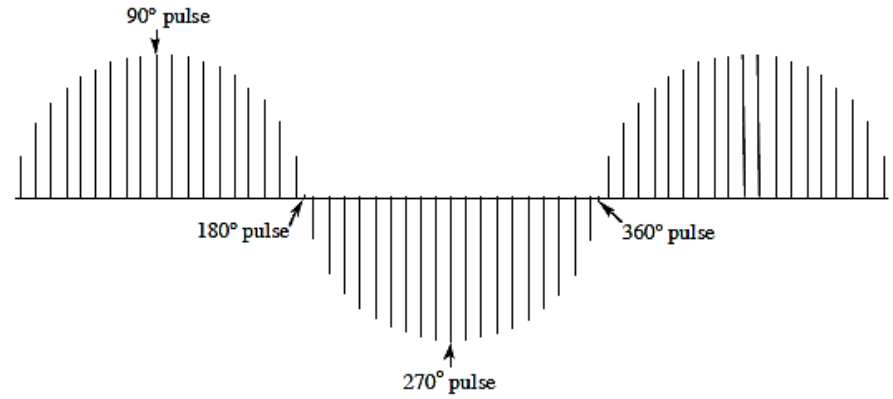
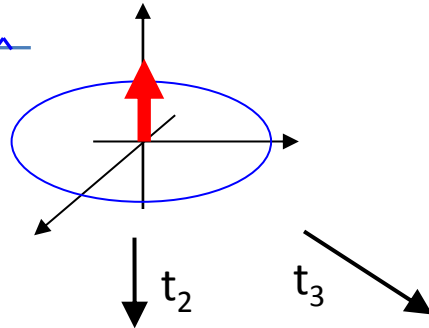
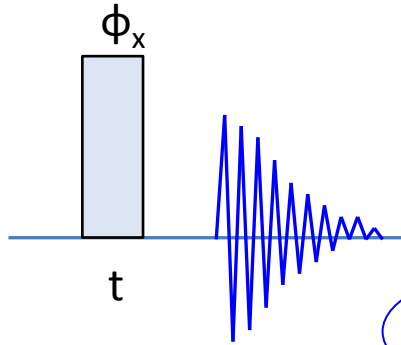


Nukleární magnetická rezonance

Lekce 4

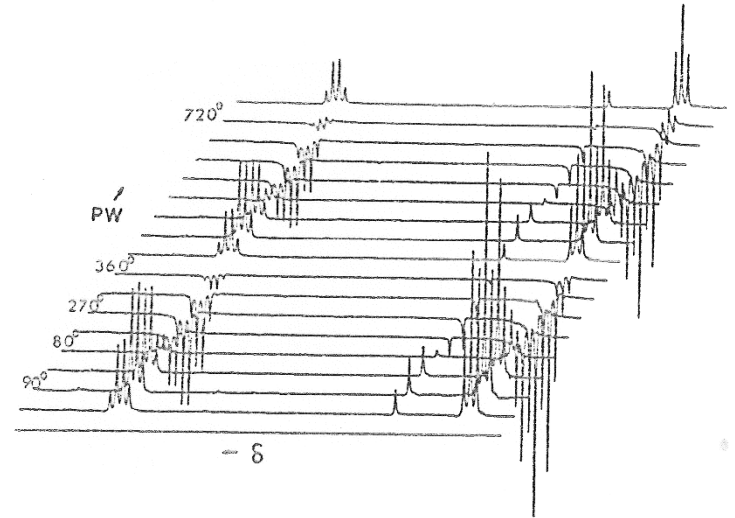
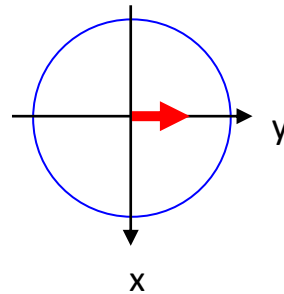
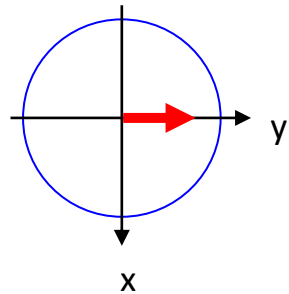
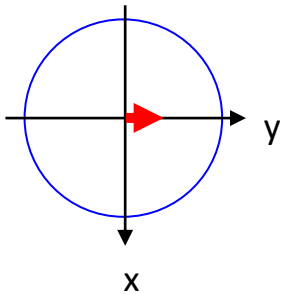
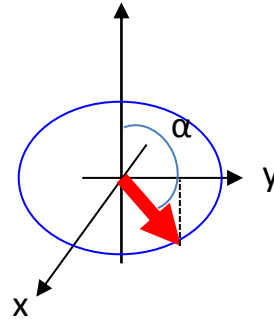
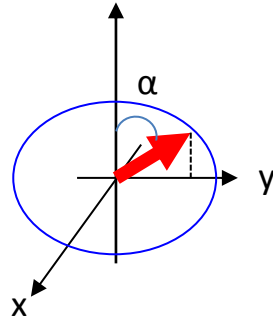
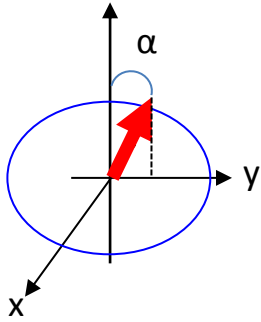
Kalibrace pulzu



t_1

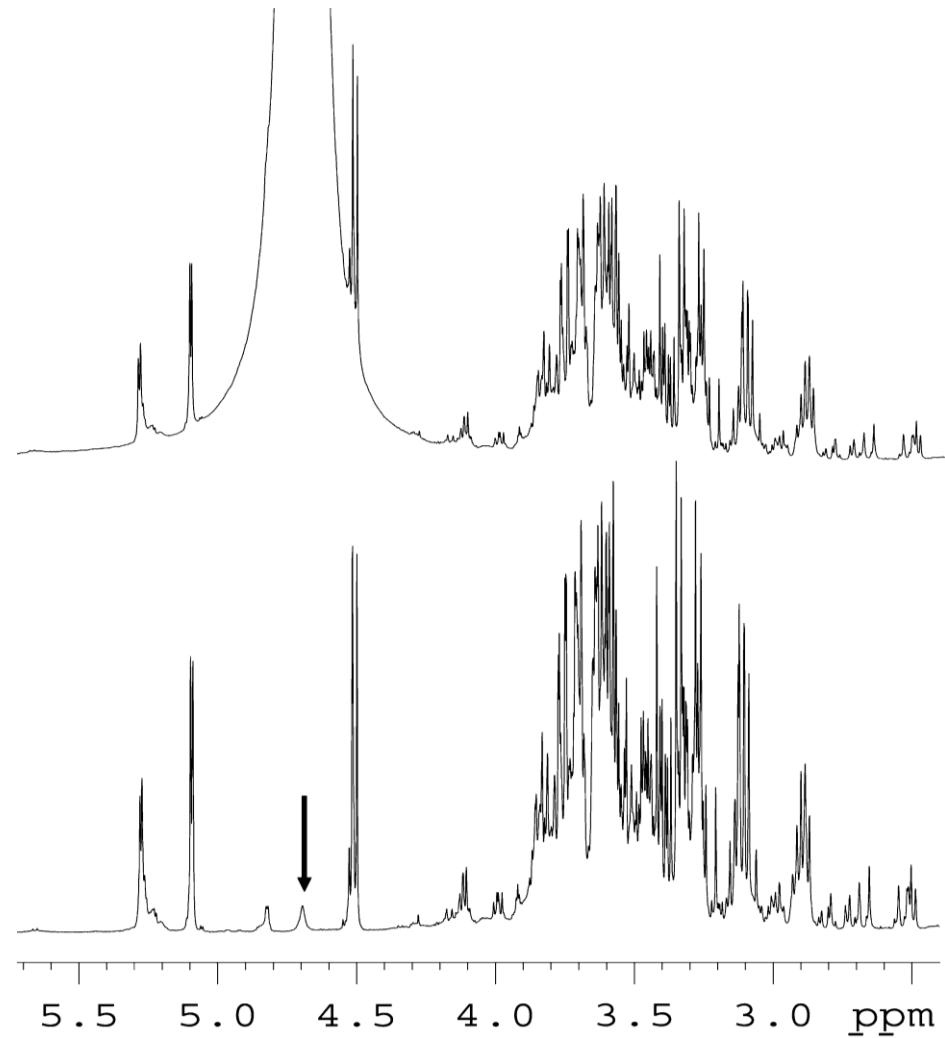
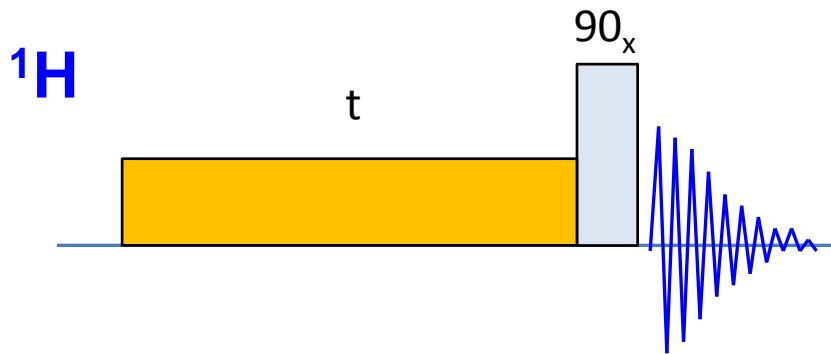
t_2

t_3

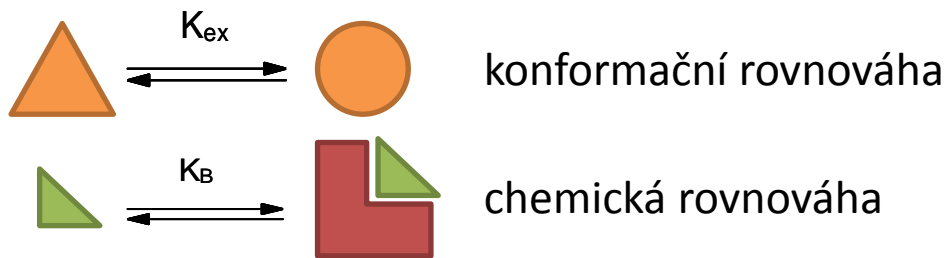
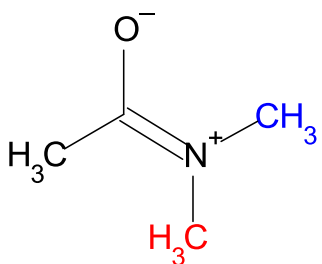


- stejný výkon, různá délka pulzu

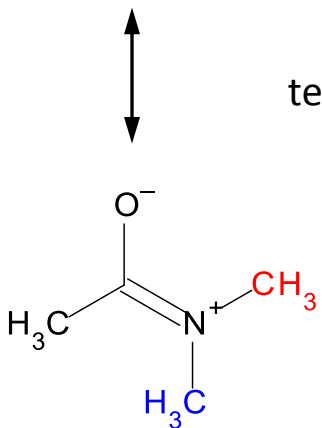
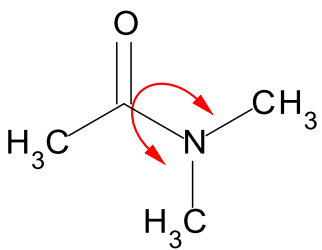
Presaturation



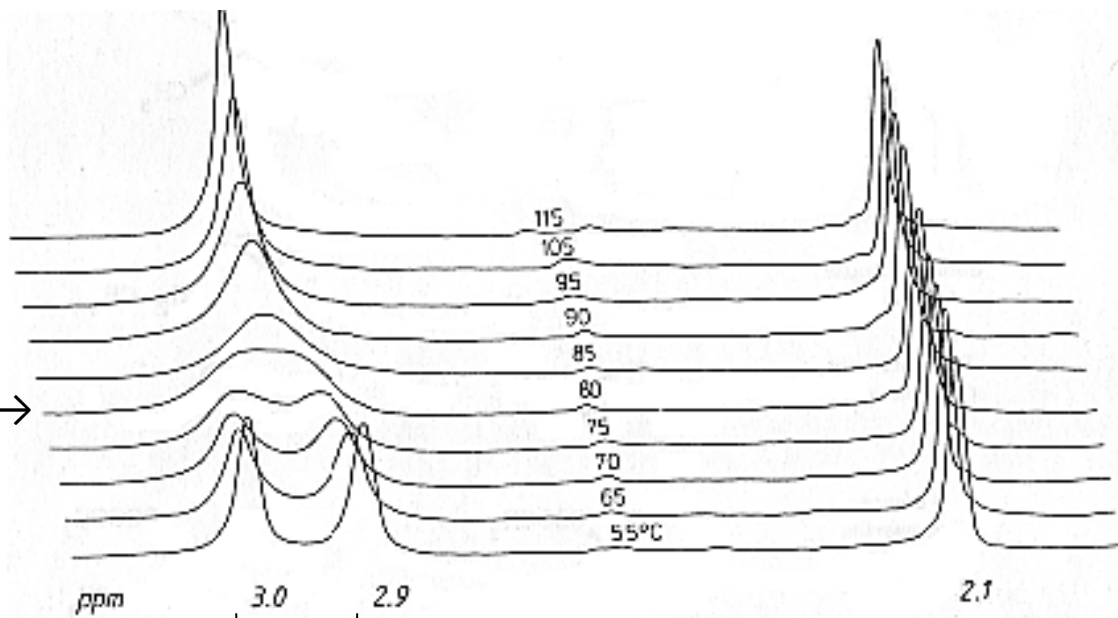
Chemická výměna



- chemická výměna – změna chemického okolí sledovaného jádra
- můžeme měřit rychlostní konstanty děje



teplota koalescence – T_c →



$\Delta\delta$ – závisí od velikosti pole

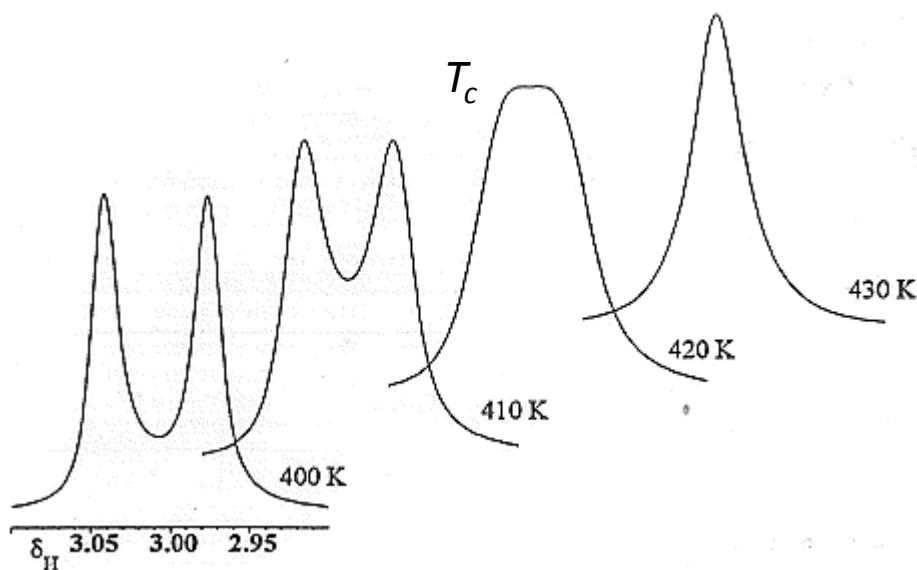
Chemická výměna

- teplota koalescence T_c – rychlost výměny k mezi jednotlivými stavy je srovnatelná s rozdílem chemických posunů $\Delta\delta$

$$k = A e^{-\frac{E_A}{RT}}$$

$$k_{T_c} = \frac{\sqrt{2\pi\Delta\delta}}{2}$$

- koalescence – 2. derivace signálu v bodě $\frac{\delta_A + \delta_B}{2} = 0$

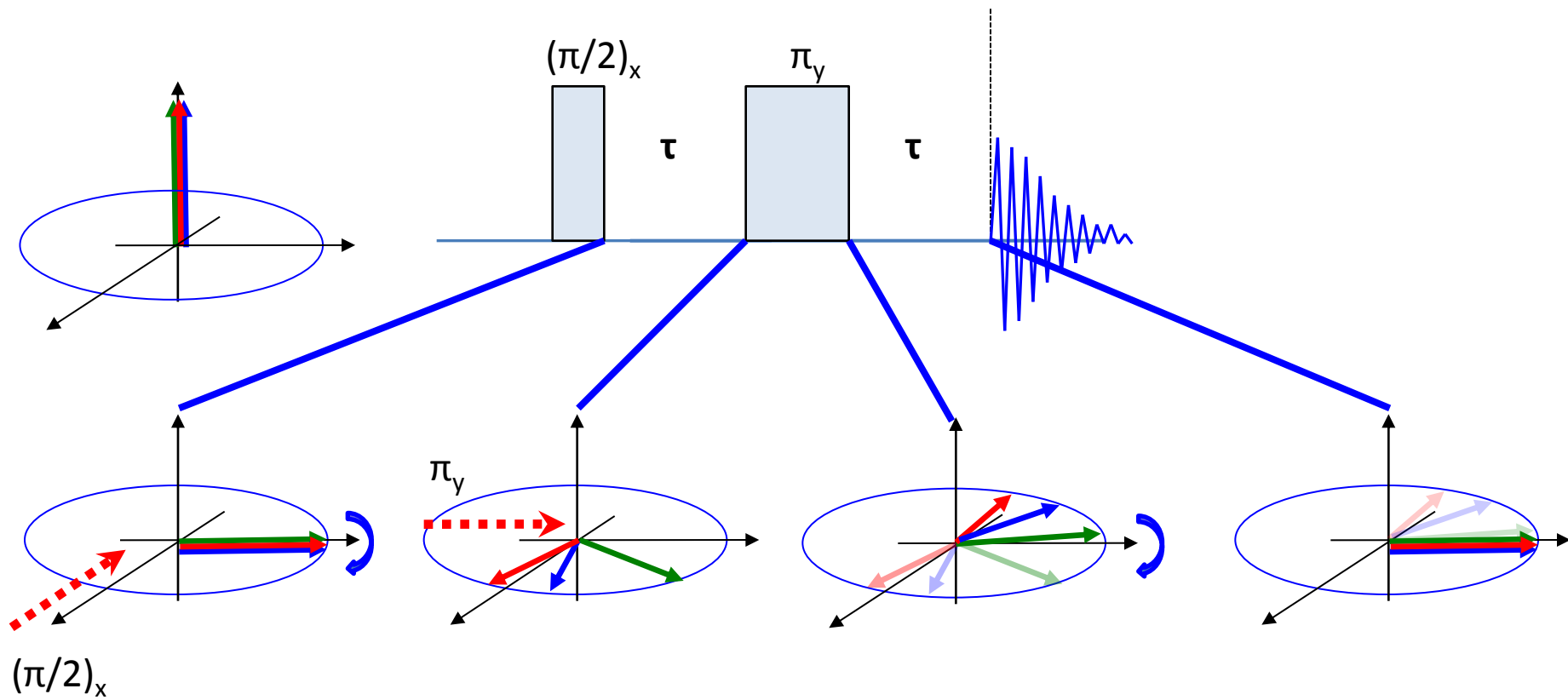


- dva režimy chemických výměn:
 $k \ll \Delta\delta$ – pomalá výměna
 $k \gg \Delta\delta$ – rychlá výměna

Spinové echo

Vývoj chemického posunu během časové periody 2τ se středovým 180° pulzem - všechny spiny se po uplynutí 2τ začínají během akvizice vyvíjet se stejnou počáteční fází = refokusace signálu.

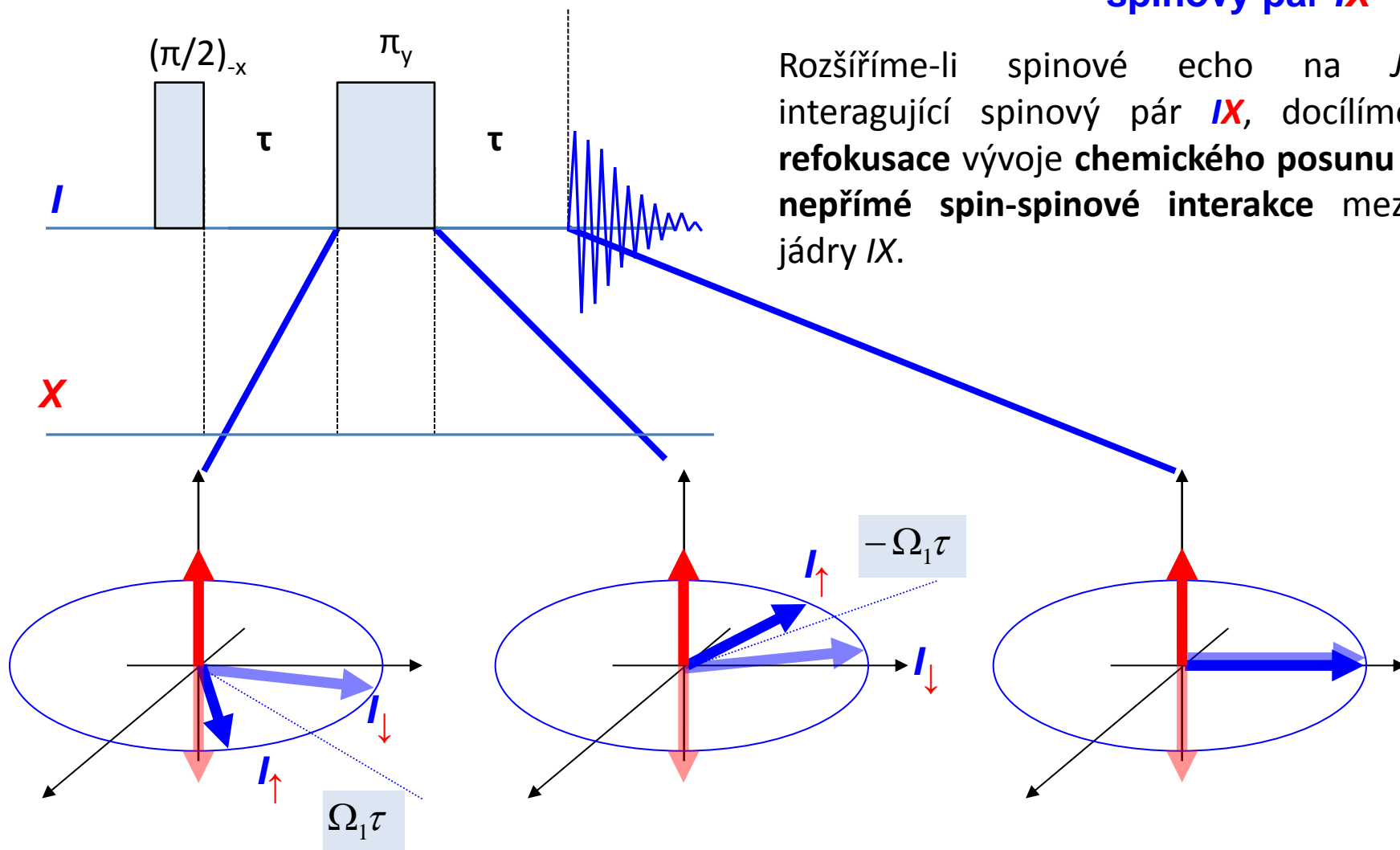
$I_1 I_2 I_3$



Heteronukleární spinové echo

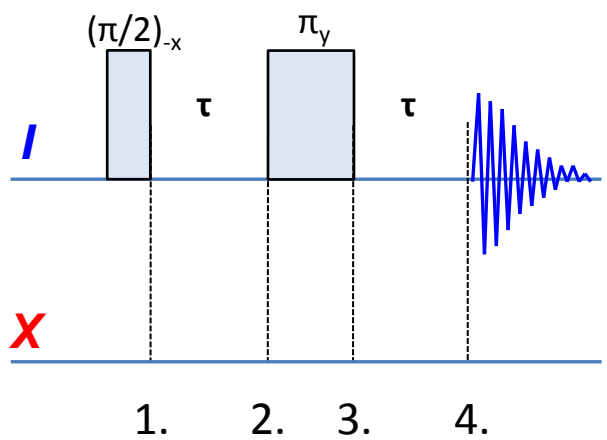
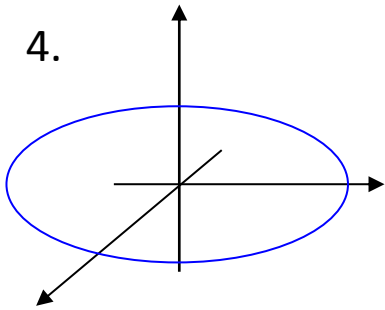
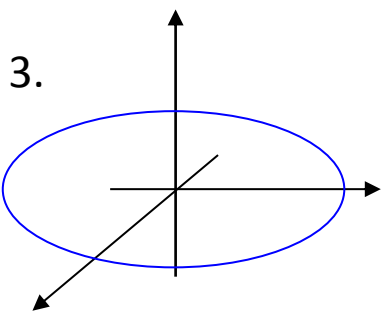
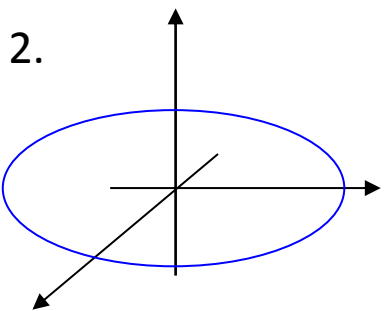
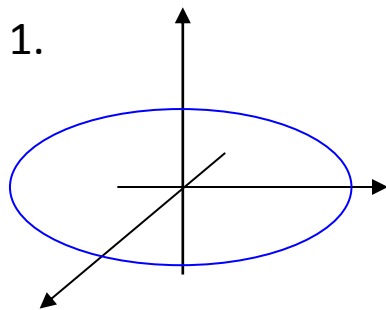
spinový pár I_X

Rozšíříme-li spinové echo na J -interagující spinový pár I_X , docílíme **refokusace** vývoje **chemického posunu** i **nepřímé spin-spinové interakce** mezi jádry I_X .

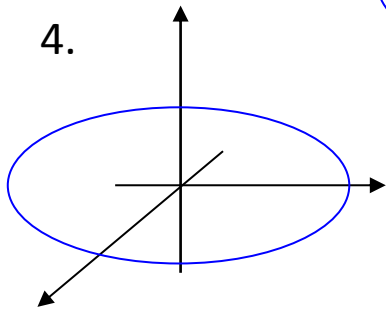
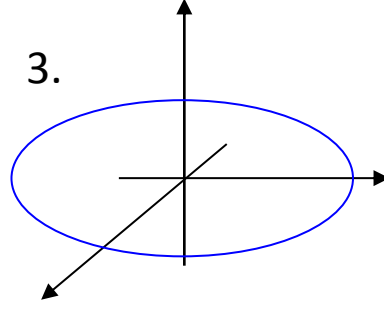
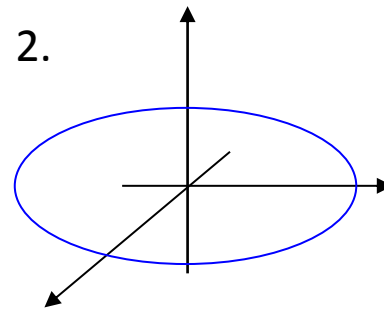
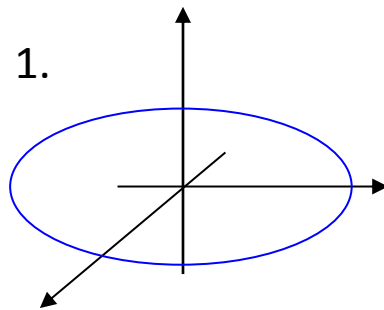


Heteronukleární spinové echo

vývoj chemického posunu

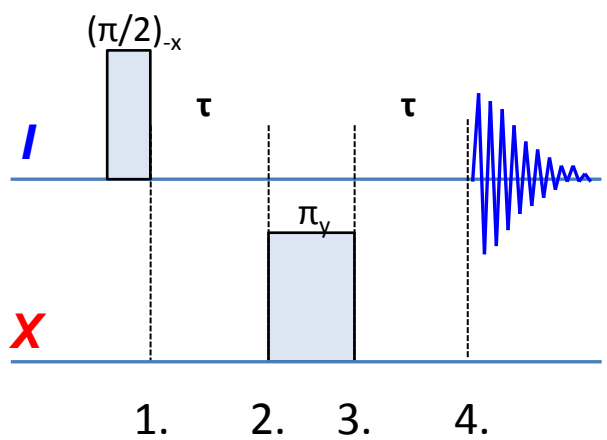
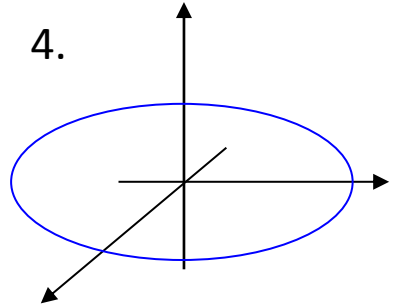
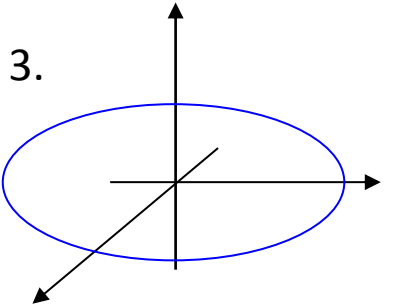
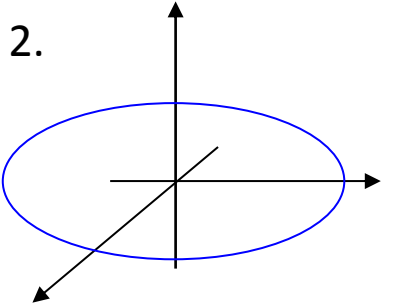
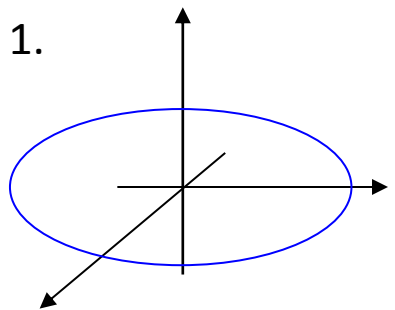


vývoj J -interakce

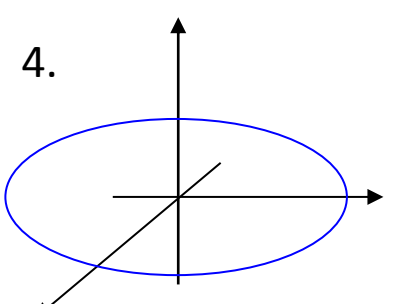
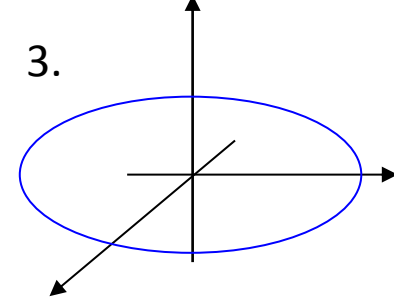
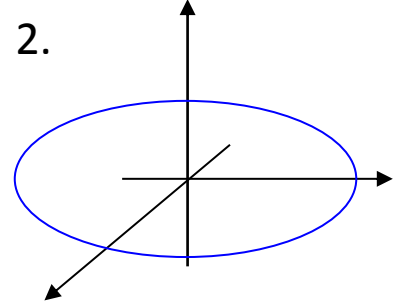
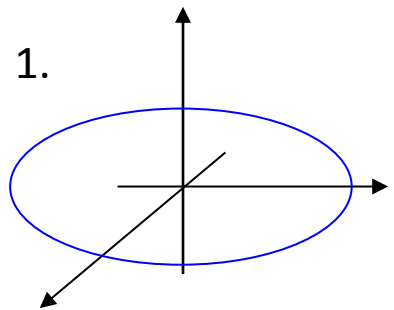


Heteronukleární spinové echo

vývoj chemického posunu



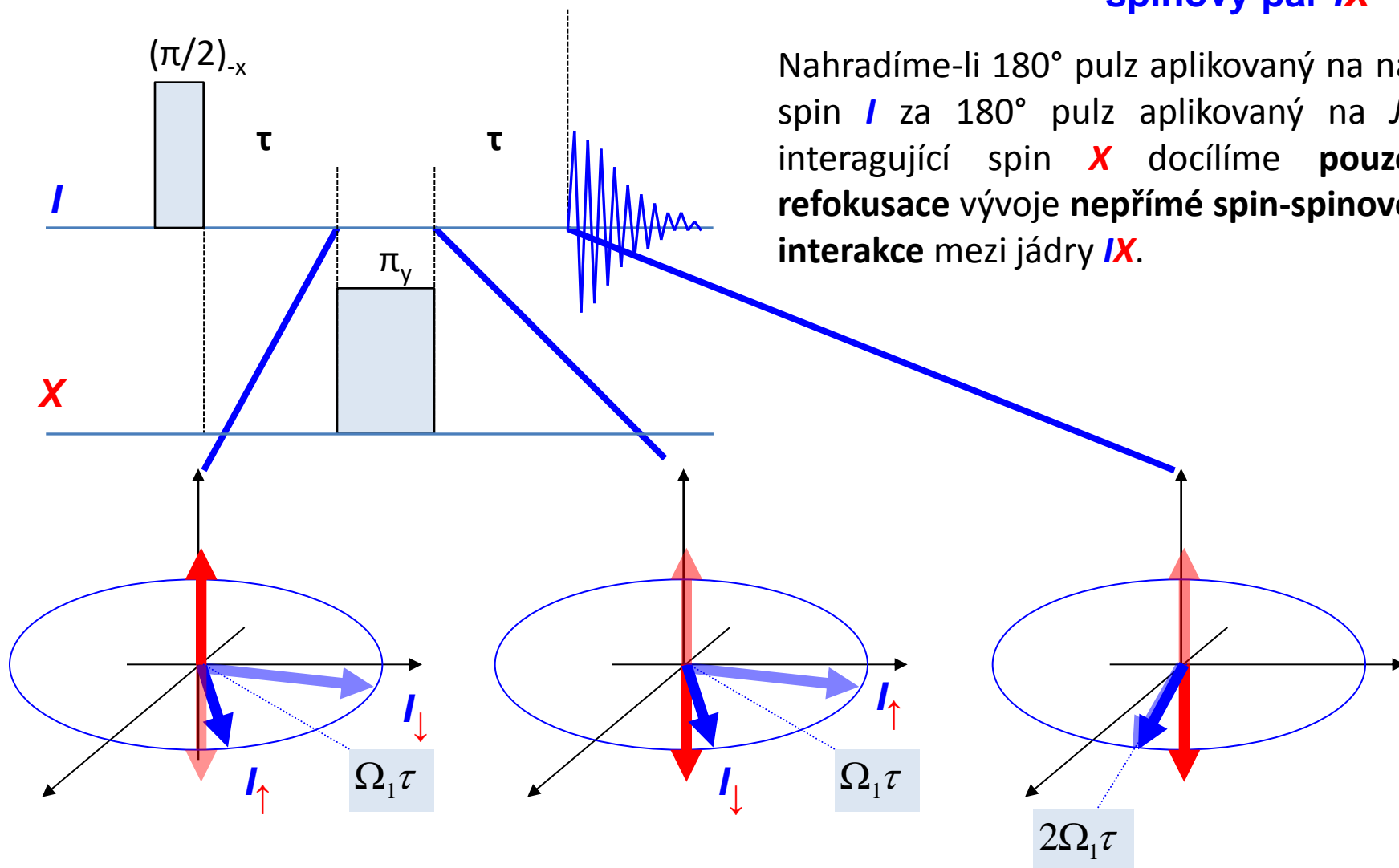
vývoj J -interakce



Heteronukleární spinové echo

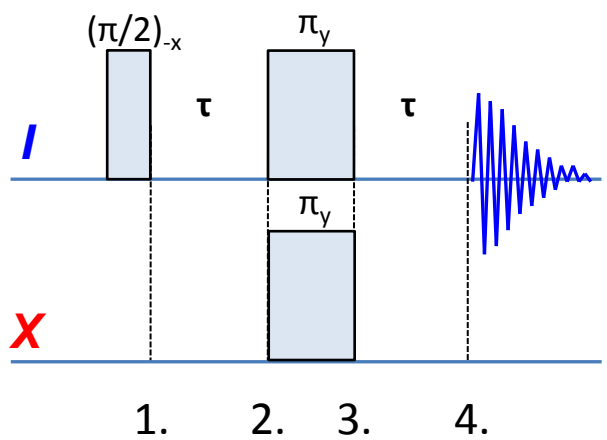
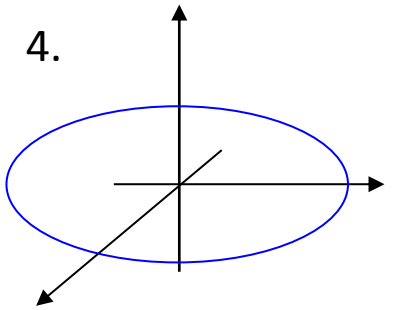
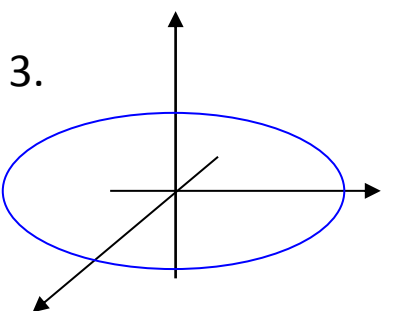
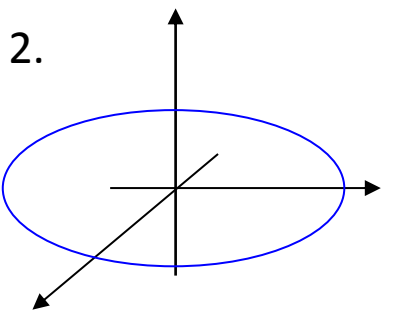
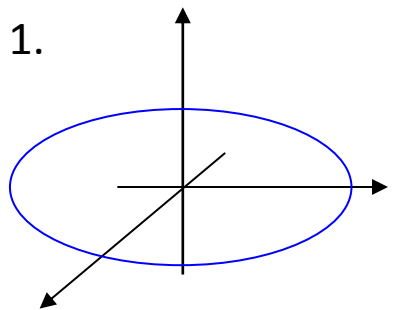
spinový pár I X

Nahradíme-li 180° pulz aplikovaný na spin I za 180° pulz aplikovaný na J -interagující spin X docílíme **pouze refokusace** vývoje **nepřímé spin-spinové interakce** mezi jádry I X .

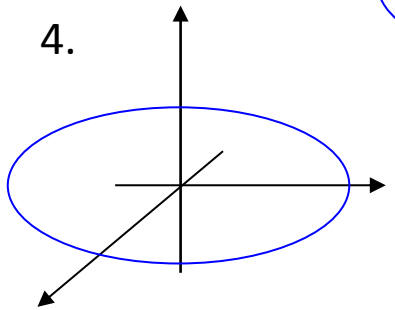
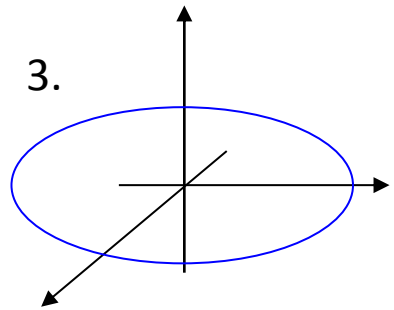
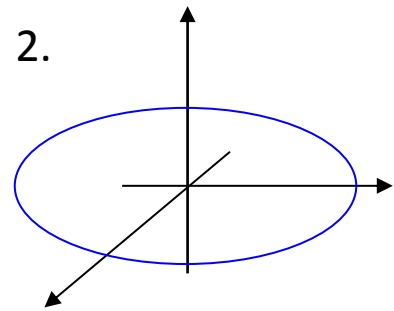
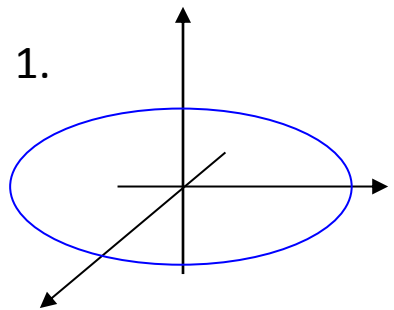


Heteronukleární spinové echo

vývoj chemického posunu



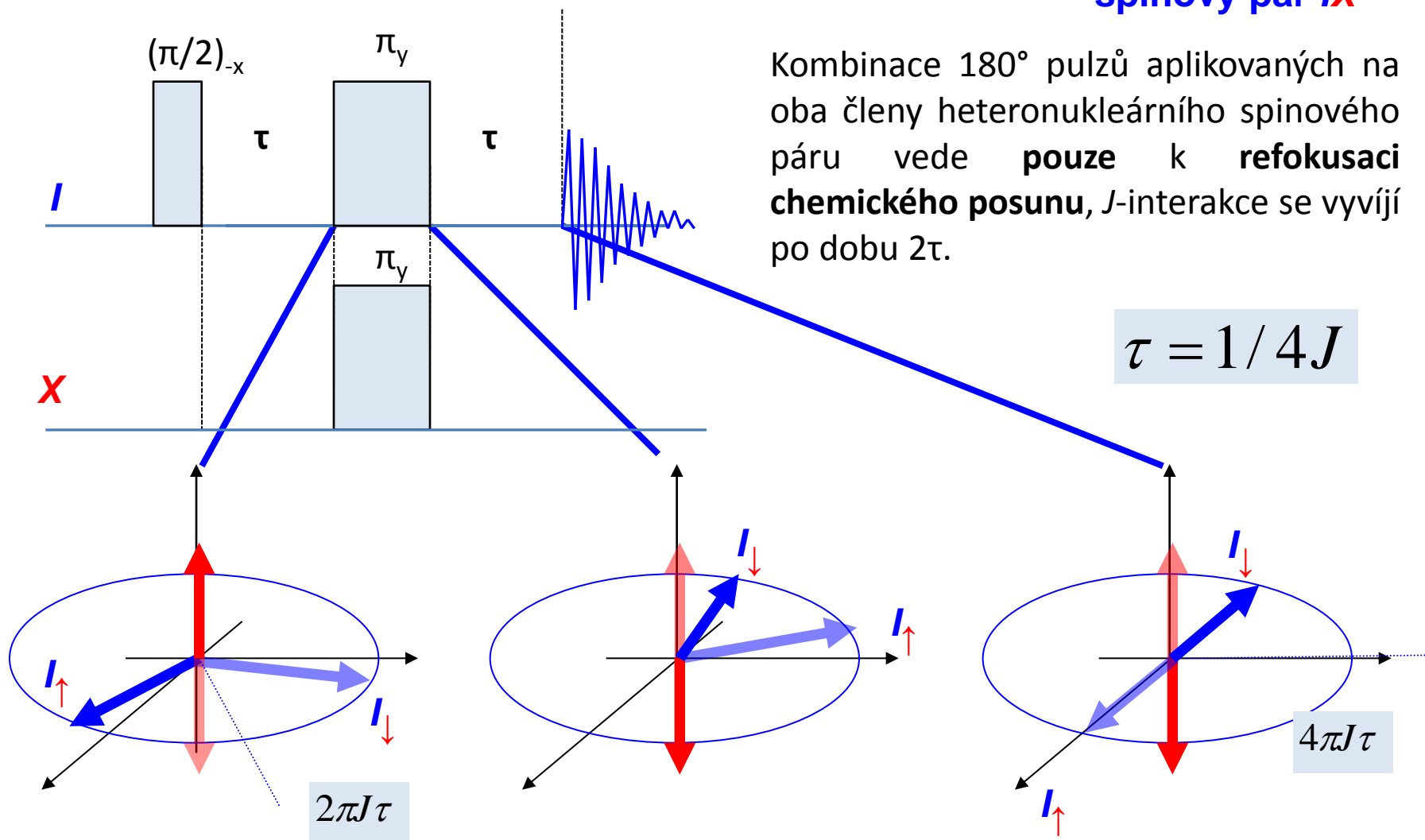
vývoj J -interakce



Heteronukleární spinové echo

spinový pár I_X

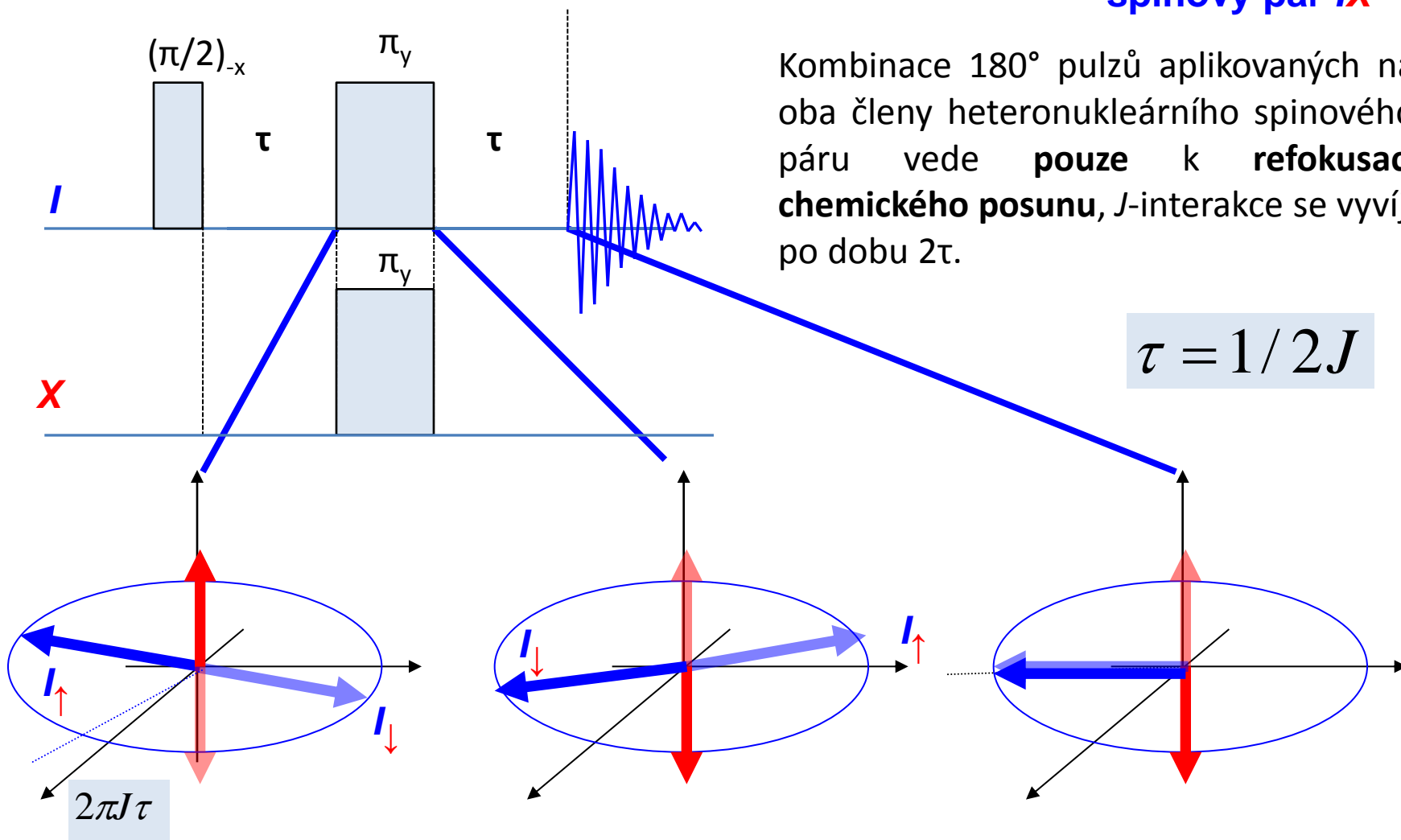
Kombinace 180° pulzů aplikovaných na oba členy heteronukleárního spinového páru vede **pouze** k **refokusaci chemického posunu**, J -interakce se vyvíjí po dobu 2τ .



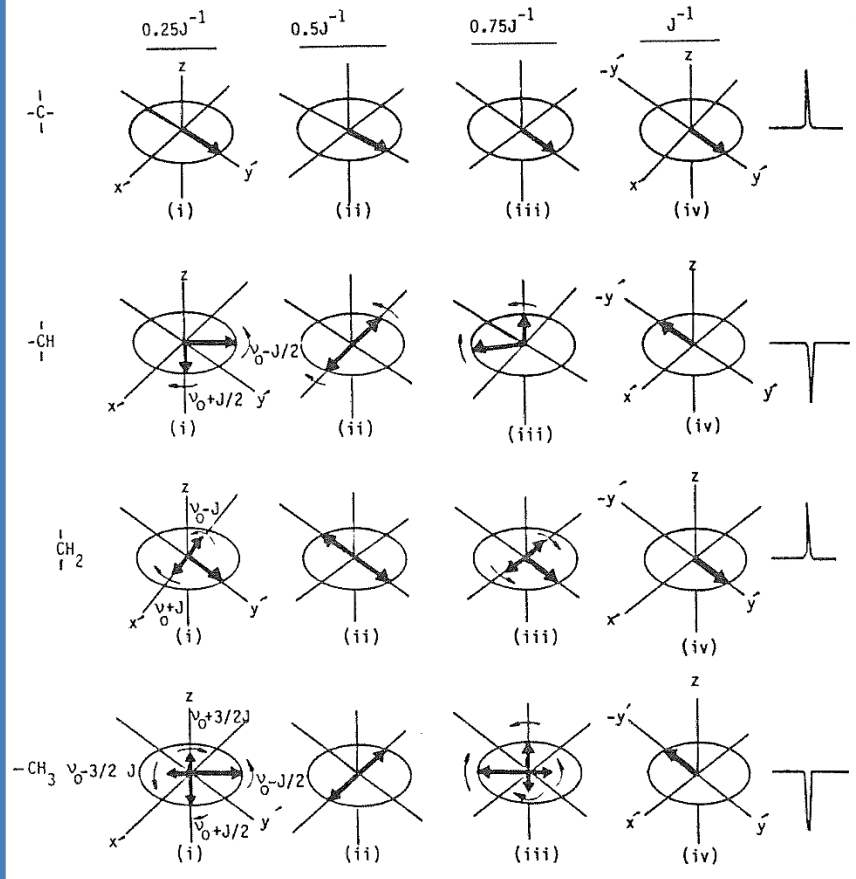
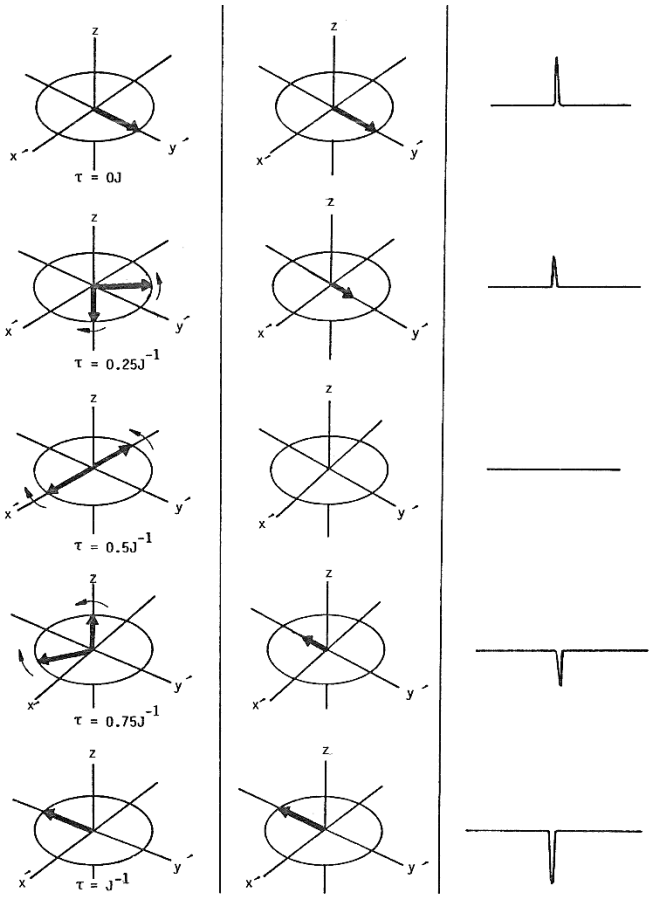
Heteronukleární spinové echo

spinový pár I X

Kombinace 180° pulzů aplikovaných na oba členy heteronukleárního spinového páru vede **pouze** k **refokusaci chemického posunu**, J -interakce se vyvíjí po dobu 2τ .

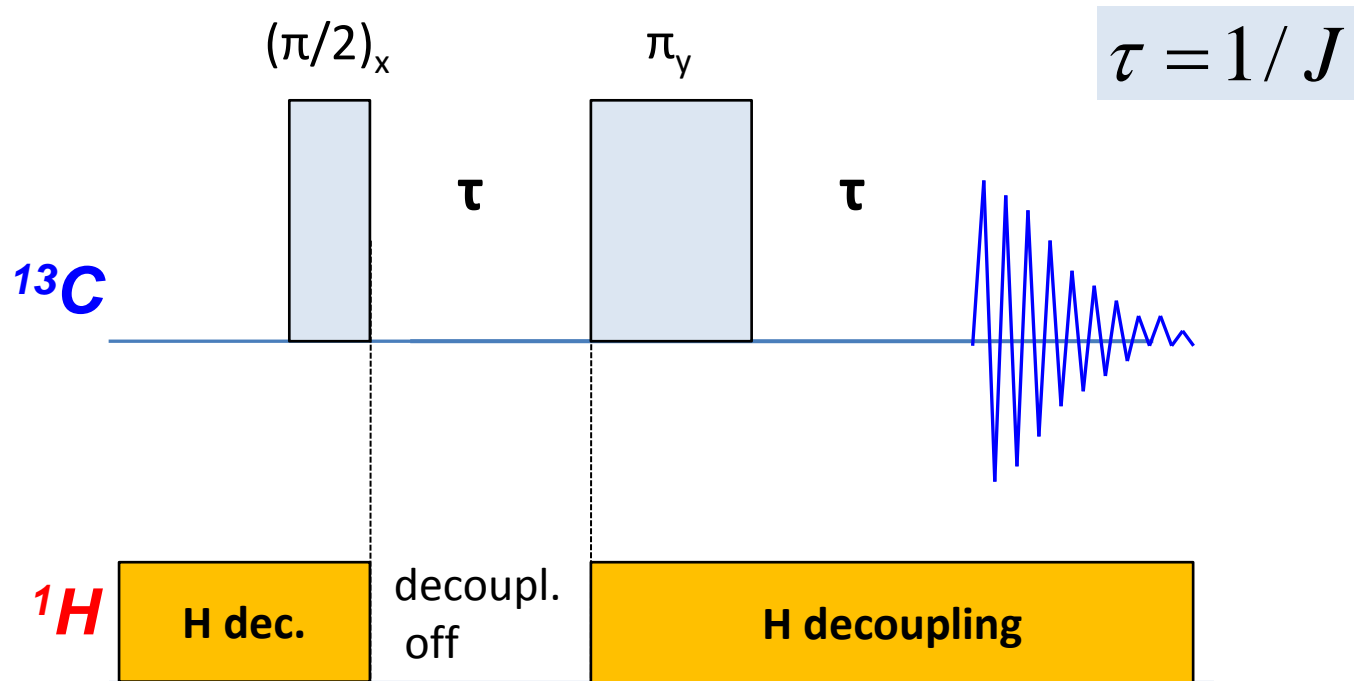


I-S (¹H-¹³C)

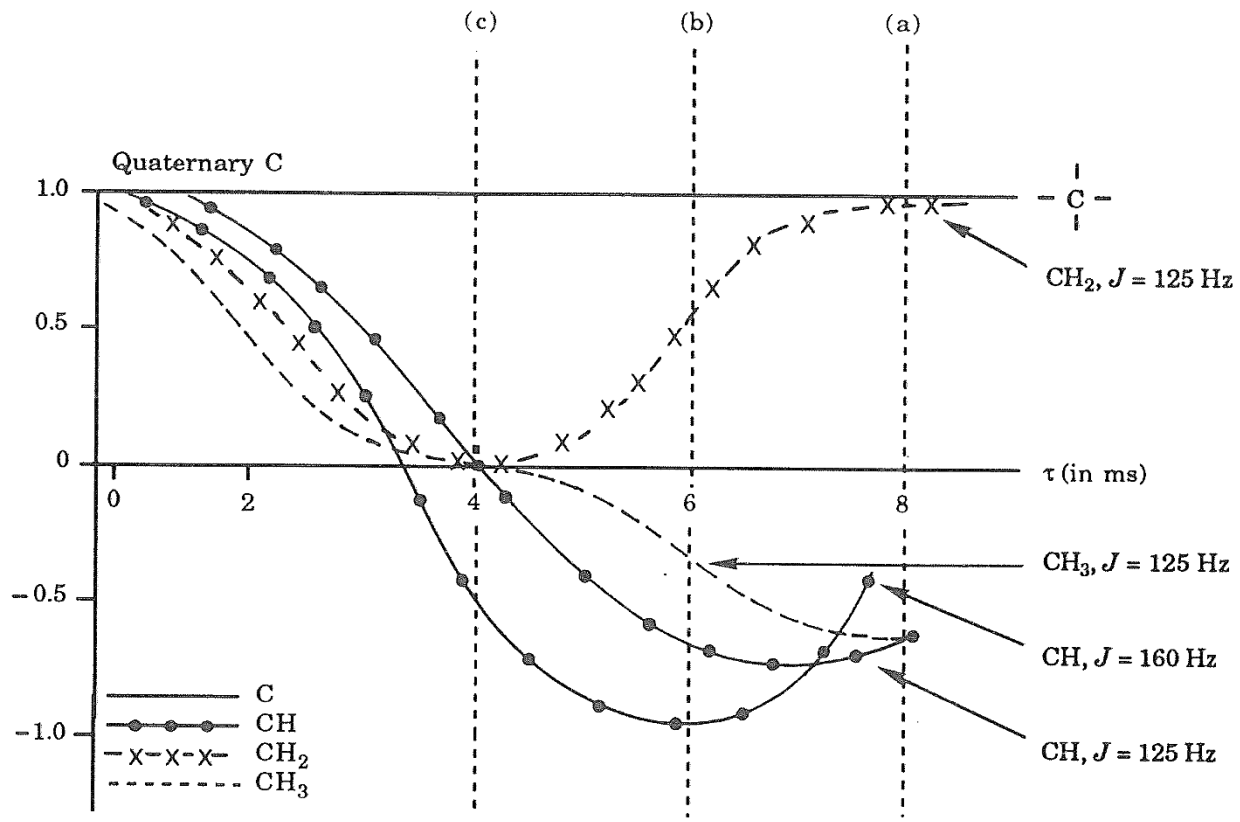


	$\frac{\nu_b - \nu_a}{2\pi} = J$
	$\frac{\nu_b - \nu_a}{2\pi} = J$ $\frac{\nu_c - \nu_a}{2\pi} = 2J$
	$\frac{\nu_b - \nu_a}{2\pi} = J$ $\frac{\nu_c - \nu_a}{2\pi} = 2J$ $\frac{\nu_d - \nu_a}{2\pi} = 3J$

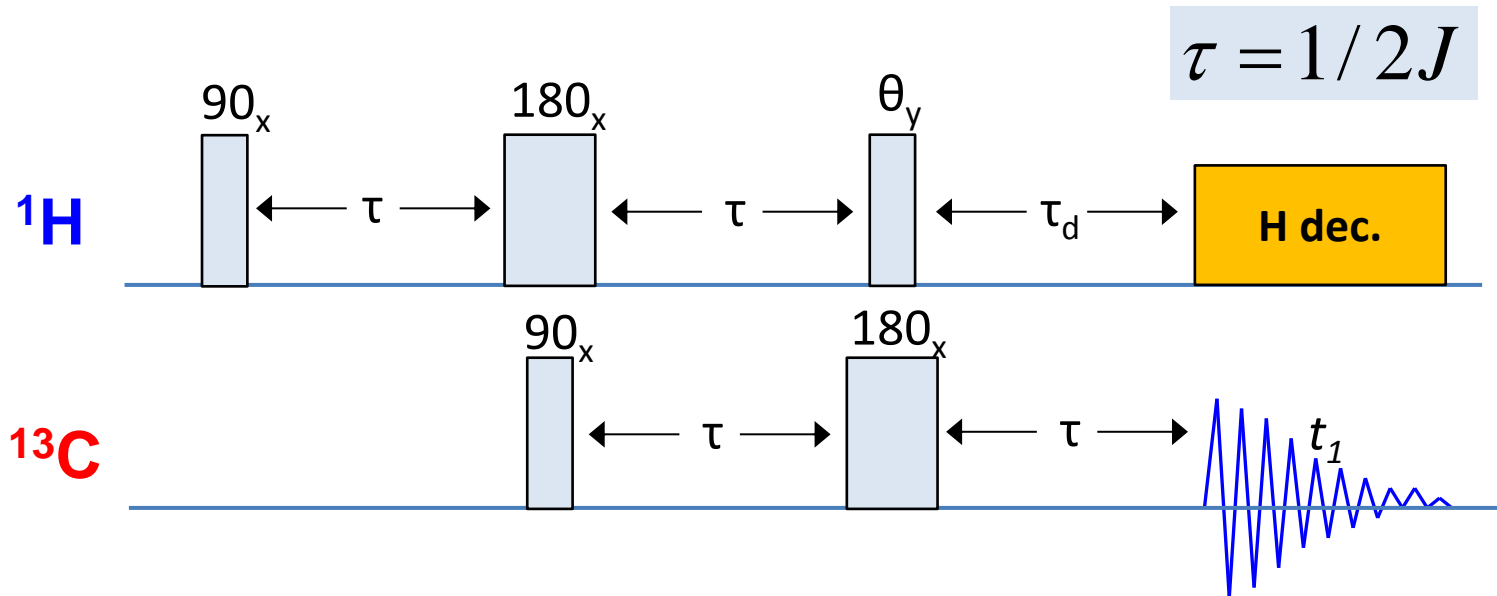
APT – Attached proton test



- Editační technika založená na vývoji systému dle počtu H atomů vázaných na ^{13}C



DEPT – Distortionless Enhancement by Polarization Transfer



$\theta = 45^\circ$ - ve spektru jsou všechny signály pozitivní

$\theta = 90^\circ$ - ve spektru jsou pouze signály CH

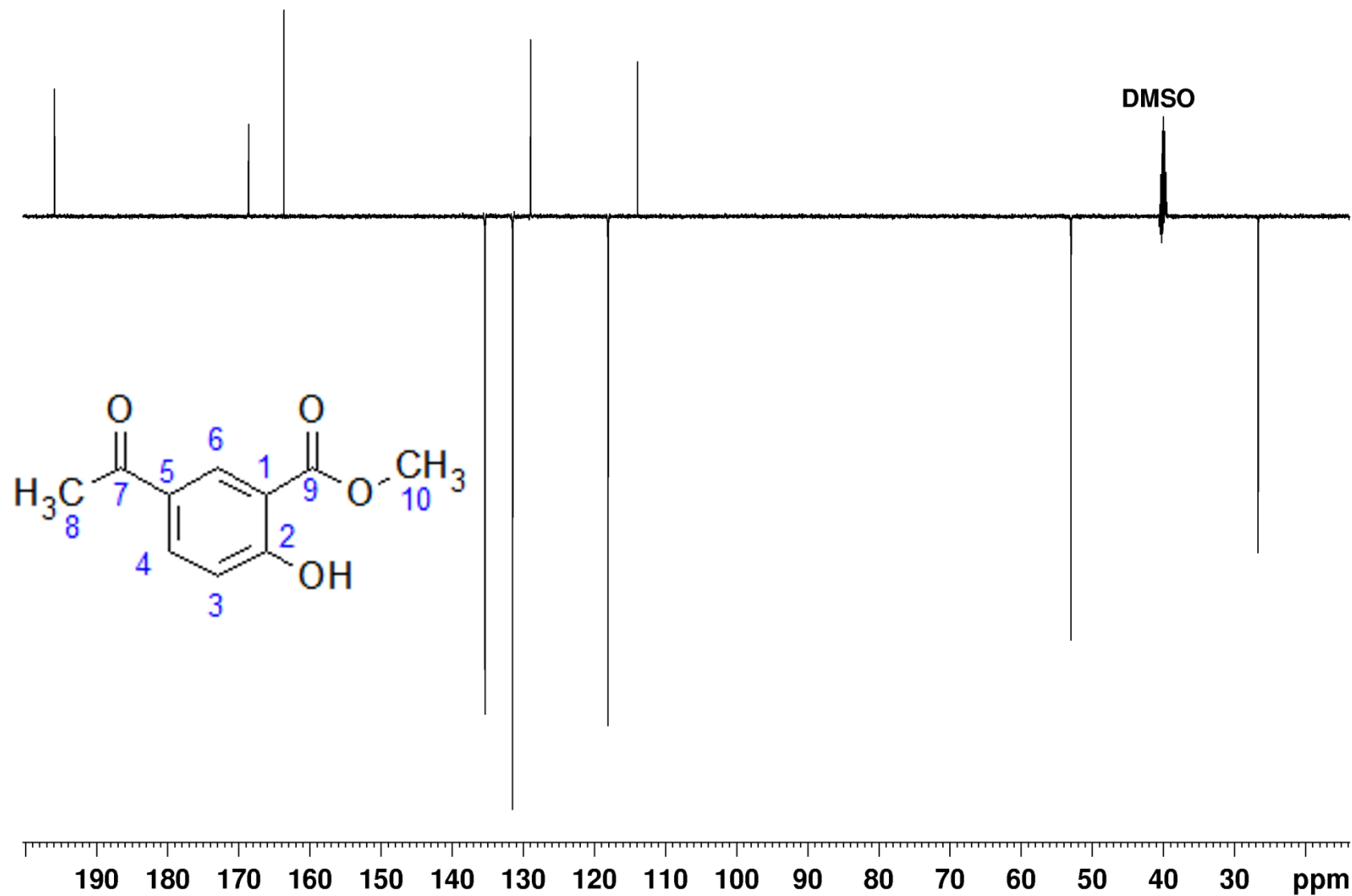
$\theta = 135^\circ$ - signály CH_3 a CH (+) mají opačnou fázi než CH_2 (-)

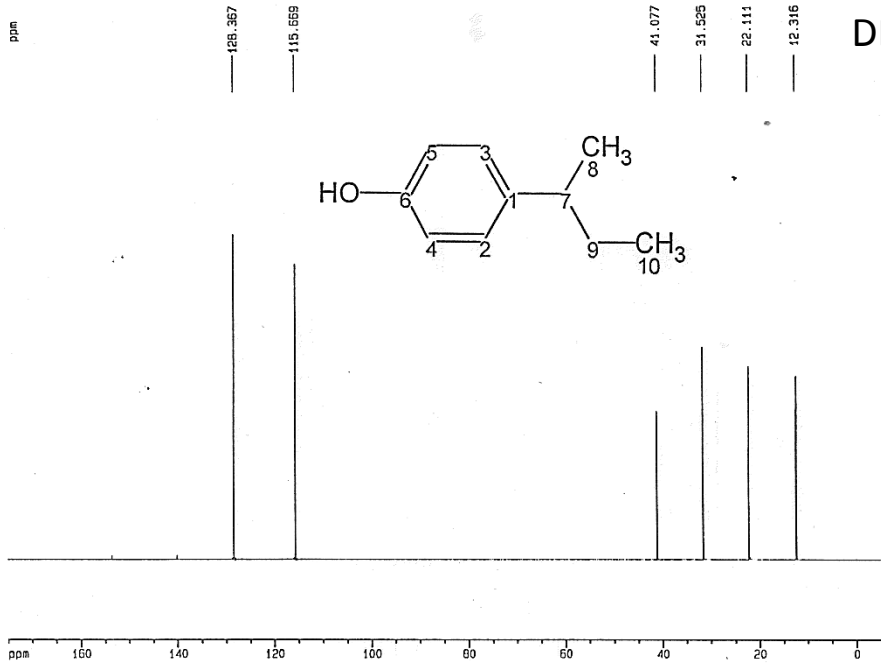
- Editační technika založená na přenosu polarizace

DEPT – Distortionless Enhancement by Polarization Transfer

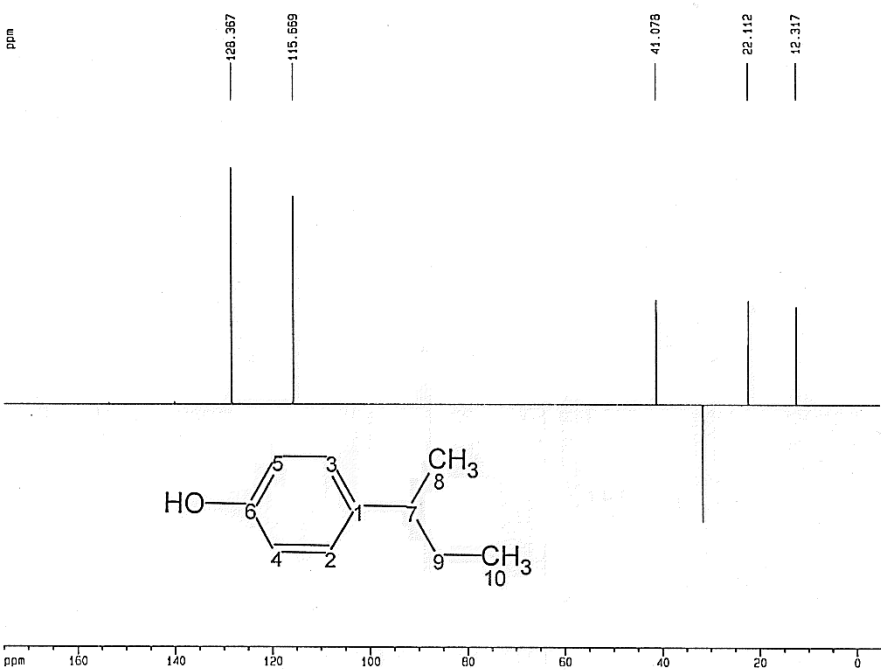
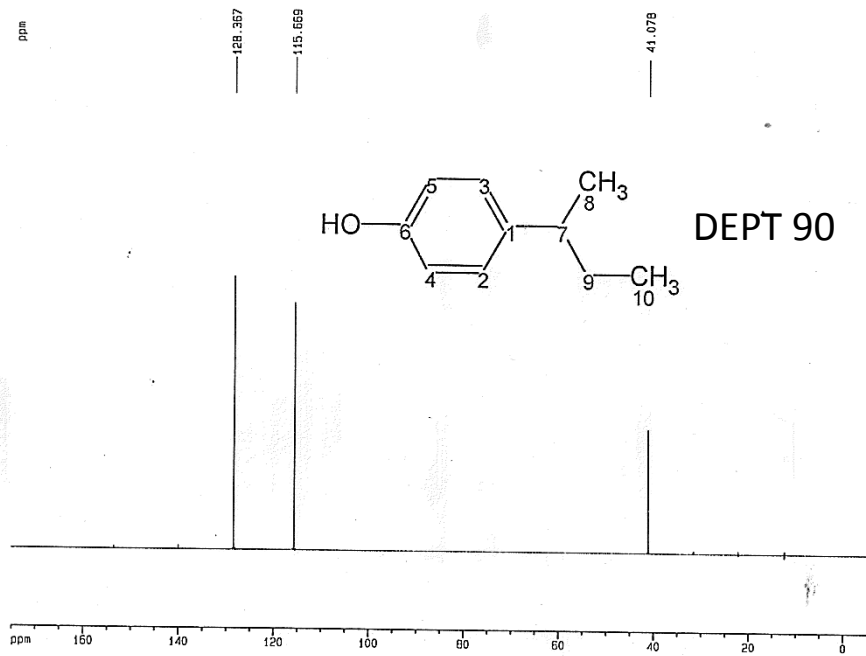
	CH	CH ₂	CH ₃		C _q
45	+	+	+		0
90	+	0	0		0
135	+	-	+		0
¹³ C	+	+	+		+

^{13}C APT





DEPT – 4-(sec.butyl) fenol



	CH	CH ₂	CH ₃		Cq
45	+	+	+		0
90	+	0	0		0
135	+	-	+		0
¹³ C	+	+	+		+

DEPT 135