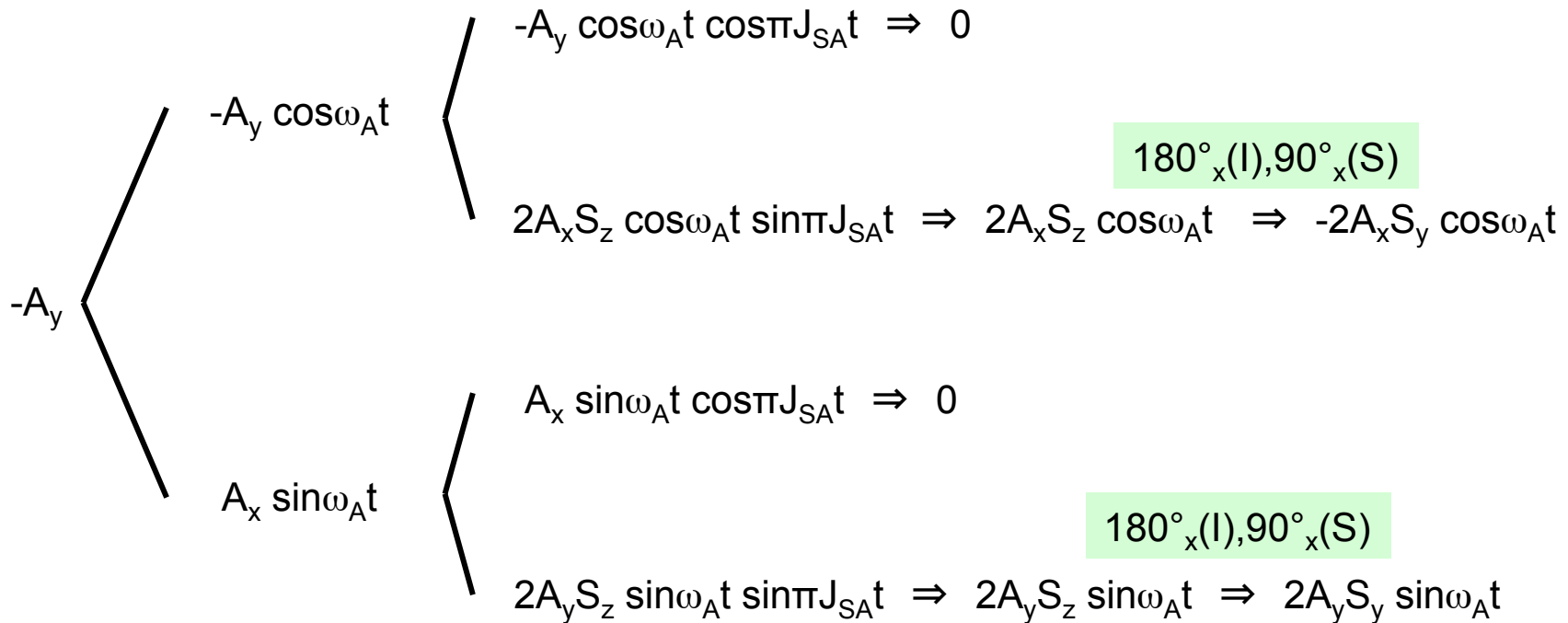


ω_A

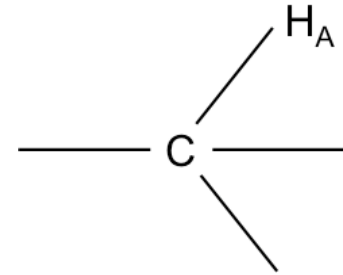
J_{SA}

σ_1

σ_2



CH \emptyset DEPT



σ_2

ω_A

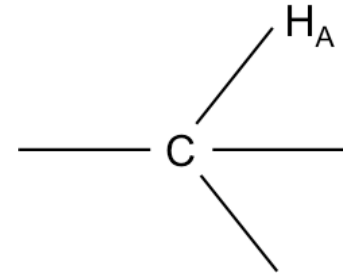
$$-2A_x S_y \cos \omega_A t \begin{cases} -2A_x S_y \cos \omega_A t \cos \omega_A t \\ -2A_y S_y \cos \omega_A t \sin \omega_A t \end{cases}$$

$$2A_y S_y \sin \omega_A t \begin{cases} 2A_y S_y \sin \omega_A t \cos \omega_A t \\ -2A_x S_y \sin \omega_A t \sin \omega_A t \end{cases}$$

+)

$$\begin{aligned} & -2A_x S_y (\cos \omega_A t \cos \omega_A t + \sin \omega_A t \sin \omega_A t) \\ & = -2A_x S_y \end{aligned}$$

CH ρ DEPT



ω_S

J_{AS}

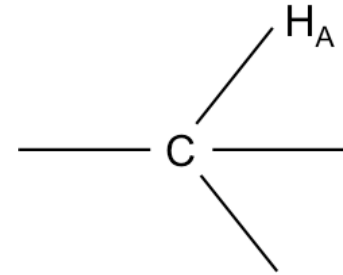
σ_3

$\beta_y(I), 180_x(S)$

σ_4

$$\begin{array}{l}
 -2A_x S_y \\
 \begin{array}{l}
 \nearrow -2A_x S_y \cos \omega_S t \Rightarrow -2A_x S_y \cos \omega_S t \\
 \searrow 2A_x S_x \sin \omega_S t \Rightarrow 2A_x S_x \sin \omega_S t
 \end{array} \\
 \begin{array}{l}
 \nearrow 2A_x S_y \cos \omega_S t \cos \beta \\
 \searrow -2A_z S_y \cos \omega_S t \sin \beta \\
 \nearrow 2A_x S_x \sin \omega_S t \cos \beta \\
 \searrow -2A_z S_x \sin \omega_S t \sin \beta
 \end{array}
 \end{array}$$

CH ρ DEPT



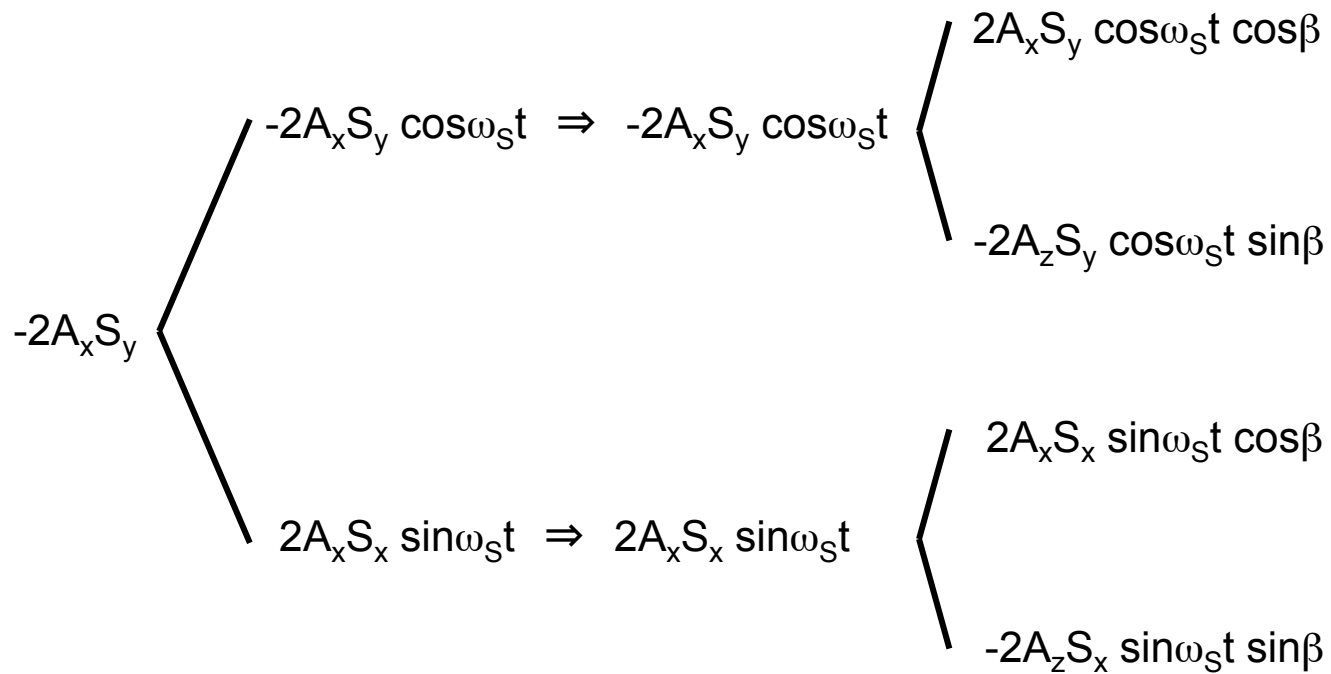
ω_S

J_{AS}

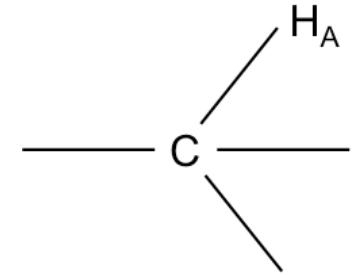
σ_3

$\beta_y(I), 180_x(S)$

σ_4



CH \emptyset DEPT



ω_S

J_{SA}

σ_5

$$-2A_z S_y \cos \omega_S t \sin \beta \left\{ \begin{array}{l} -2A_z S_y \cos \omega_S t \cos \omega_S t \sin \beta \\ 2A_z S_x \cos \omega_S t \sin \omega_S t \sin \beta \end{array} \right.$$

$$-2A_z S_x \sin \omega_S t \sin \beta \left\{ \begin{array}{l} -2A_z S_x \sin \omega_S t \cos \omega_S t \sin \beta \\ -2A_z S_y \sin \omega_S t \sin \omega_S t \sin \beta \end{array} \right.$$

+))

$$-2A_z S_y \cos \omega_S t \cos \omega_S t \cos \pi J_{SA} t \sin \beta \Rightarrow 0$$

$$S_x \cos \omega_S t \cos \omega_S t \sin \pi J_{SA} t \sin \beta \Rightarrow S_x \cos \omega_S t \cos \omega_S t \sin \beta$$

$$2A_z S_x \cos \omega_S t \sin \omega_S t \cos \pi J_{SA} t \sin \beta \Rightarrow 0$$

$$S_y \cos \omega_S t \sin \omega_S t \sin \pi J_{SA} t \sin \beta \Rightarrow S_y \cos \omega_S t \sin \omega_S t \sin \beta$$

$$-2A_z S_x \sin \omega_S t \cos \omega_S t \cos \pi J_{SA} t \sin \beta \Rightarrow 0$$

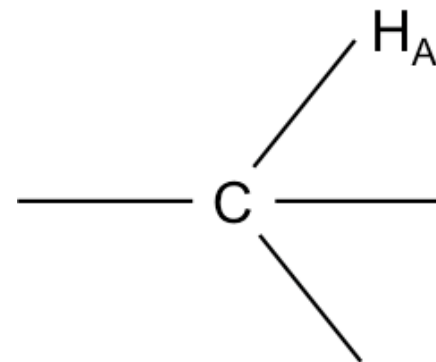
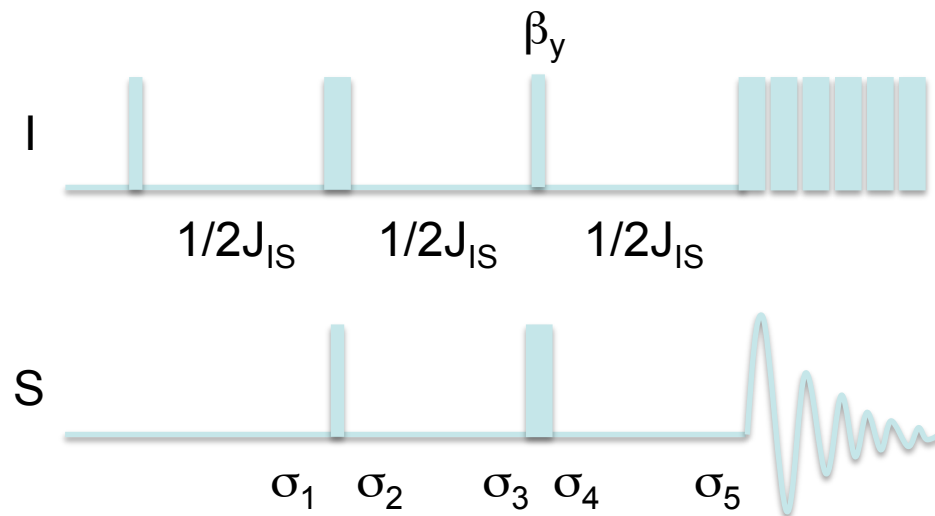
$$-S_y \sin \omega_S t \cos \omega_S t \sin \pi J_{SA} t \sin \beta \Rightarrow -S_y \sin \omega_S t \cos \omega_S t \sin \beta$$

$$-2A_z S_y \sin \omega_S t \sin \omega_S t \cos \pi J_{SA} t \sin \beta \Rightarrow 0$$

$$S_x \sin \omega_S t \sin \omega_S t \sin \pi J_{SA} t \sin \beta \Rightarrow S_x \sin \omega_S t \sin \omega_S t \sin \beta$$

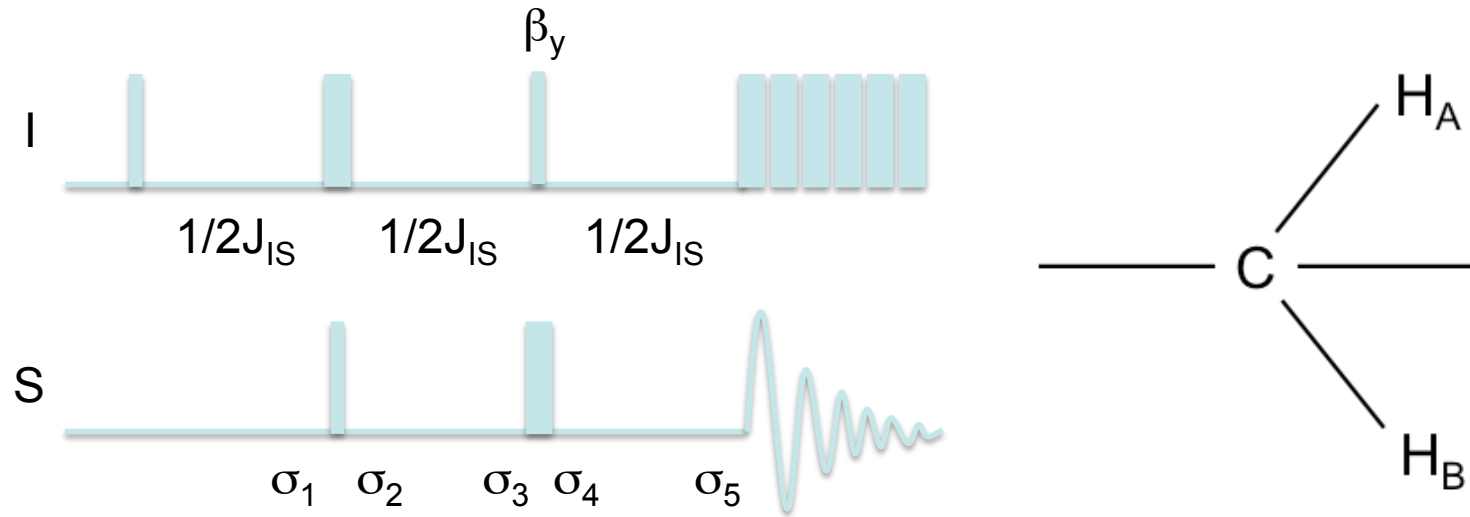
$$S_x (\cos \omega_A t \cos \omega_A t + \sin \omega_A t \sin \omega_A t) \sin \beta = S_x \sin \beta$$

CHのDEPT まとめ



1. 化学シフト項は全てリフォーカスする。
2. Jカップリング項のみ計算する。
3. σ_4 でIスピンの成分がx,y成分のときはリフォーカスしない。

CH₂のDEPT



Q6. I₂Sスピン系において、 σ_1 でのプロダクトオペレータを表示せよ。

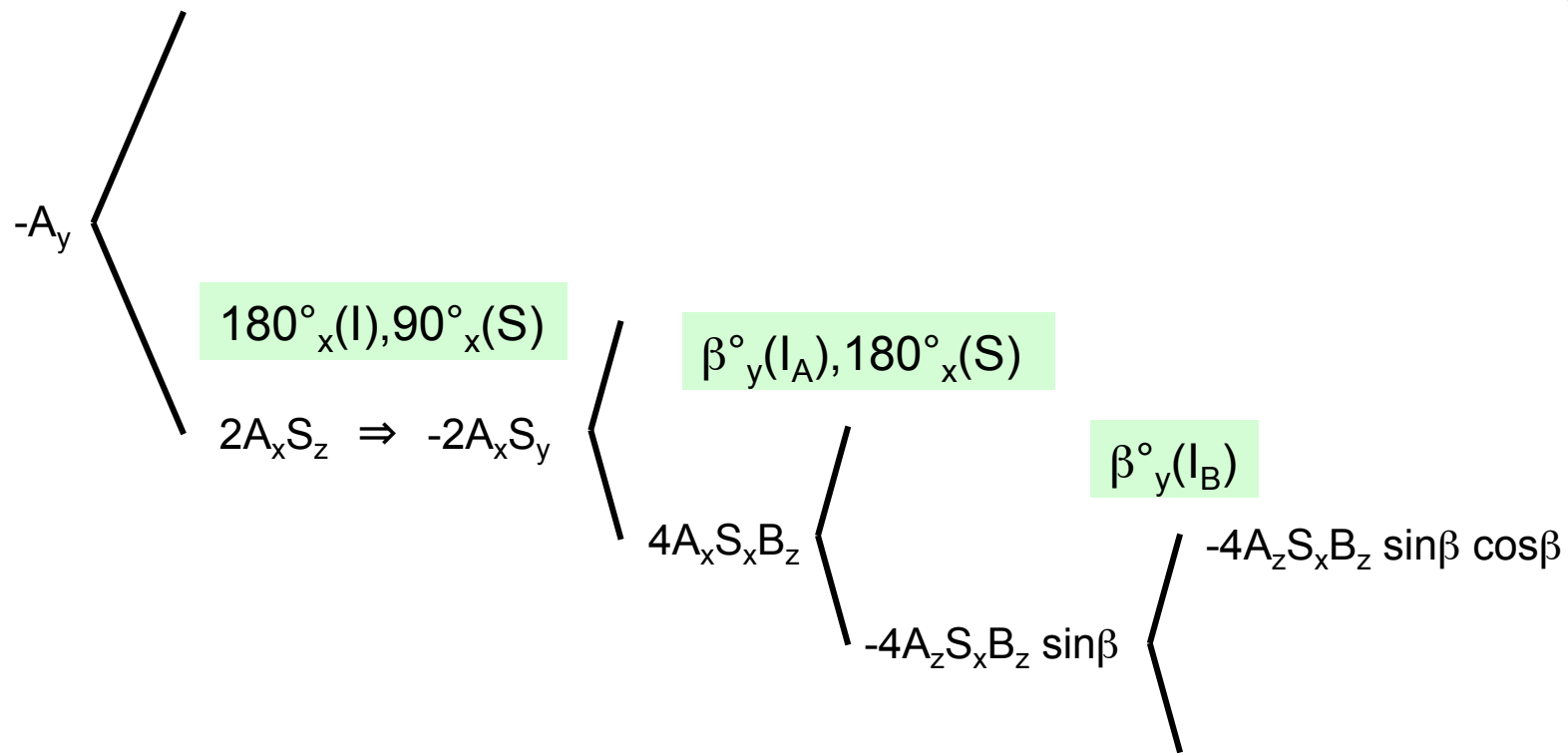
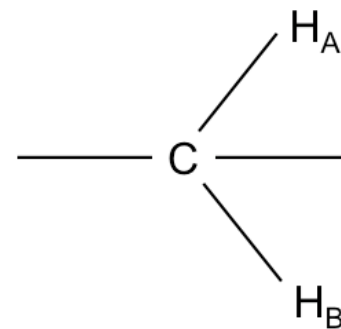
Q7. I₂Sスピン系において、 σ_2 でのプロダクトオペレータを表示せよ。

Q8. I₂Sスピン系において、 σ_3 でのプロダクトオペレータを表示せよ。

Q9. I₂Sスピン系において、 σ_4 でのプロダクトオペレータを表示せよ。

Q10. I₂Sスピン系において、 σ_5 でのプロダクトオペレータを表示せよ。

CH₂のDEPT



J_{SA}

σ_1

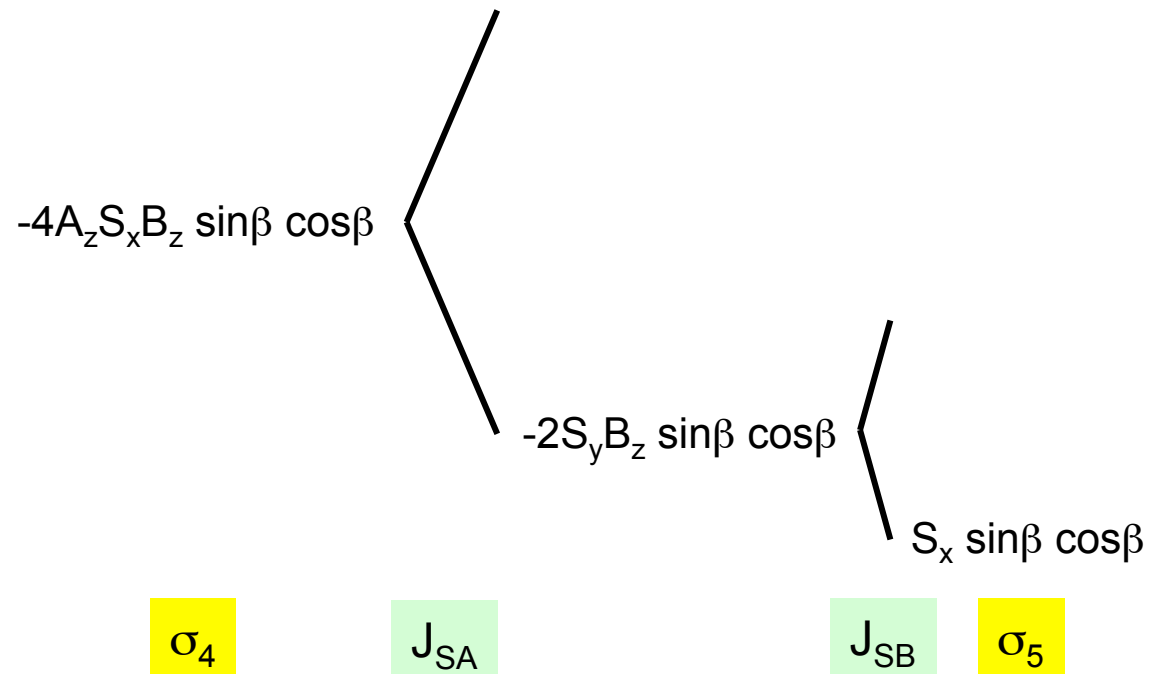
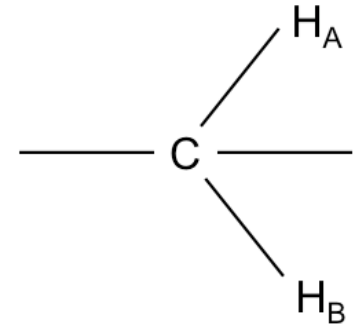
σ_2

J_{SB}

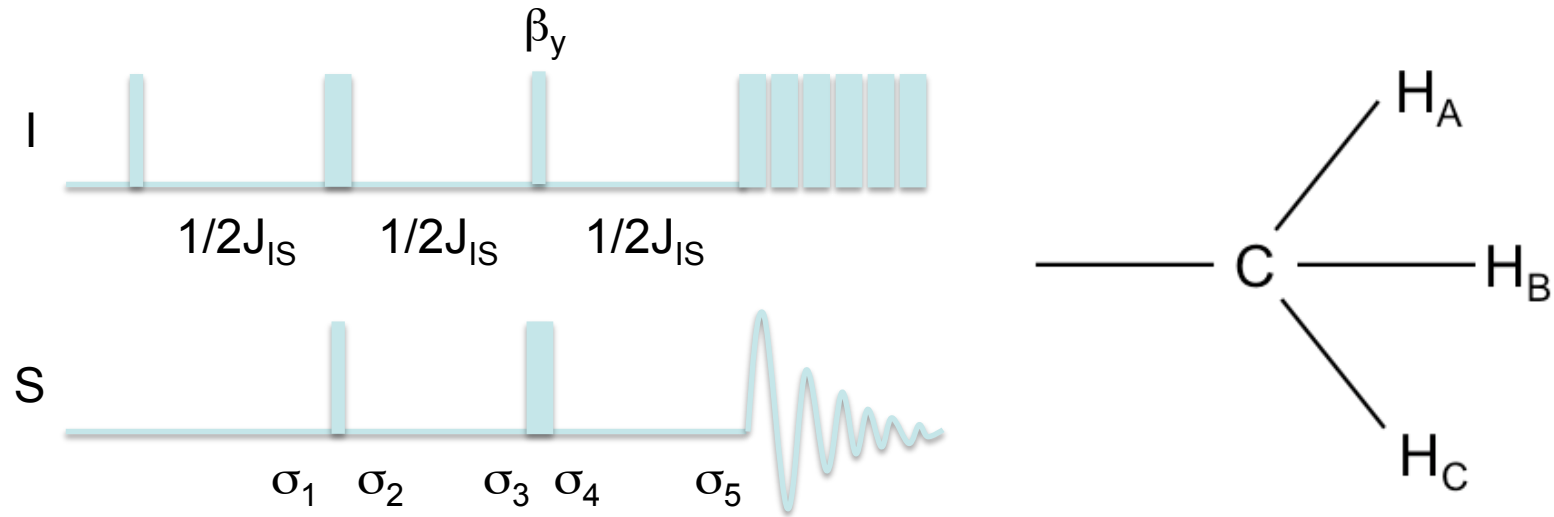
σ_3

σ_4

CH₂のDEPT

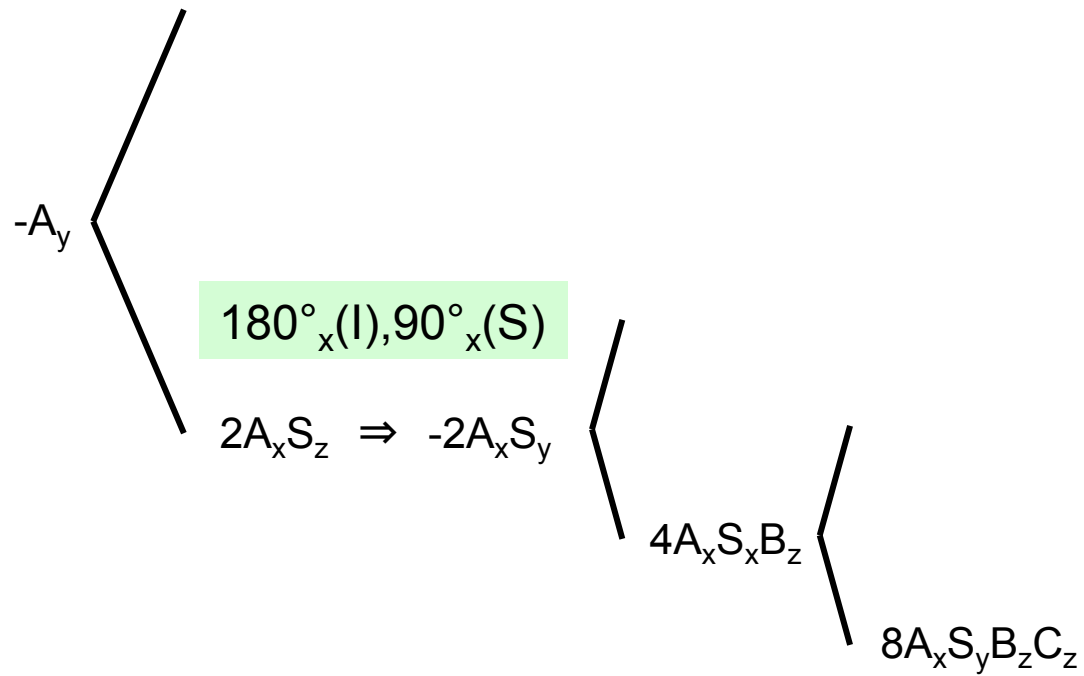
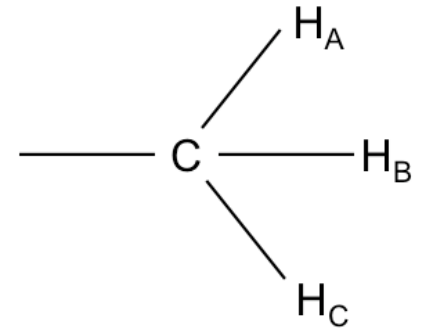


CH₃のDEPT 演習

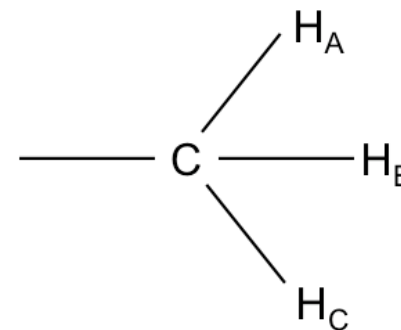


- Q11. I_3S スピン系において、 σ_1 でのプロダクトオペレータを表示せよ。
- Q12. I_3S スピン系において、 σ_2 でのプロダクトオペレータを表示せよ。
- Q13. I_3S スピン系において、 σ_3 でのプロダクトオペレータを表示せよ。
- Q14. I_3S スピン系において、 σ_4 でのプロダクトオペレータを表示せよ。
- Q15. I_3S スピン系において、 σ_5 でのプロダクトオペレータを表示せよ。

CH₃のDEPT



CH₃のDEPT



$\beta^\circ_y(I_A), 180^\circ_x(S)$

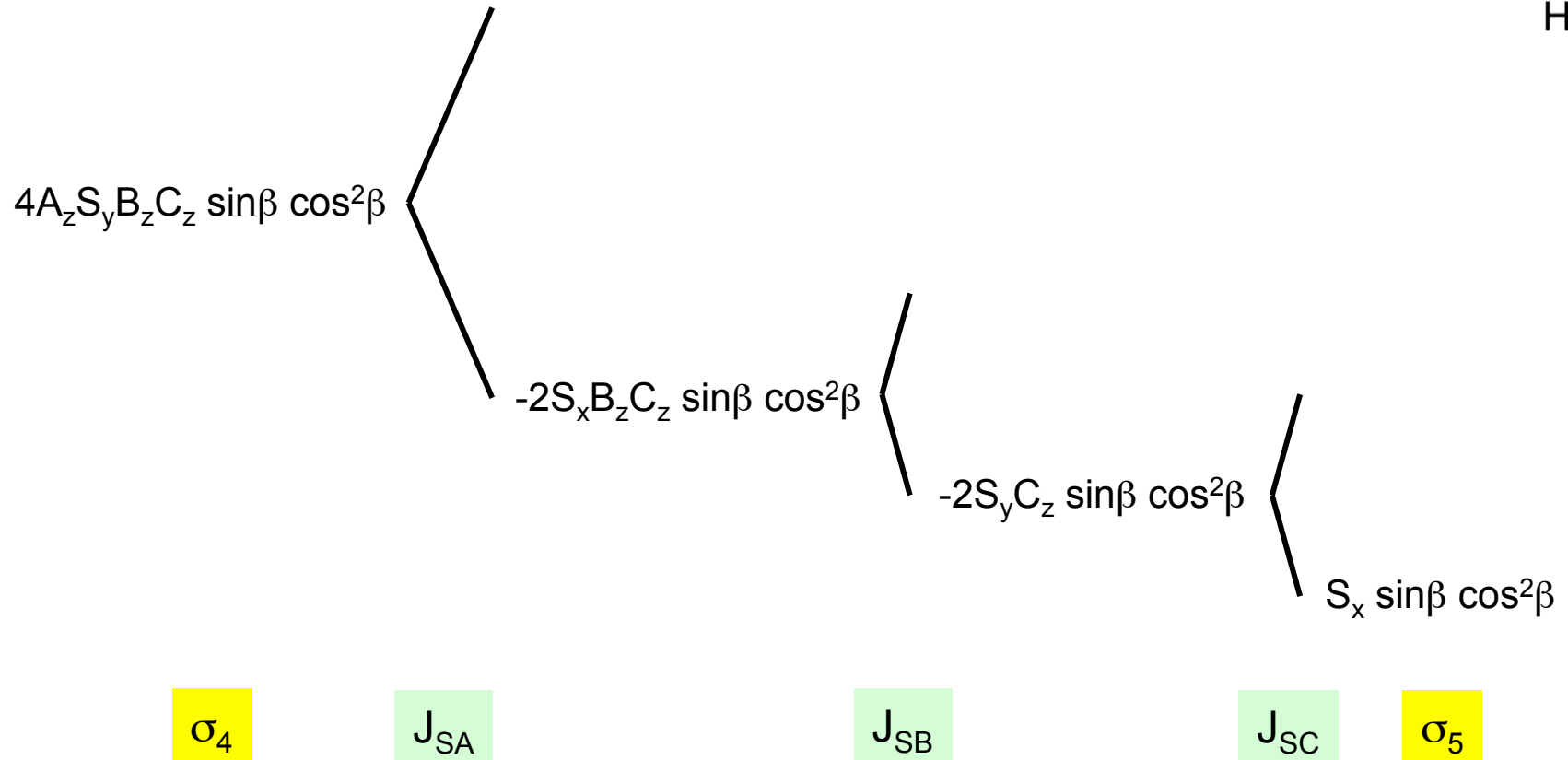
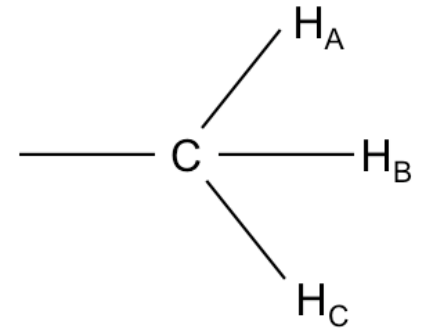
$\beta^\circ_y(I_C)$

$$4A_x S_y B_z C_z \left\{ \begin{array}{l} 4A_z S_y B_z C_z \sin\beta \\ 4A_z S_y B_z C_z \sin\beta \cos\beta \end{array} \right. \left\{ \begin{array}{l} 4A_z S_y B_z C_z \sin\beta \cos^2\beta \end{array} \right.$$

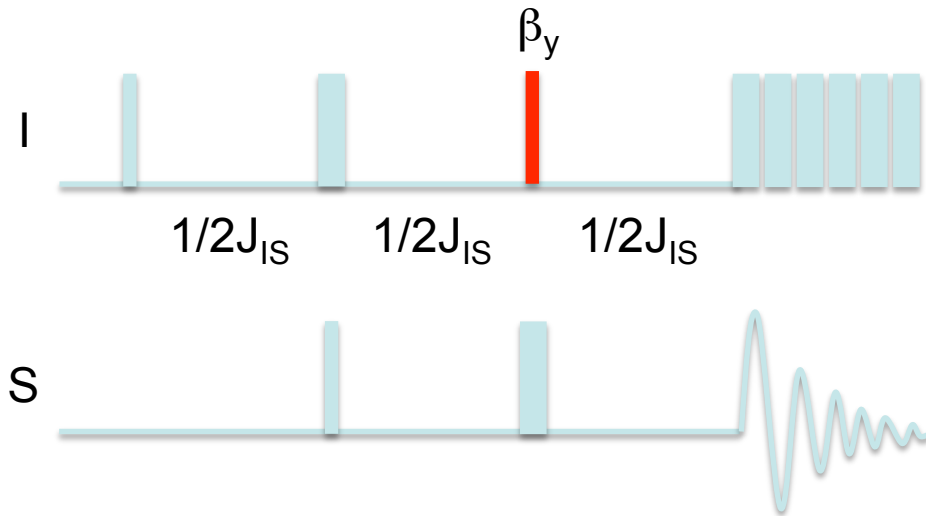
σ_3

σ_4

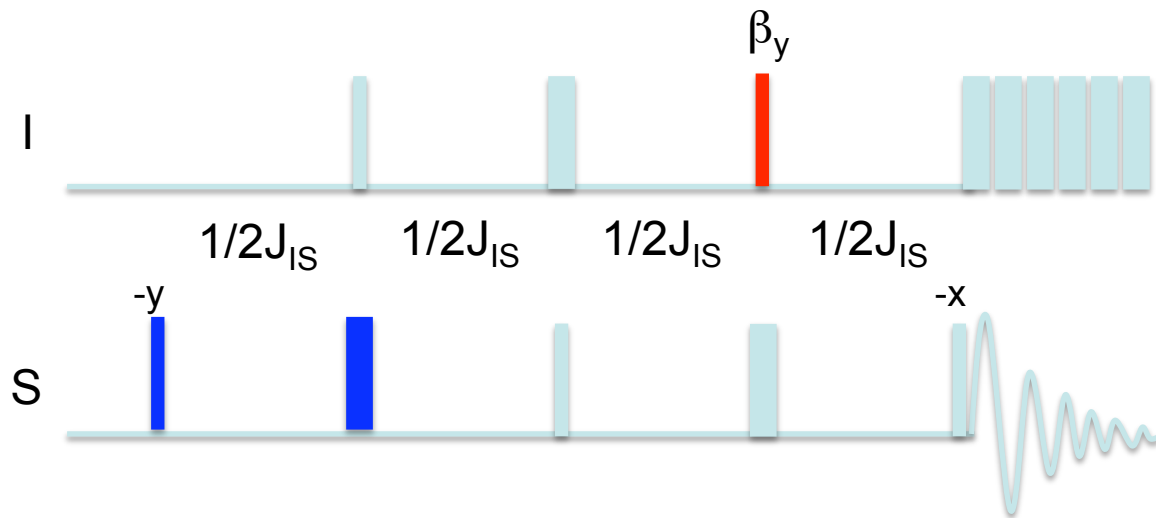
CH₃のDEPT



DEPTQ



DEPT
1-3級¹³Cの検出



DEPTQ
4級¹³Cの検出も可能

DEPTQ 4級¹³Cスペクトル

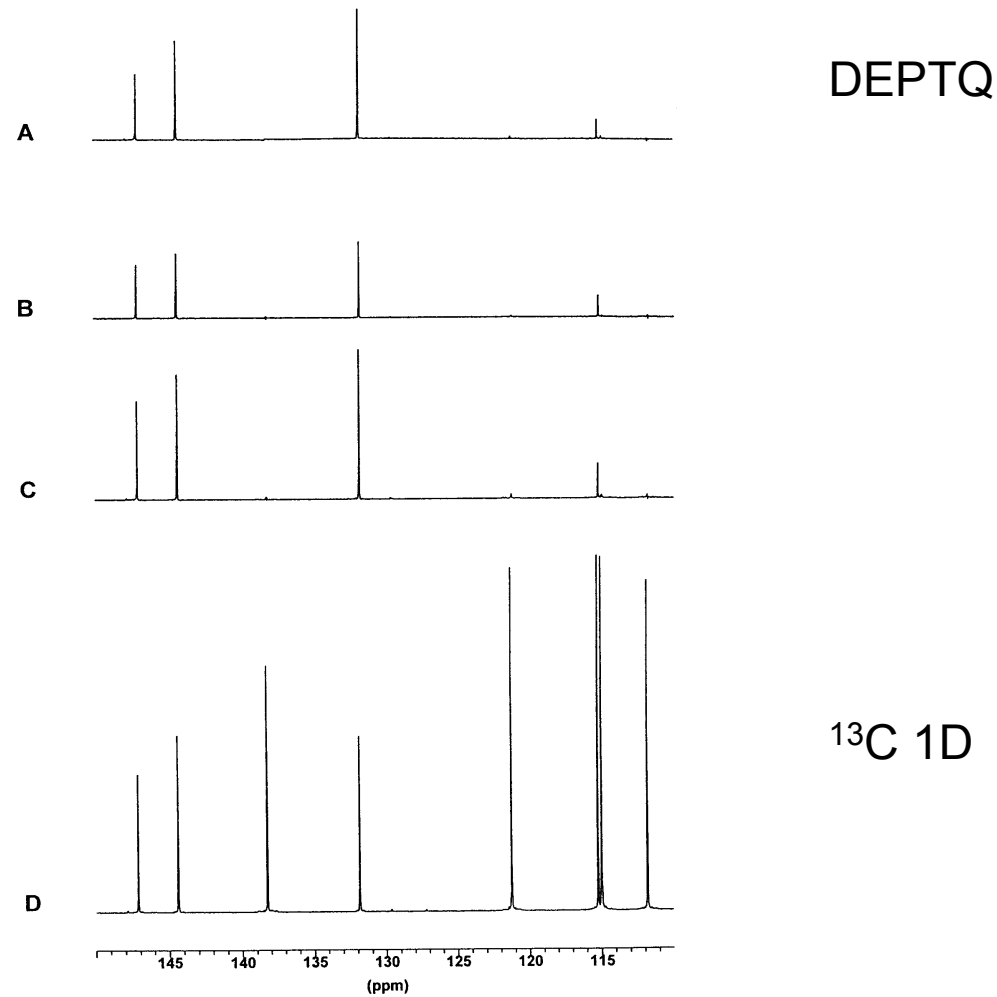
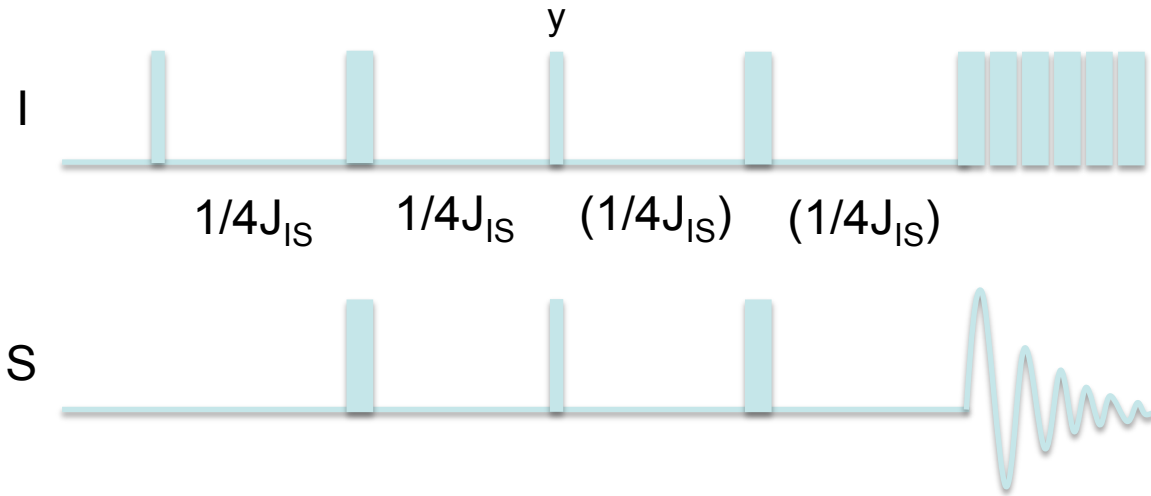


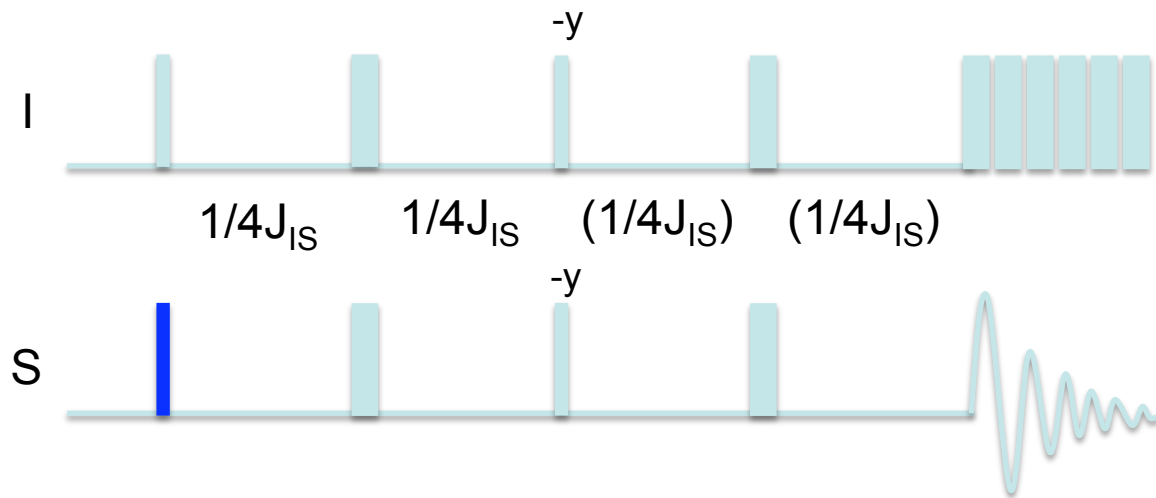
FIG. 2. Comparison of the DEPTQ, SEMUT, SEMUT-90, and the one-pulse ¹³C (reference) experiments applied to eugenol dissolved in acetone-d₆ and performed on a BRUKER DRX-400 spectrometer, with 90° pulse lengths of 9.1 and 6.2 μs for ¹H and ¹³C respectively. The DEPTQ and SEMUT experiments were set up and applied for complete spectral editing as described in the text, whereas SEMUT-90, yielding exclusively the signals of quaternary carbons, was applied for comparison. Several subexperiments with different ¹H selection pulses were performed with DEPTQ and SEMUT, and the corresponding data were stored separately. The same relaxation delay (D1 = 2 s) and the same delay for coupling evolution (D2 = 3.45 ms) were used throughout. An equal total number of scans were acquired within the same total measuring time with each experiment. As a result the corresponding C_q subspectra (expansion 110–150 ppm) obtained with DEPTQ (A), SEMUT (B), and SEMUT-90 (C) are shown together with the corresponding spectrum of the one-pulse experiment (D). The residual signal at 115.2 ppm, visible in all edited spectra, originates from the olefinic methylene group.

Burger R and Bigler P,
J Magn Reson, 1998.

PENDANT



refocused INEPT
1-3級¹³Cの検出



PENDANT
4級¹³Cの検出も可能

PENDANT

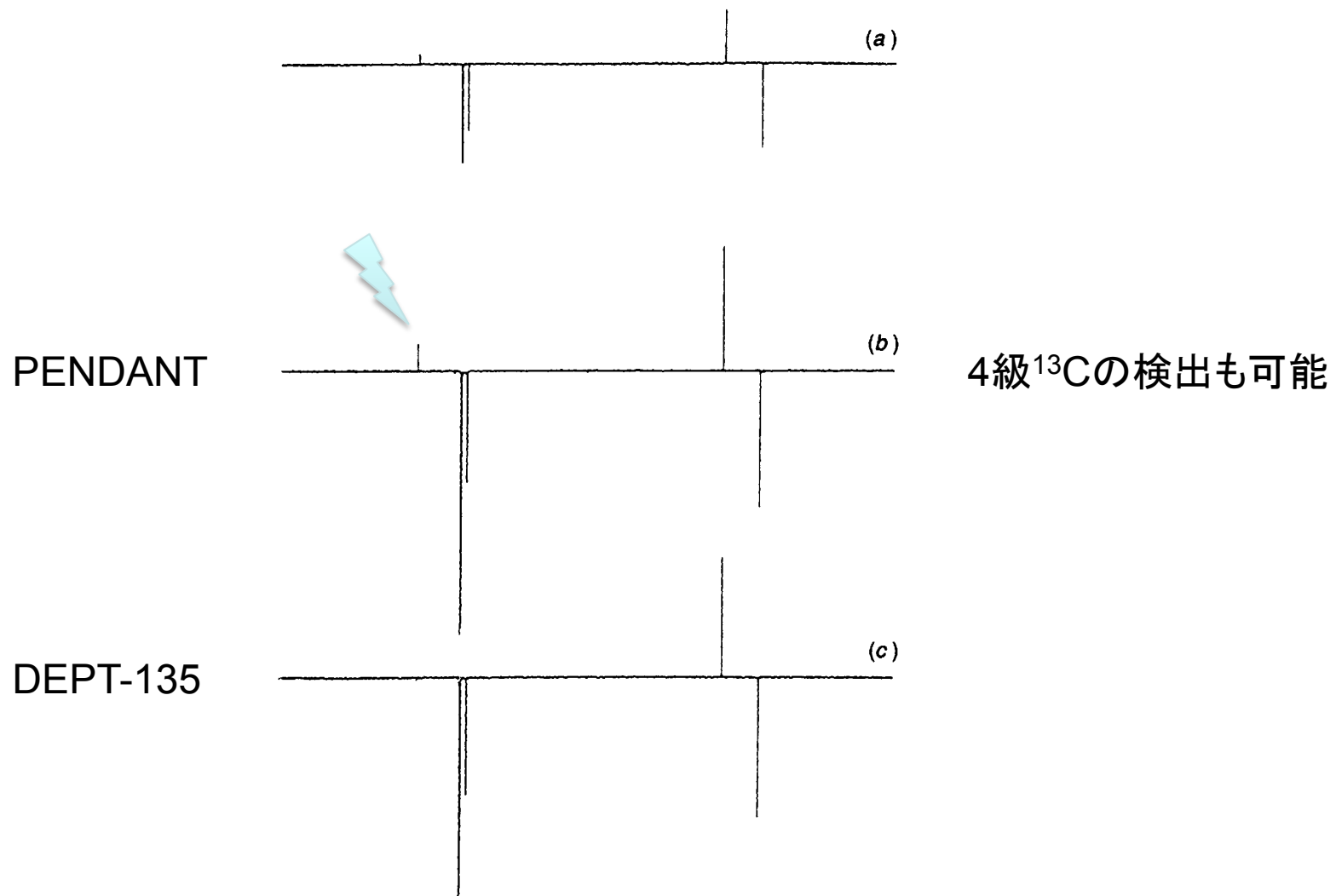


Fig. 1 Comparison of the ^1H -decoupled (a) APT (with NOE), (b) PENDANT (not phase cycled) and (c) DEPT (135°) ^{13}C spectra of ethylbenzene under equivalent conditions

Homer J and Perry MC,
Chem Commun, 1994.