

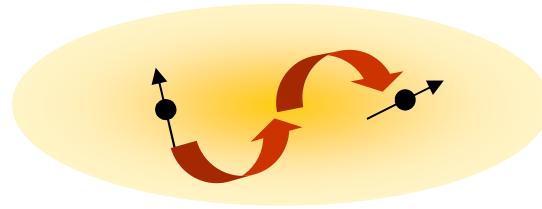
Metody dvojí rezonance

Heteronukleární J interakce, ^{13}C spektra, dekapling,
experimenty APT a DEPT

Heteronukleární J interakce

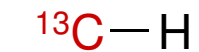
Nepřímá spin-spinová interakce

scalar coupling



interakce zprostředkovaná vazebnými elektrony

jádro „cítí“ spinový stav okolních NMR aktivních jader

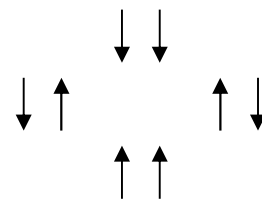
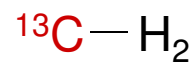


$m = -1/2$ ↓

$m = +1/2$ ↑

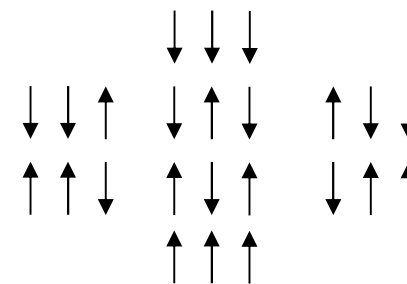
dublet

1 : 1



triplet

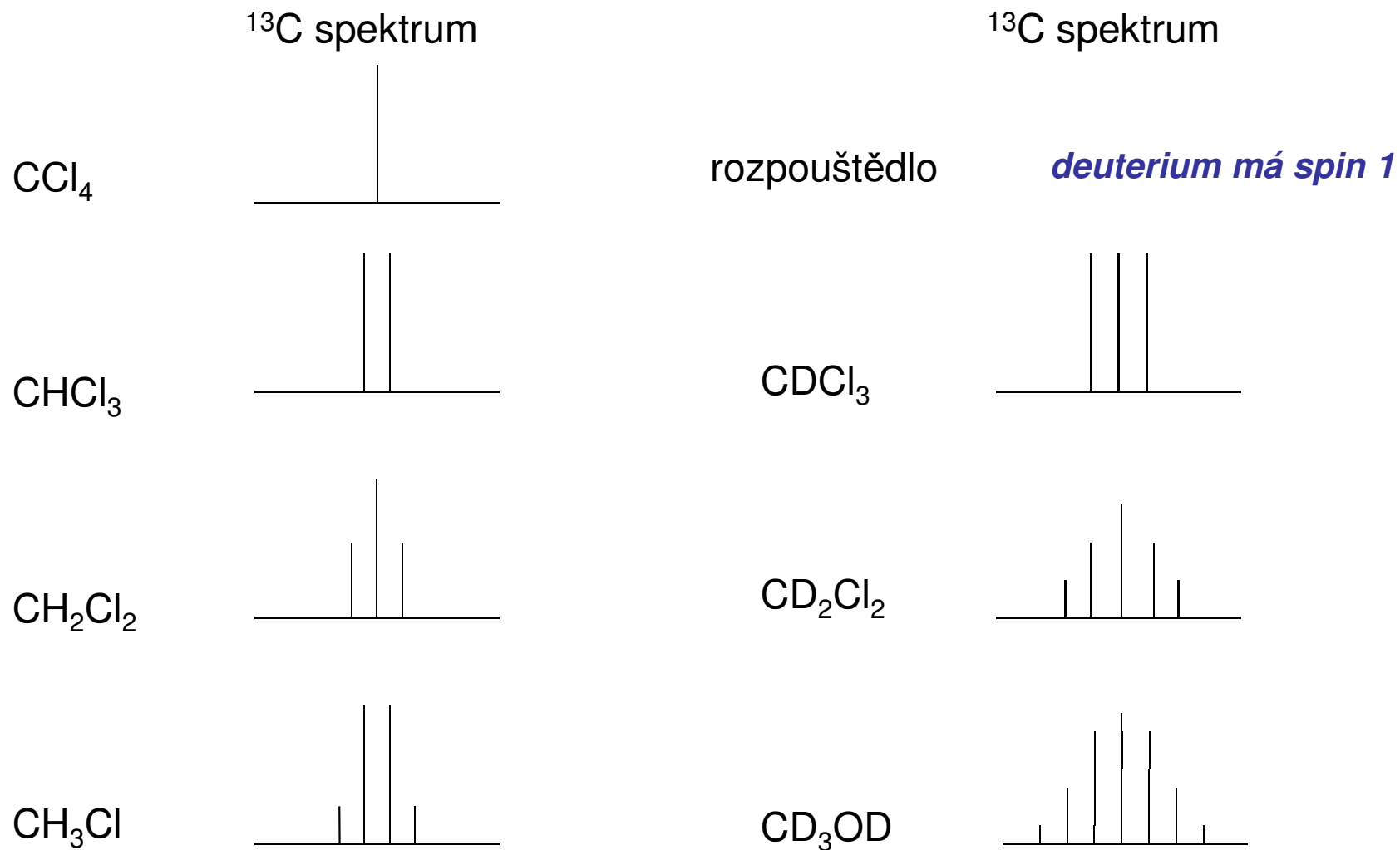
1 : 2 : 1



kvartet

1 : 3 : 3 : 1

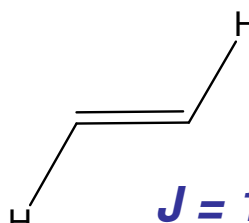
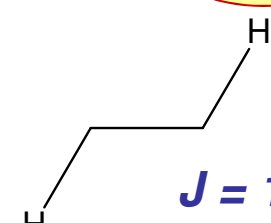
J interakce $^{13}\text{C} - ^1\text{H}$ (^2H)



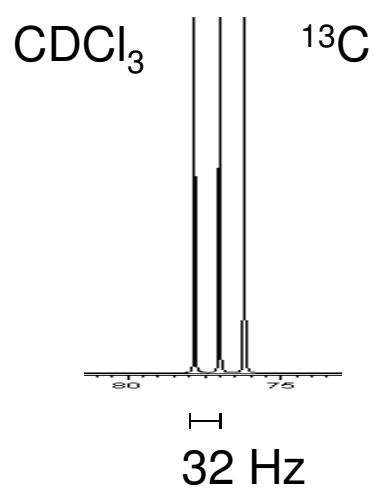
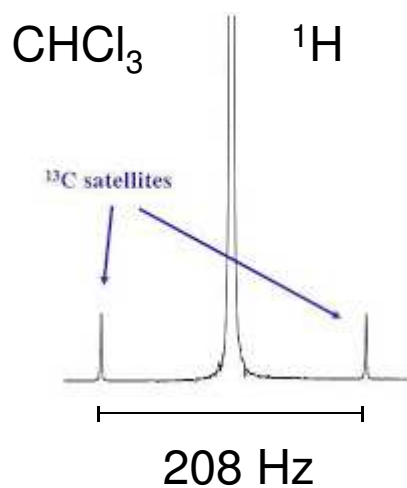
Velikost J interakce

velmi obecně závisí na

- hybridizaci

	$\text{H}_3\text{C}-\text{CH}_3$	$\text{H}_2\text{C}=\text{CH}_2$	C_6H_6	$\text{HC}\equiv\text{CH}$
$^1J_{\text{CH}}$	124,9	156,4	158,4	249,0
$^3J_{\text{HH}}$		 <p>$J = 17 \text{ Hz}$</p>		 <p>$J = 10 \text{ Hz}$ (při zabráněné rotaci)</p>

- gyromagnetickém poměru jader v interakci



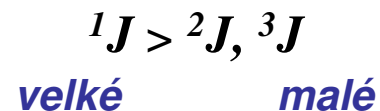
$$\frac{J_{\text{CH}}}{J_{\text{CD}}} = \frac{\gamma_{\text{H}}}{\gamma_{\text{D}}}$$

$$= 6.51$$

Velikost J interakce

velmi obecně závisí na

- **počtu vazeb**



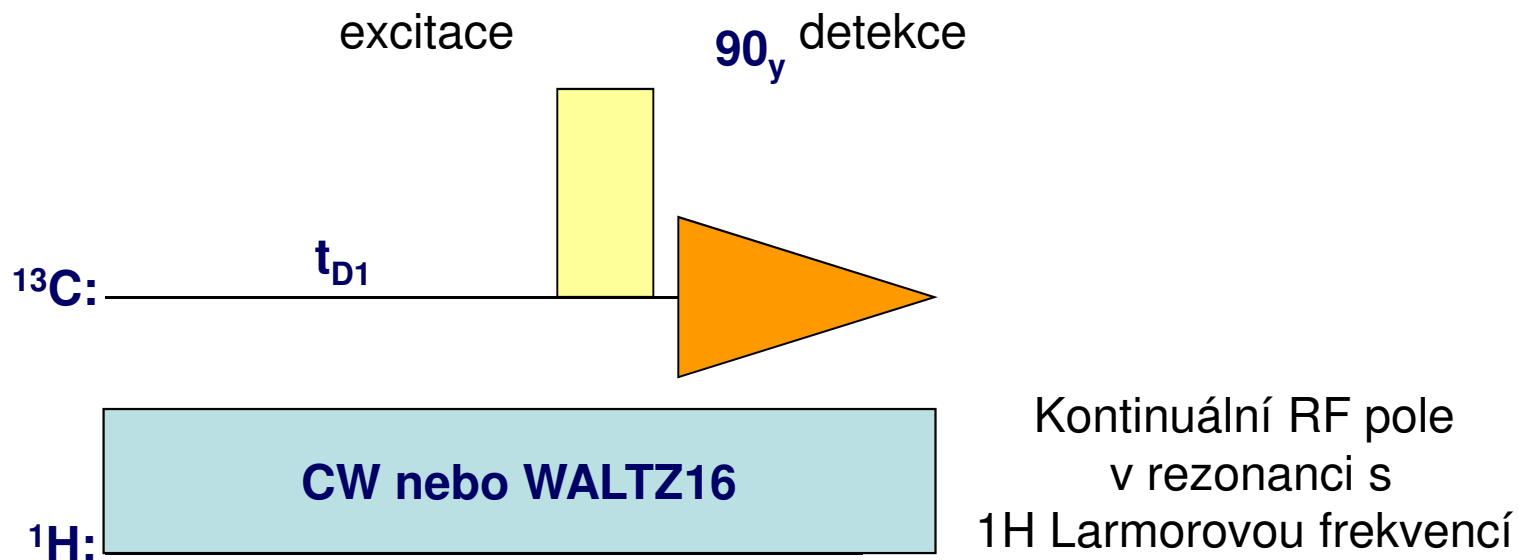
- **geometrii – „překryvu orbitalů“**

větší/lepší překryv orbitalů ⇒ větší J

- Karplusova křivka
- cis – trans
- axiální – ekvatoriální

- **elektronegativitě a dalších faktorech**

Dekapling a ^{13}C spektrum



saturace – vyrovnání obsazenosti hladin

nukleární Overhauserův efekt

NOE navýšení (až o 199%) intenzity
 ^{13}C s přímo vázanými vodíky

závisí na relaxaci - lokální pohyblivosti

^{13}C spektra nejsou kvantitativní

- NOE
- nedostatečná relaxace

měření lze nastavit i pro kvantitativní odezvu

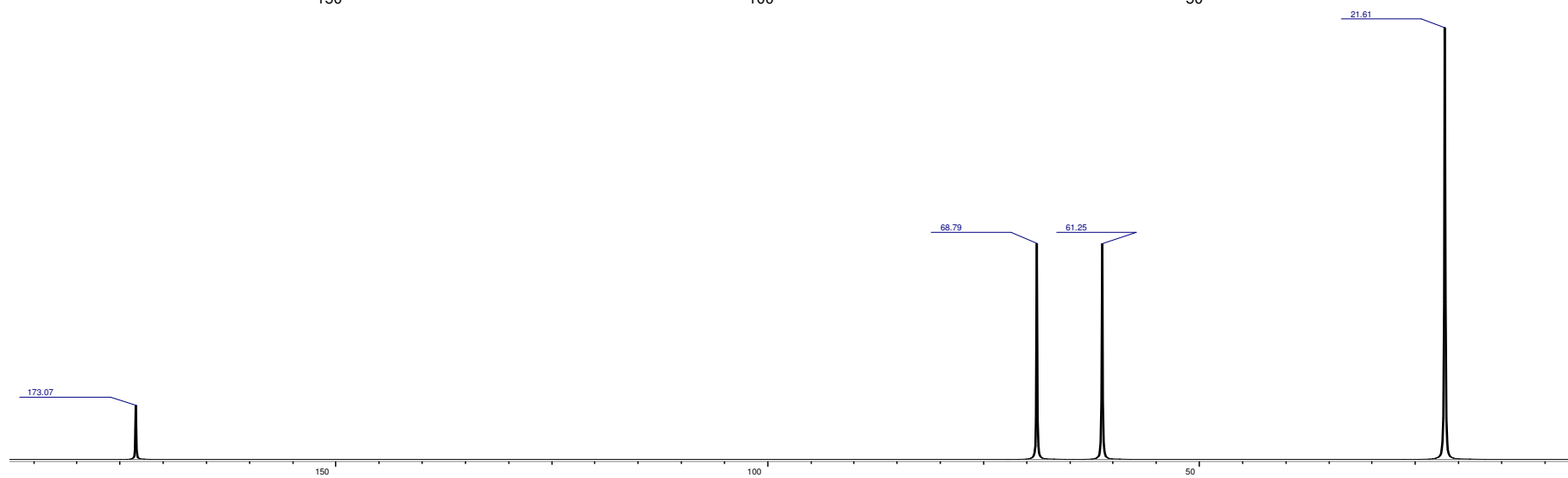
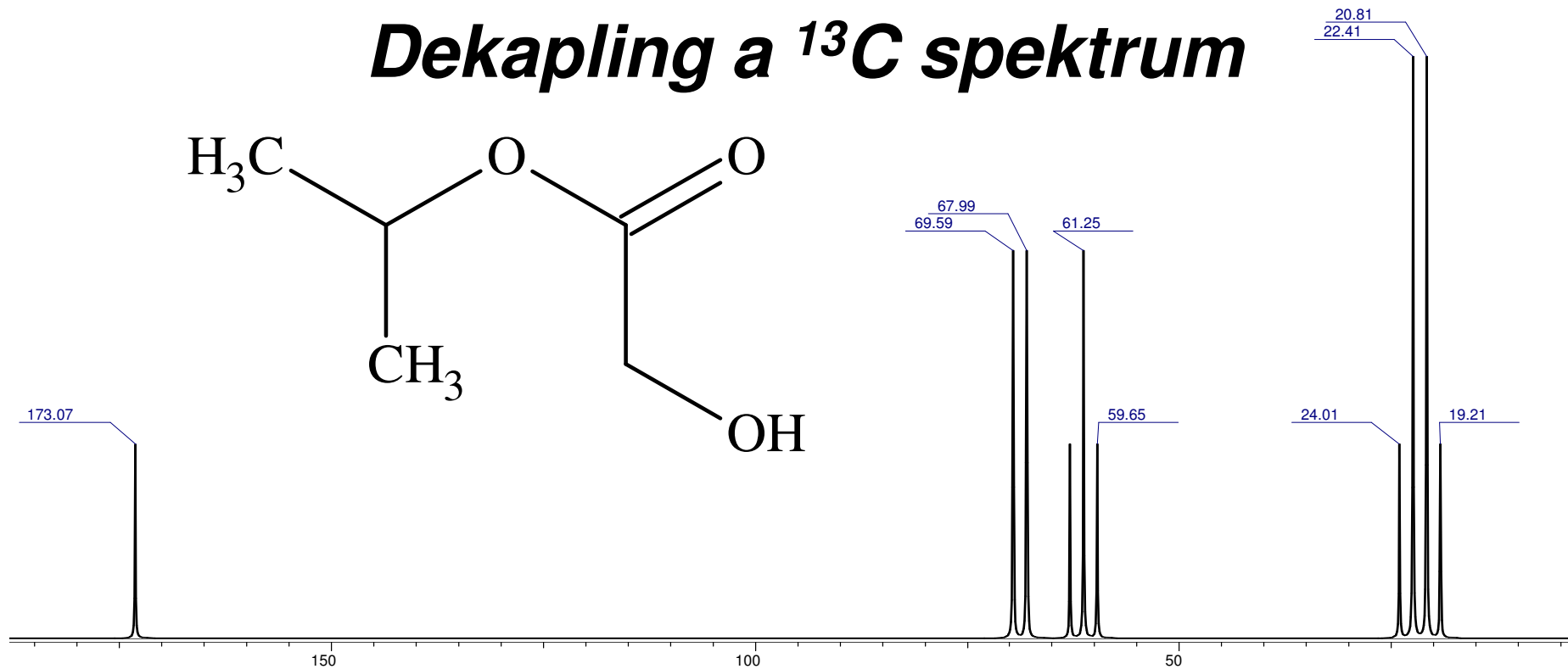
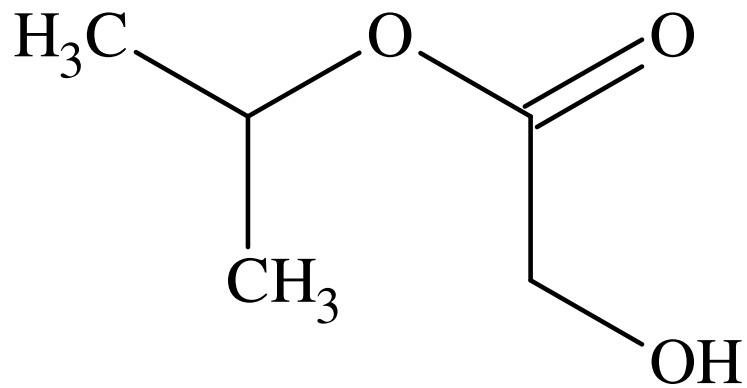
rychlé přeskoky

efektivně spin 0

„zrušení“ J interakce

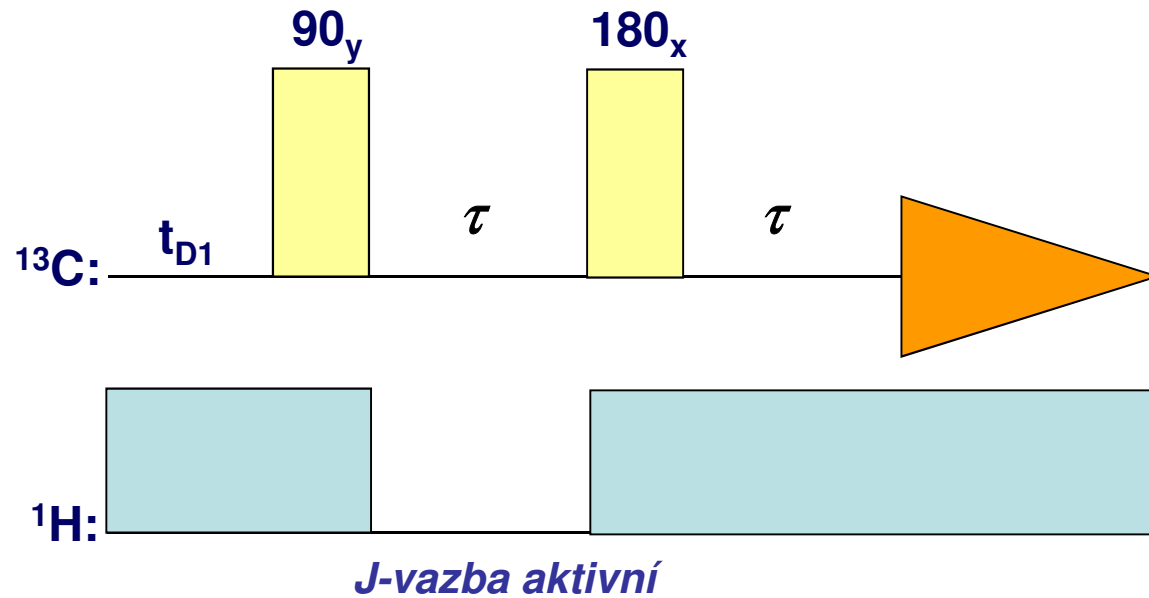
decoupling

Dekapling a ^{13}C spektrum

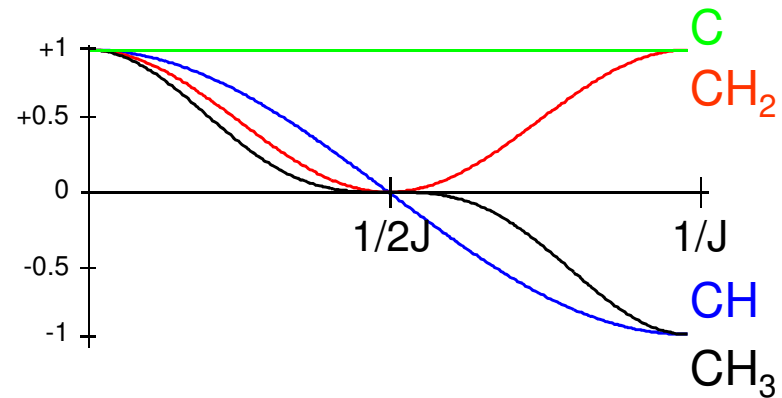


Využití J vazby

APT – attached proton test

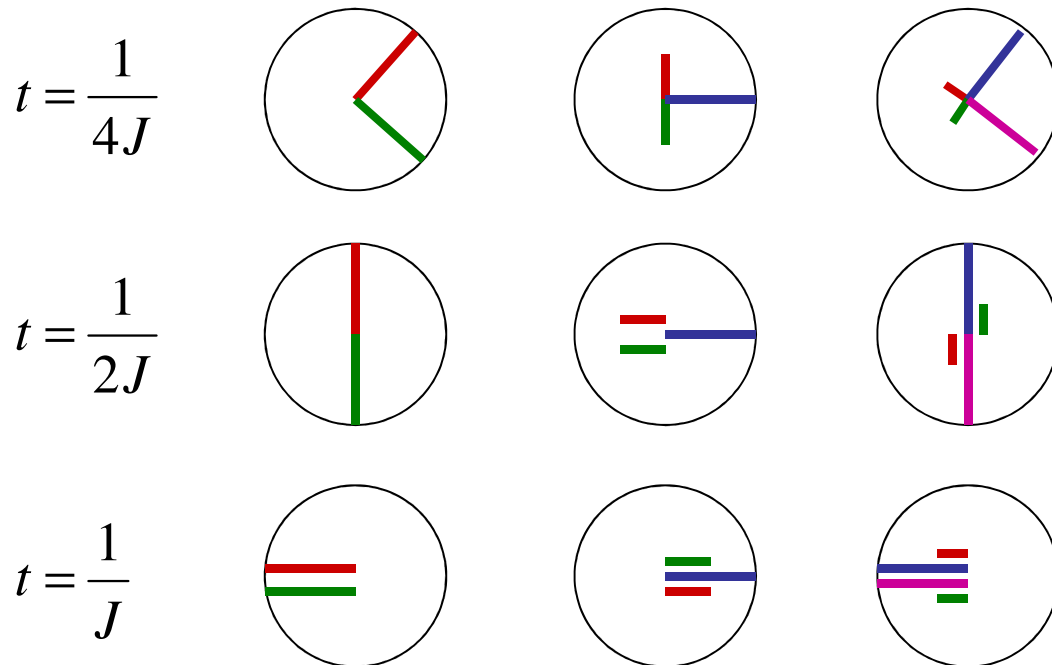
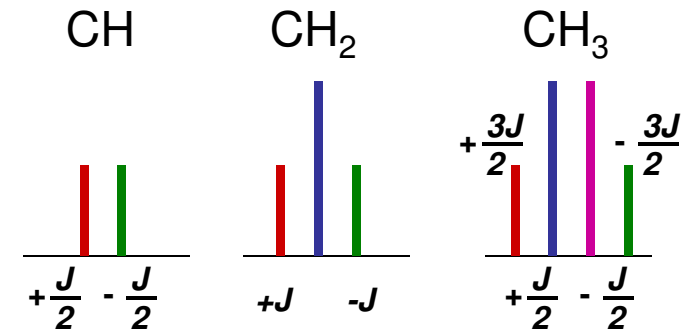
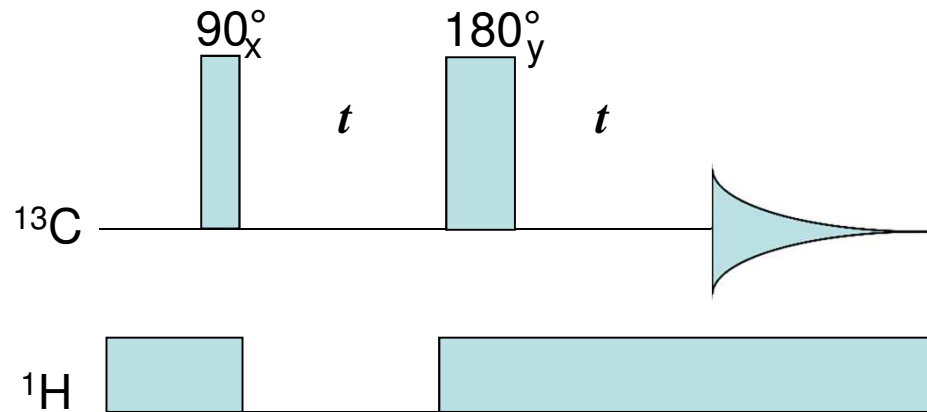


Modulace amplitudy



APT experiment

*Spinové echo refokusuje chemický posun
J vazba aktivní jen v jedné polovině echa*

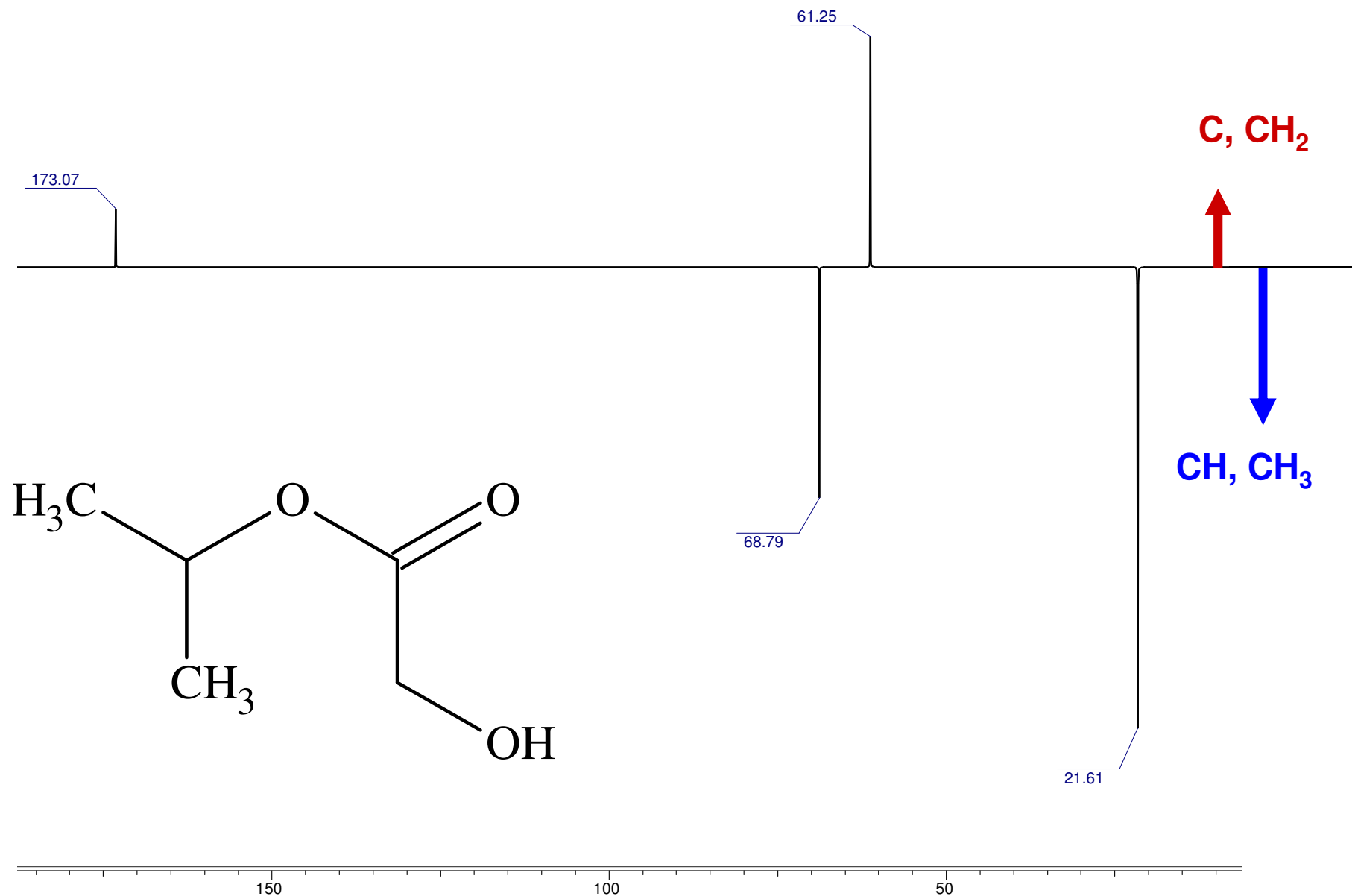


všechny signály kladné

jen kvartérní uhlíky

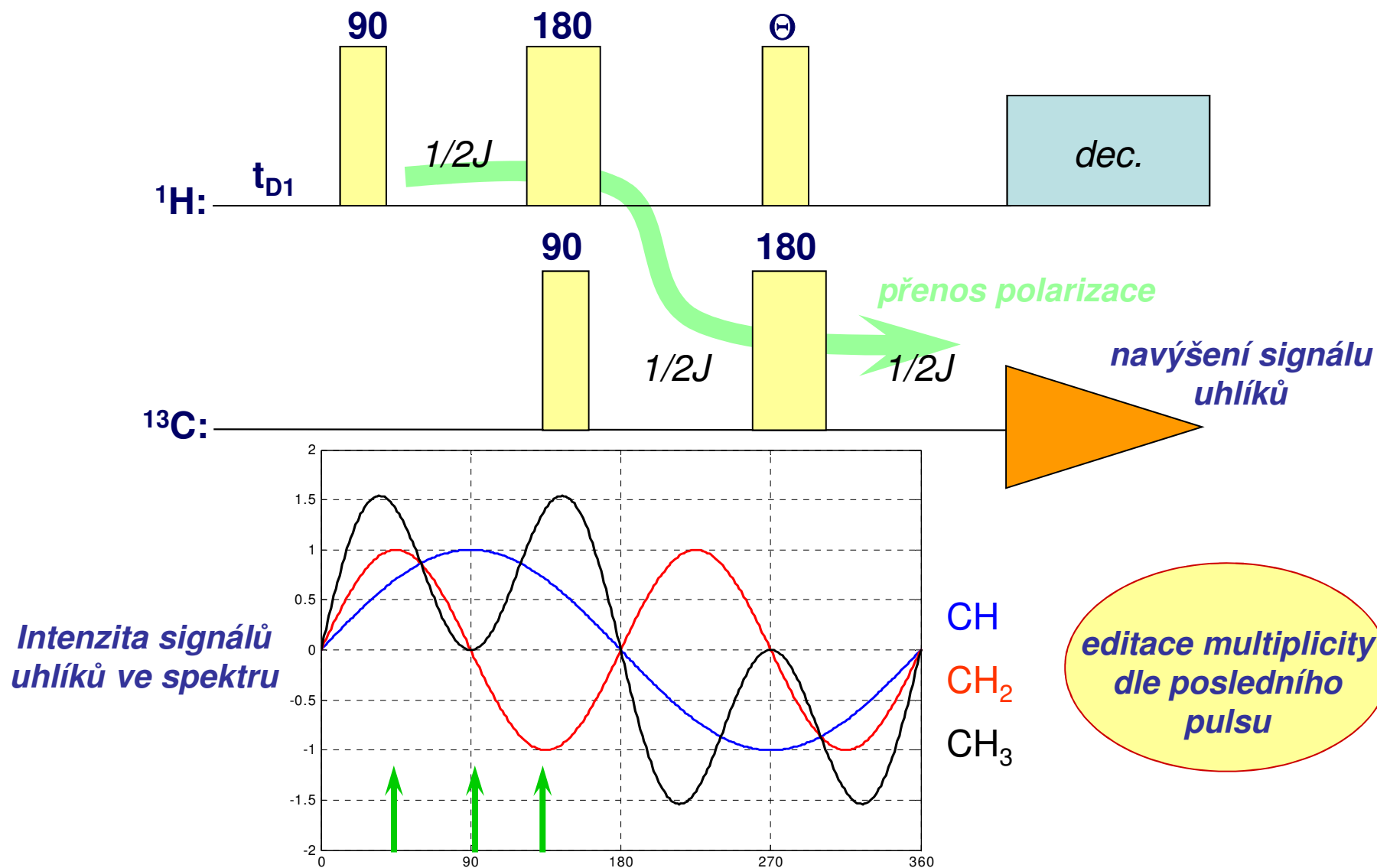
záporné kladné záporné

APT experiment



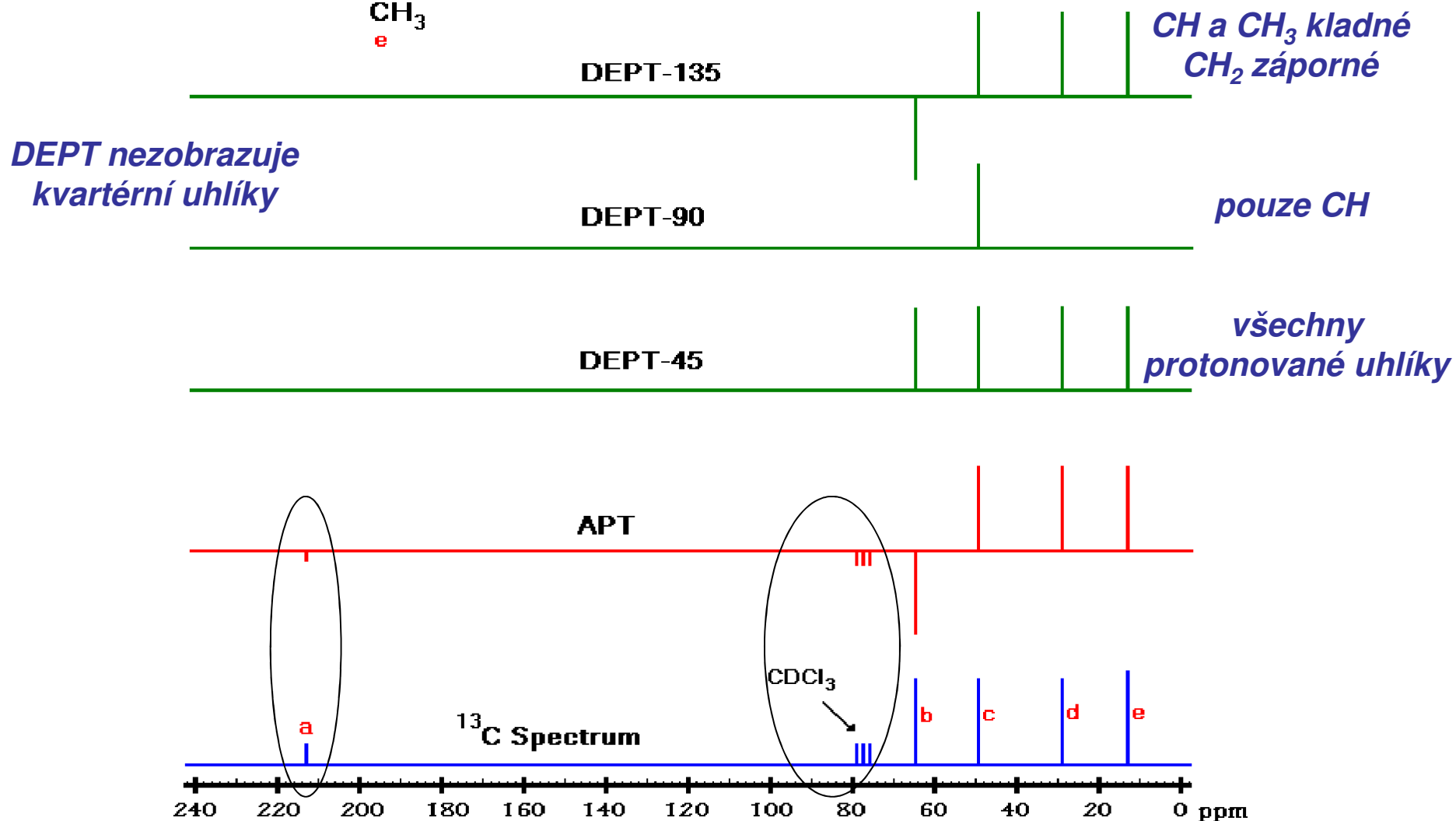
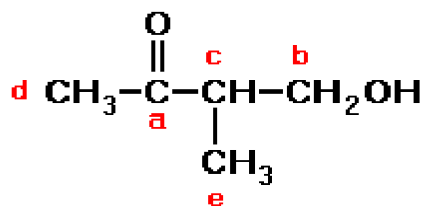
DEPT experiment

DEPT – distortionless enhancement by polarization transfer



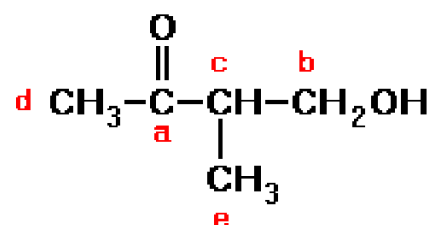
DEPT experiment

4-Hydroxy-3-Methyl-2-Butanone

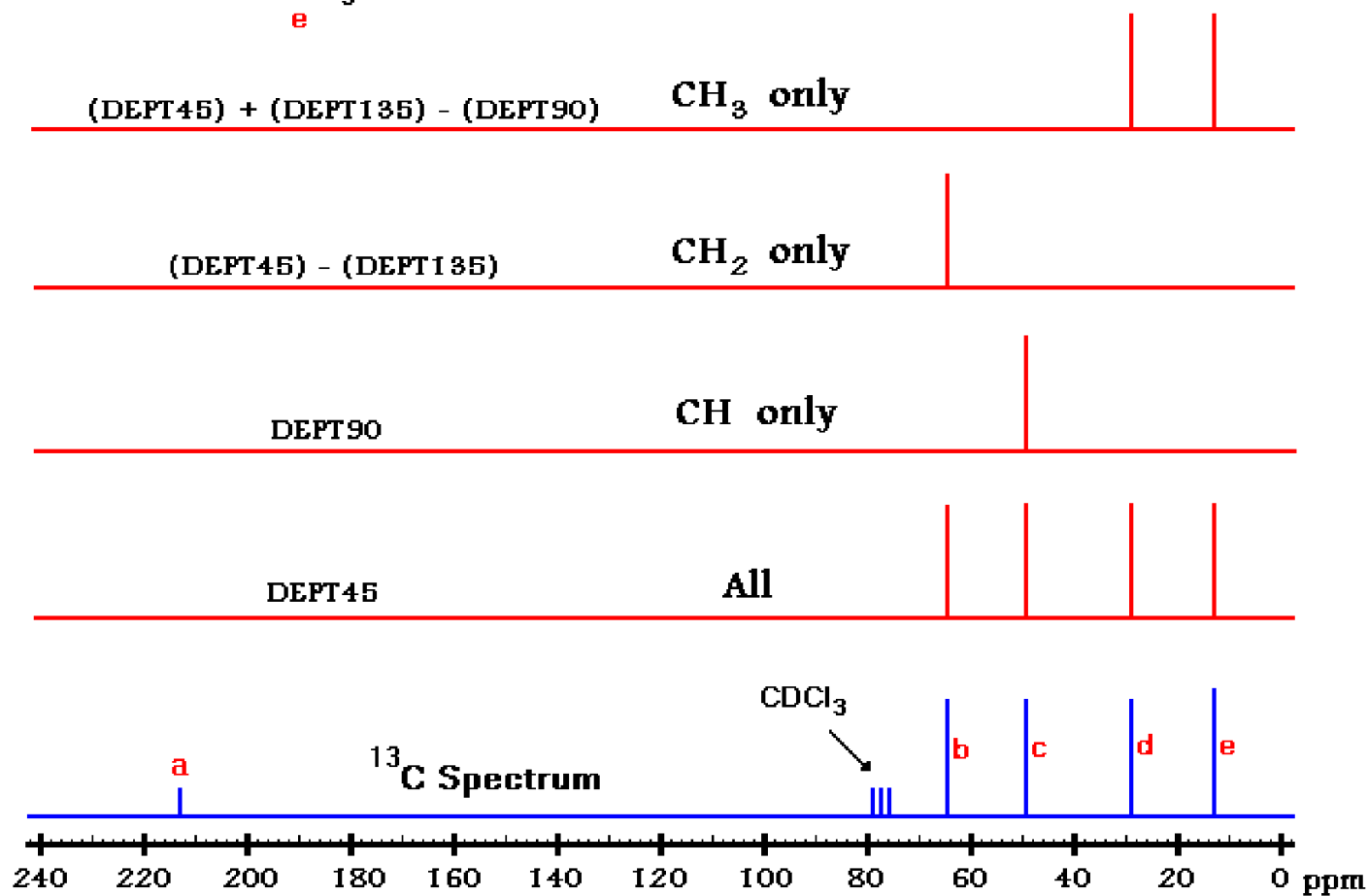


DEPT experiment

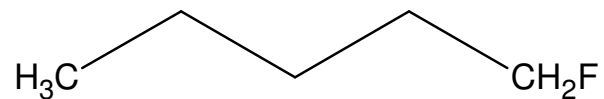
DEPT spektra lze rozdělit podle multiplicity



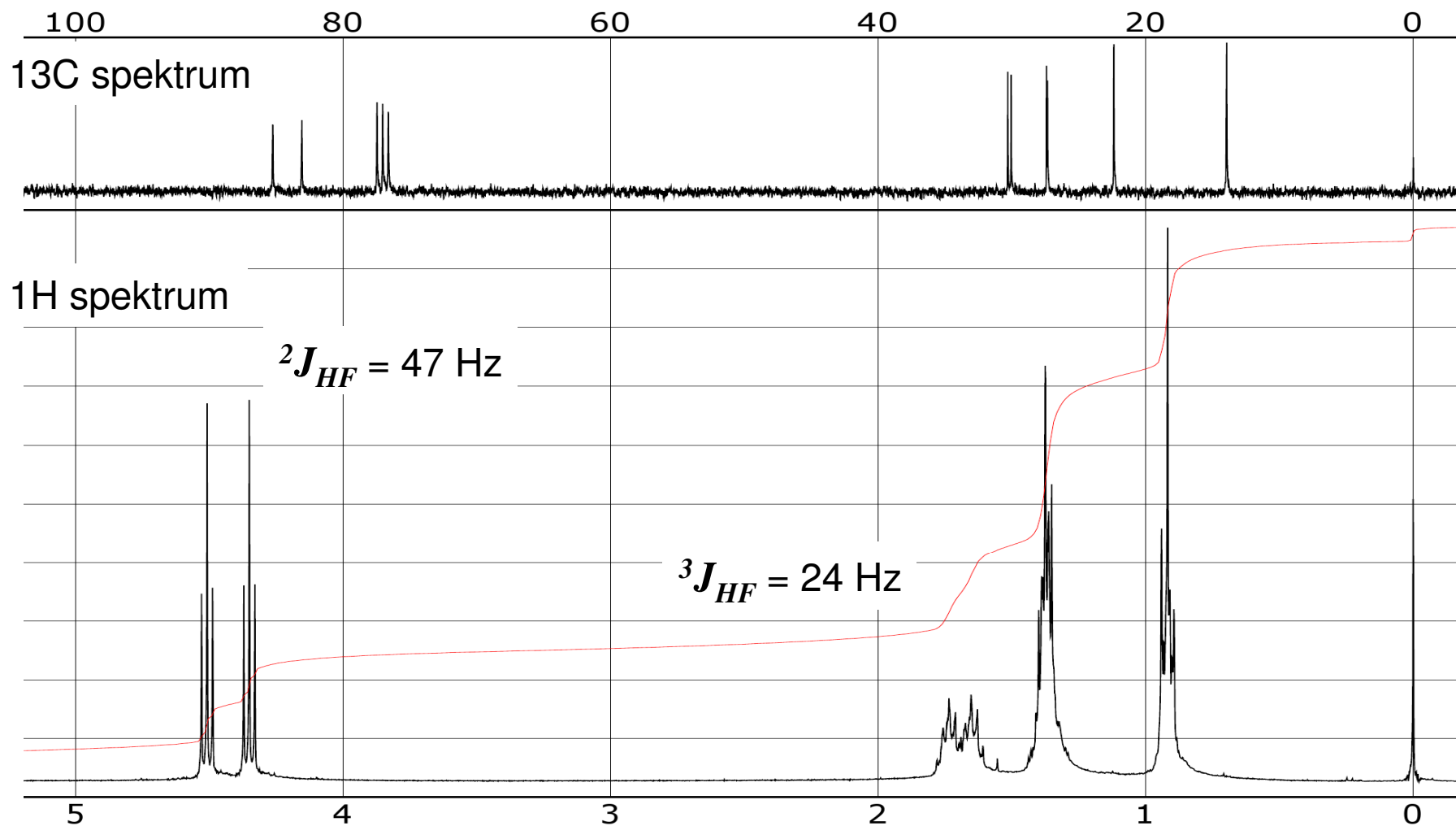
4-Hydroxy-3-Methyl-2-Butanone



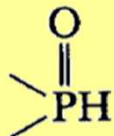
J interakce s jinými jádry: ^{-19}F



$${}^1J_{CF} = 167 \text{ Hz} \quad {}^2J_{CF} = 26 \text{ Hz} \quad {}^3J_{CF} = 7 \text{ Hz}$$



J interakce s jinými jádry: ^1H - ^{31}P

Pozor:  ~650 Hz

