

Band Selective Homonuclear Decoupling (BASHD) during ^1H and ^{13}C Detection

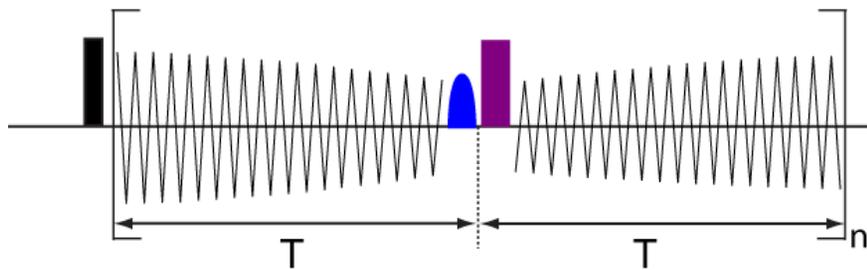
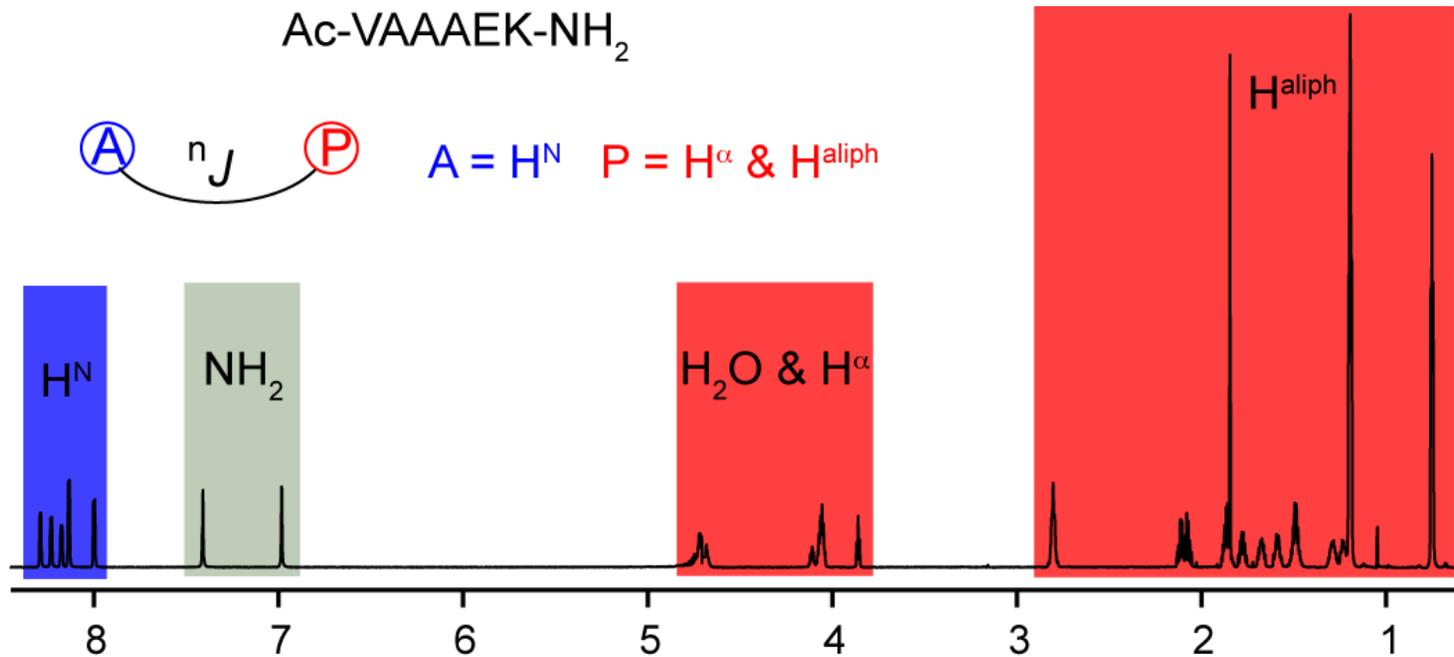
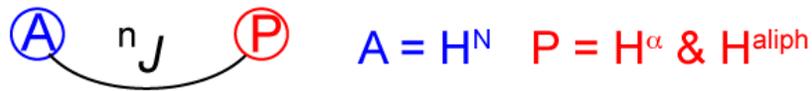
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Lab of Chemical Physics, NIDDK/NIH

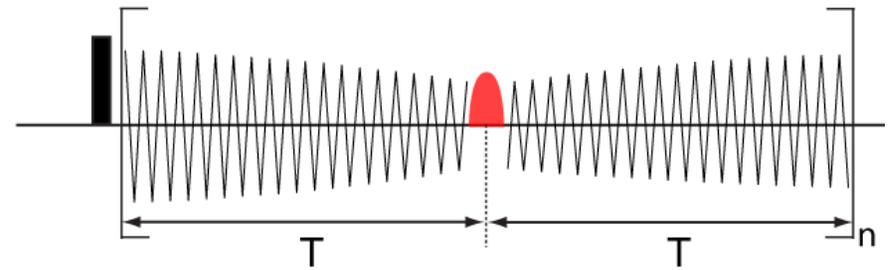
September 8, 2014



BASHD is Useful When Active or Passive Spins Resonate within a Separate Band

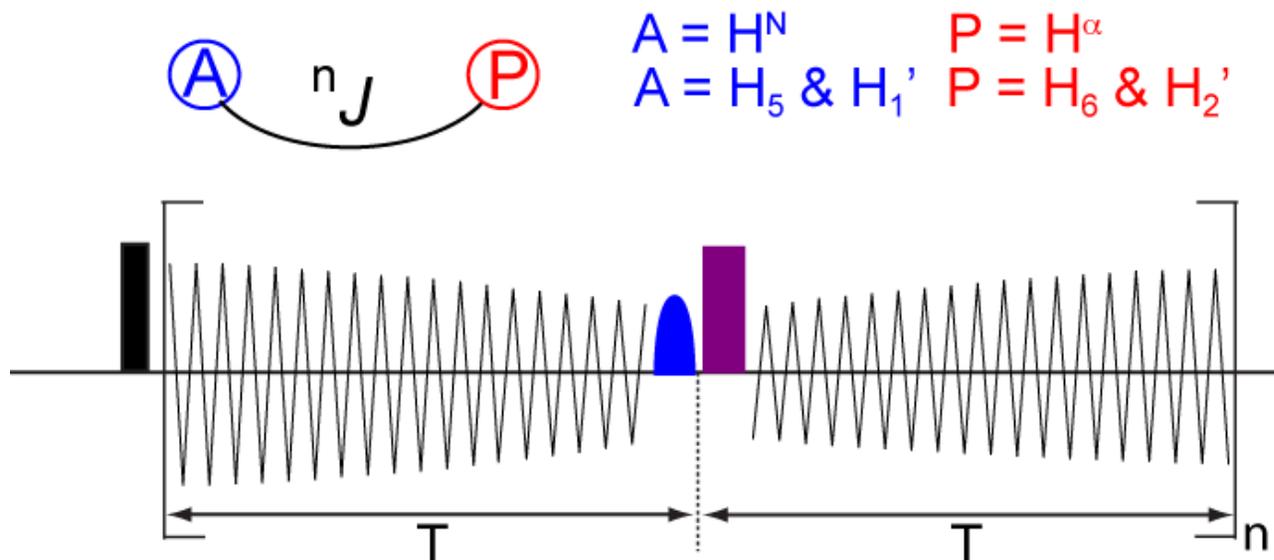


Scheme I



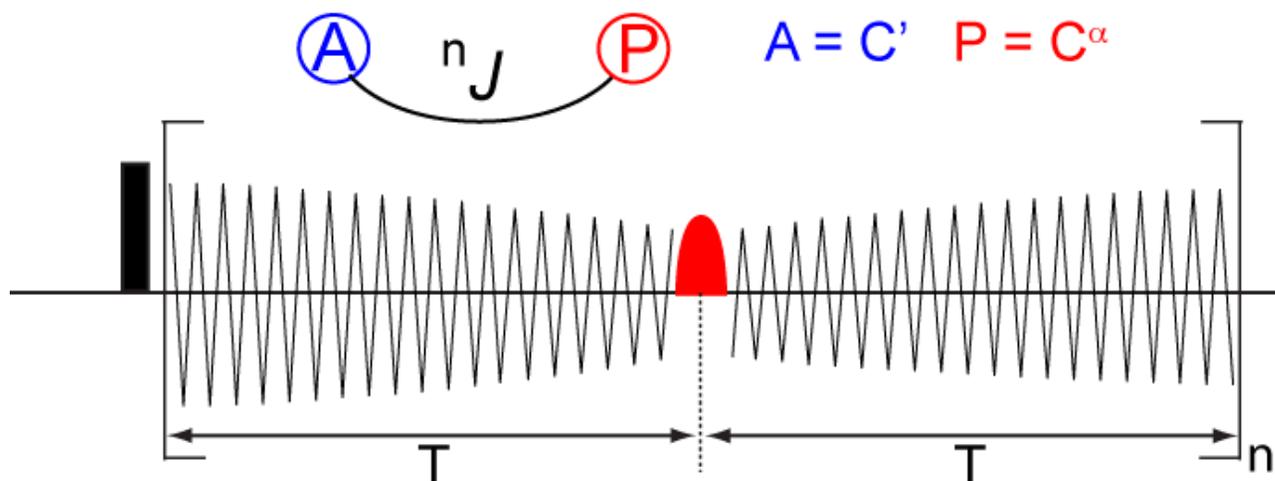
Scheme II

BASHD Scheme I



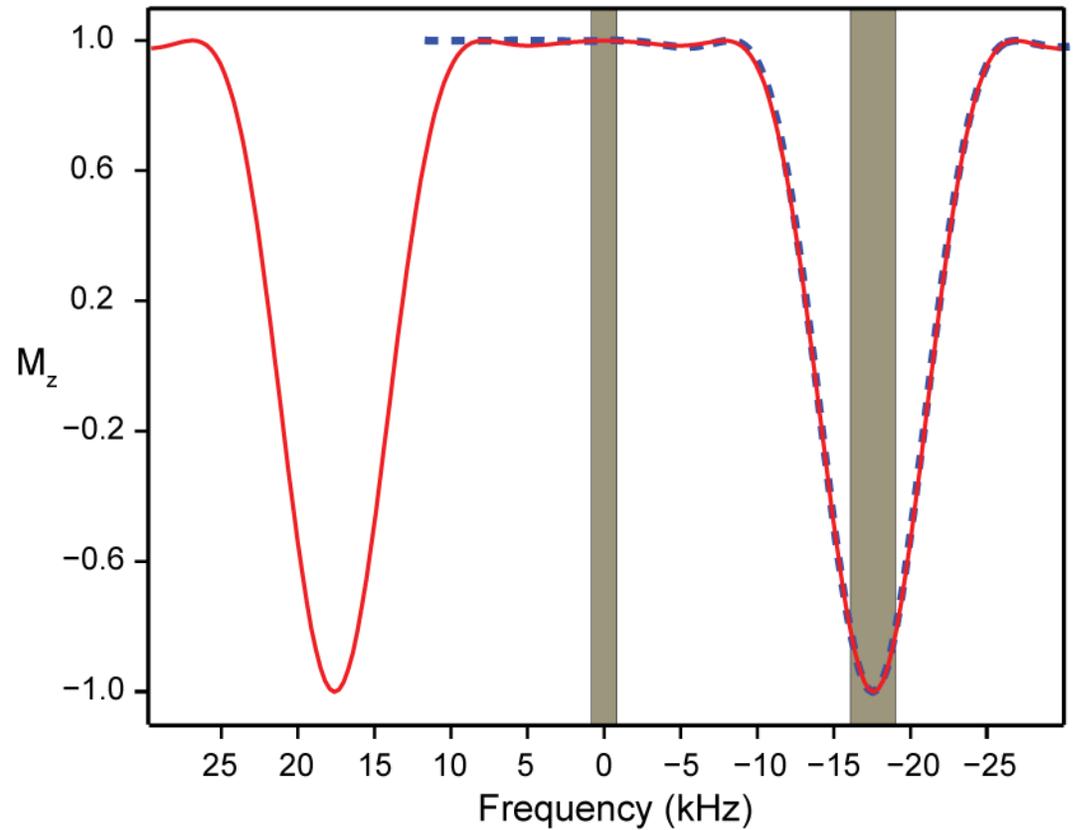
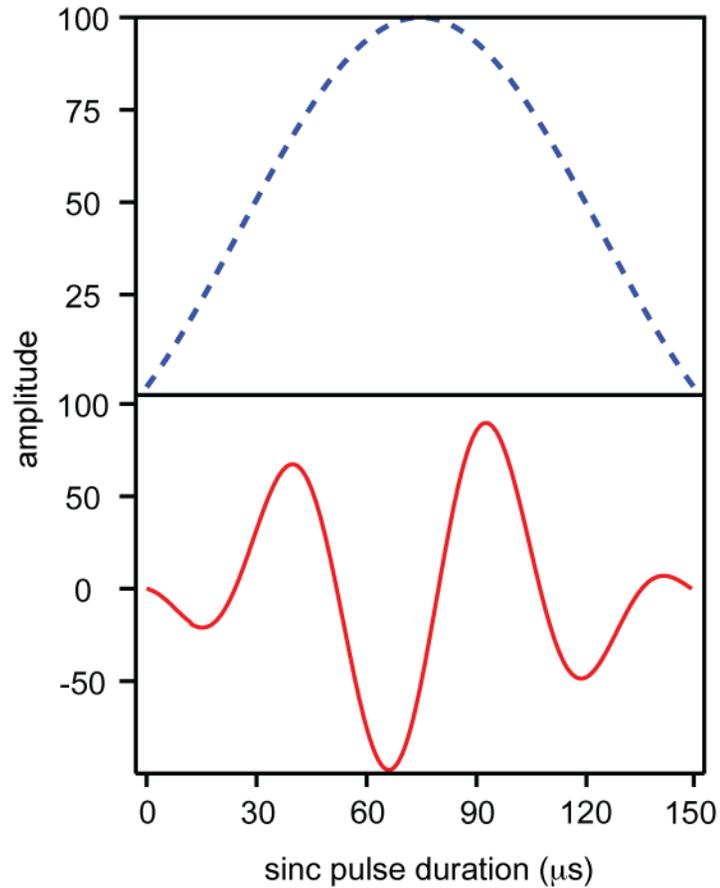
- Active spin resonance band can be selectively refocused
- All spins can be inverted with a negligible offset effect
- The total length of pulses/gradients is roughly ~3.5-4.0 ms
- Better suited for relatively small ${}^nJ_{\text{HH}}$ or ${}^nD_{\text{HH}}$
- Solvent suppression is critical
- No chemical shift evolution and no Bloch-Siegert shift

BASHD Scheme II



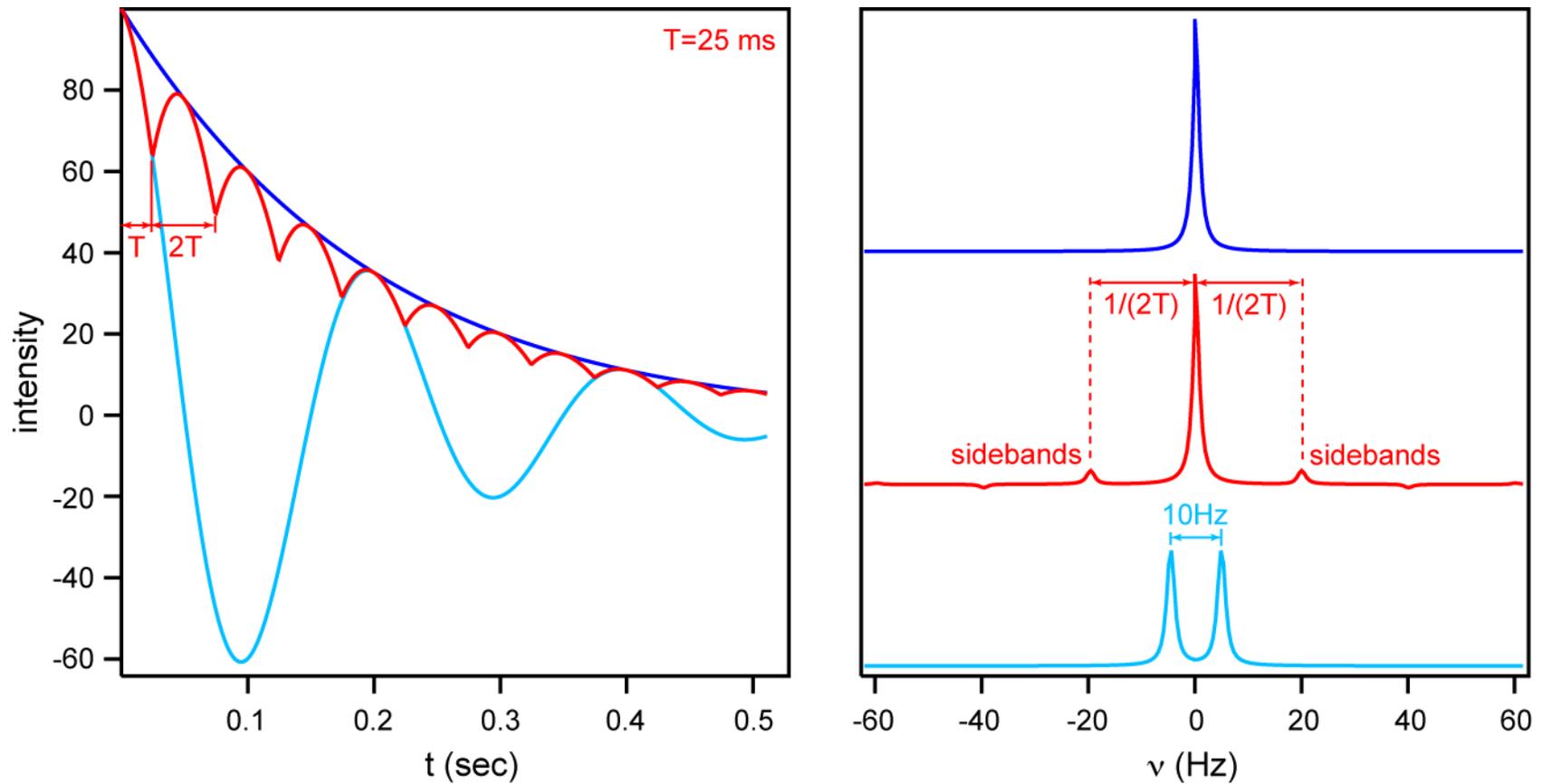
- **Passive spin resonance band can be selectively inverted**
- No refocusing for the active spins
- No gradients needed, the total length is 120-200 μs for ${}^1J_{C'C^\alpha}$
- Digitizing with receiver off during the pulse, causing intensity dip
- works well for a large band separation and large couplings
- Bloch-Siegert effect causes active peaks to shift
- Cosine modulated pulse removes constant Bloch-Siegert shift

Freq vs Amp Modulated Selective Pulse



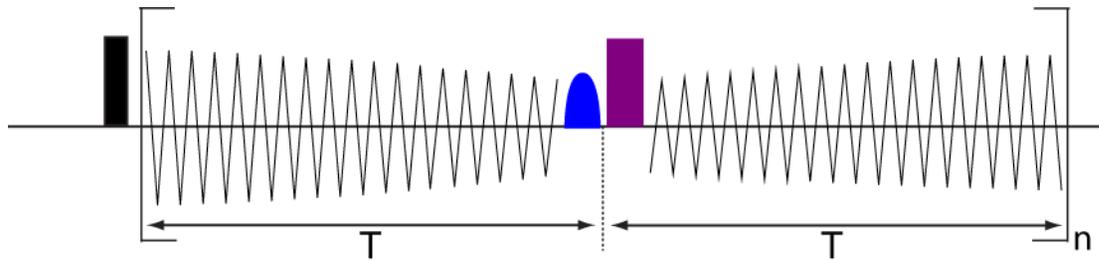
Amplitude modulation cancels the freq independent Bloch-Siegert shift

How the Delay T Impacts the Decoupling?

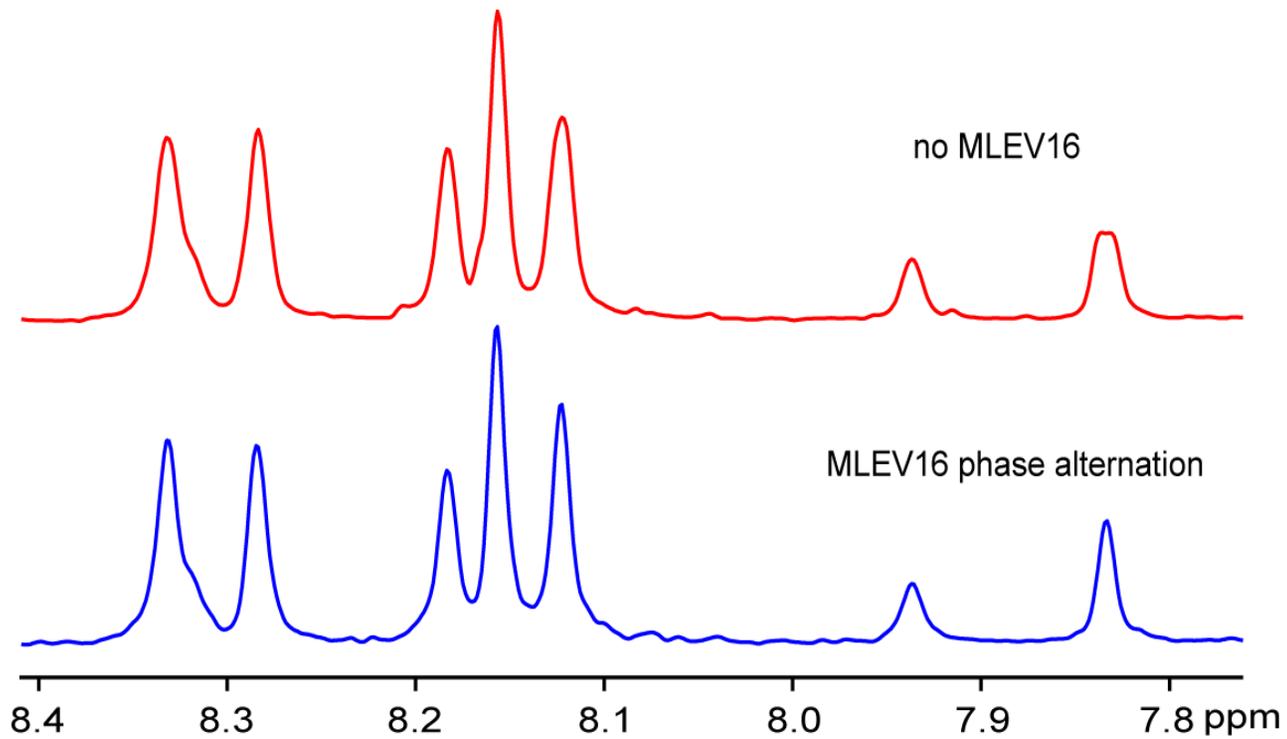


Typically $1/(10J) \leq T \leq 1/(6J)$

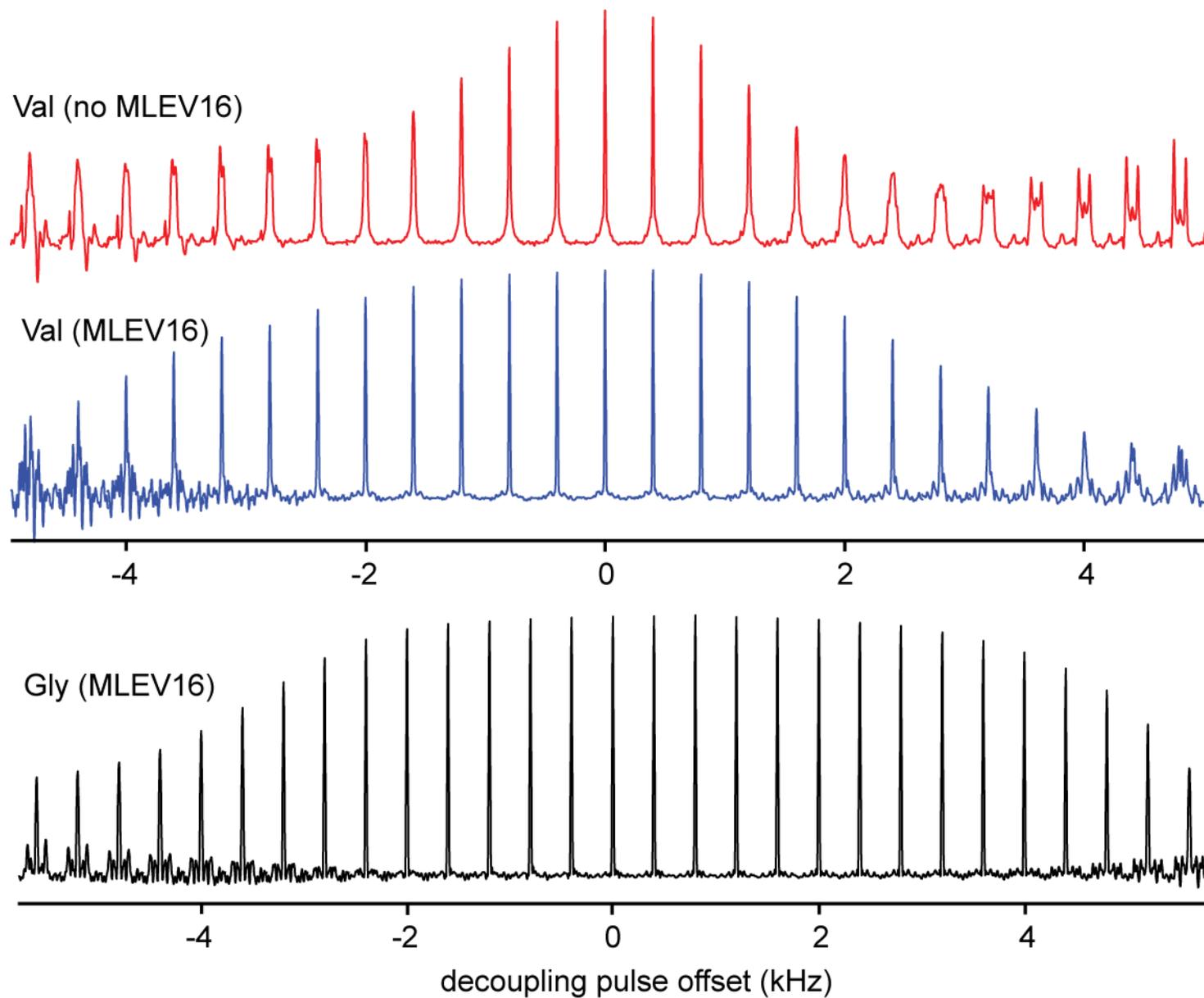
Does MLEV16 Phase Alternation Help?



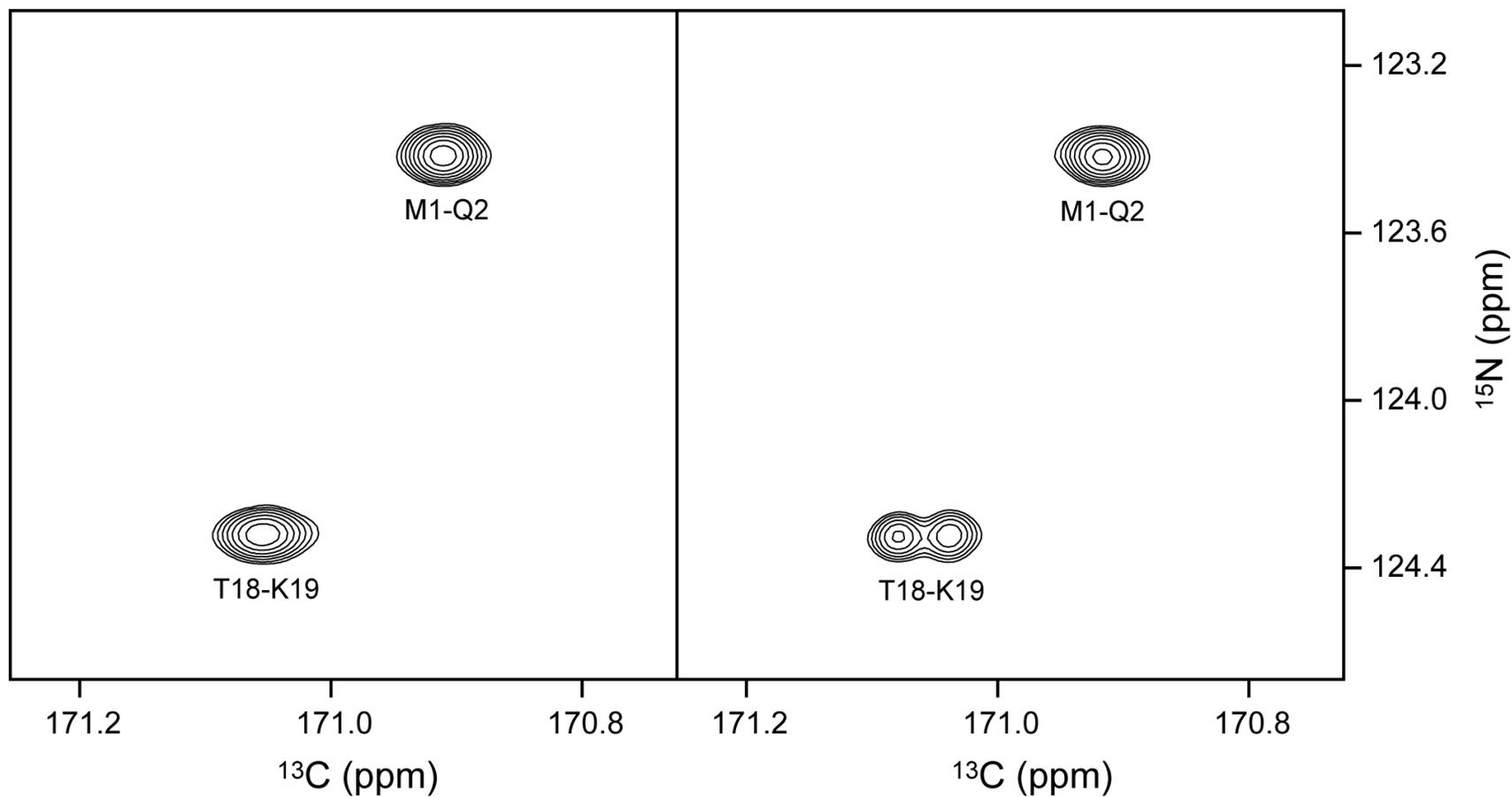
$\underline{R} \underline{R} \underline{R} \underline{R}$ $\underline{R} \underline{R} \underline{R} \underline{R}$ $\underline{R} \underline{R} \underline{R} \underline{R}$ $\underline{R} \underline{R} \underline{R} \underline{R}$
where $\underline{R}=0$, and $\underline{R}=180$



MLEV16 Improves ^{13}C BASHD Bandwidth

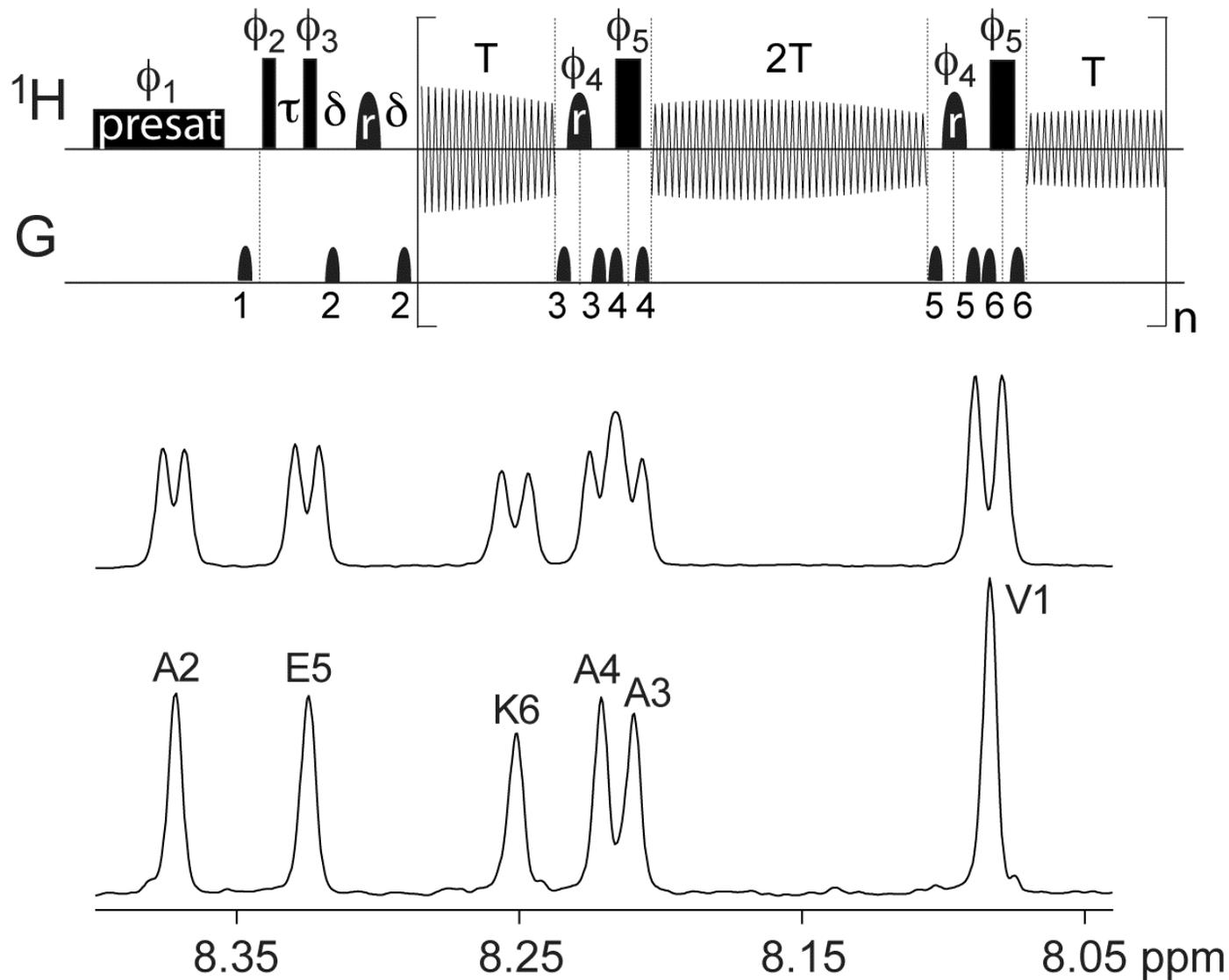


3-Spin Effect

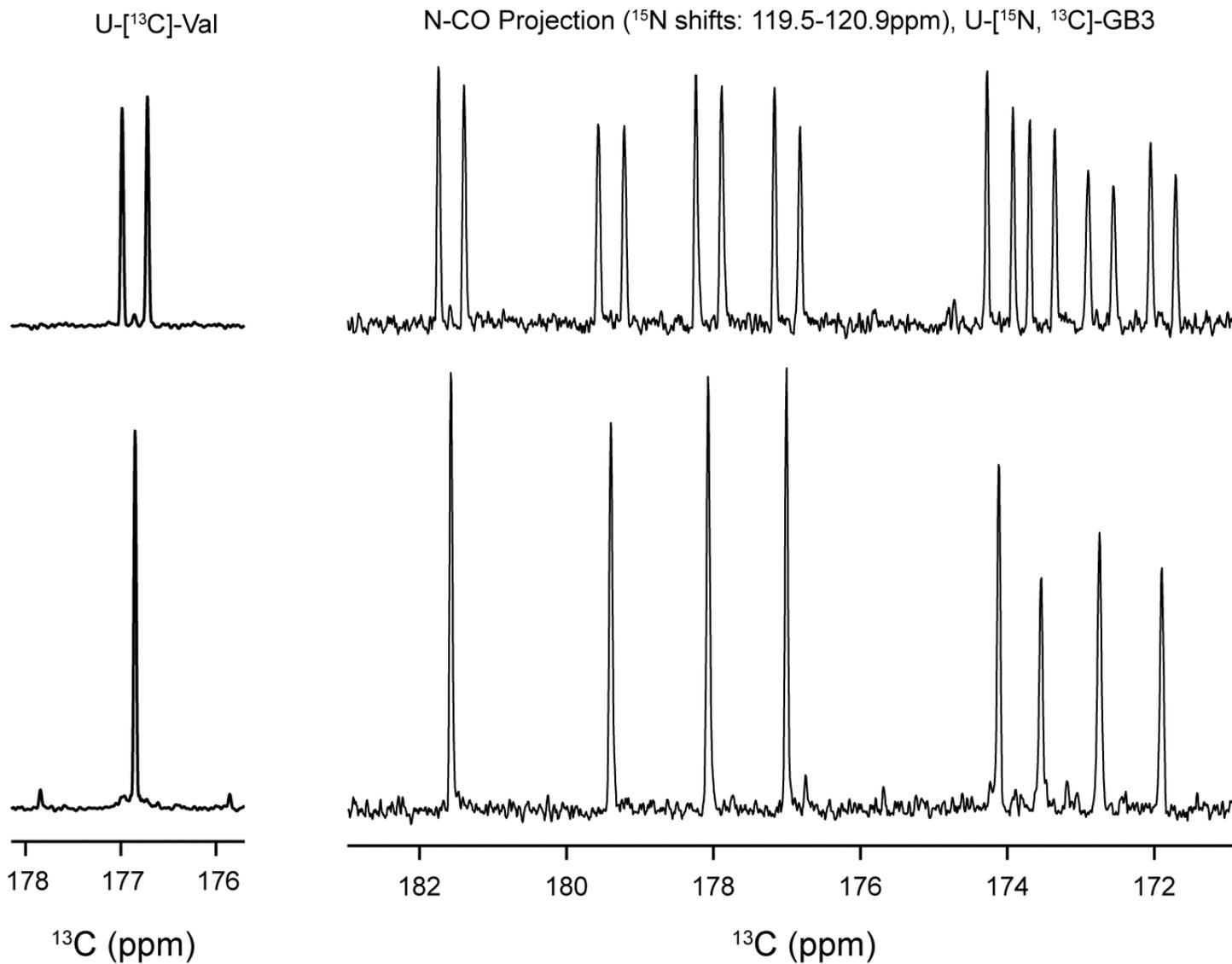


Barker et al., JMR, 1985
Shaka et al., JMR, 1987
Ying et al., JBNMR, 2014

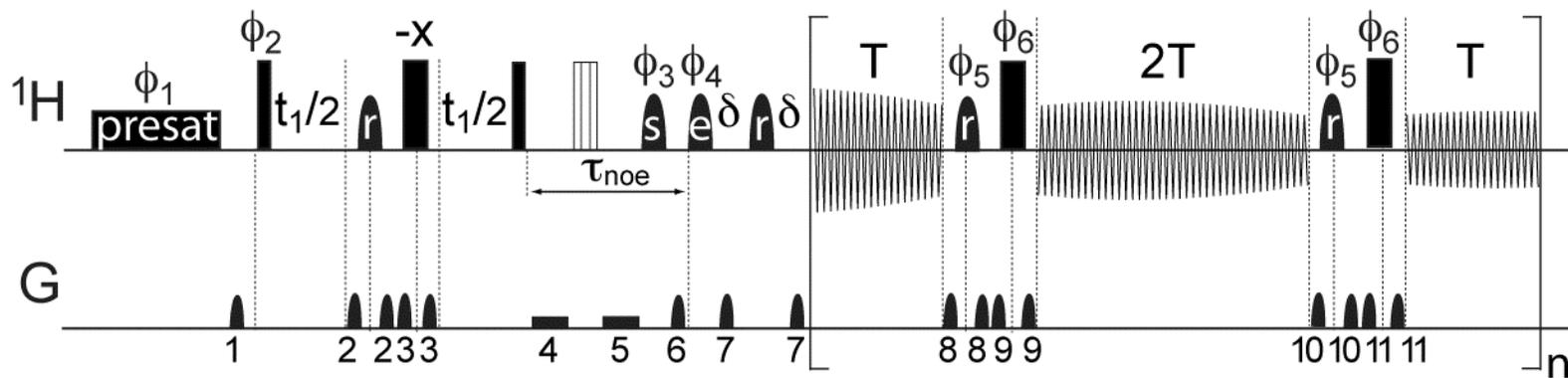
Observing H^N with H^α BASHD



$^{13}\text{C}'$ Detection with $^{13}\text{C}\alpha$ BASHD

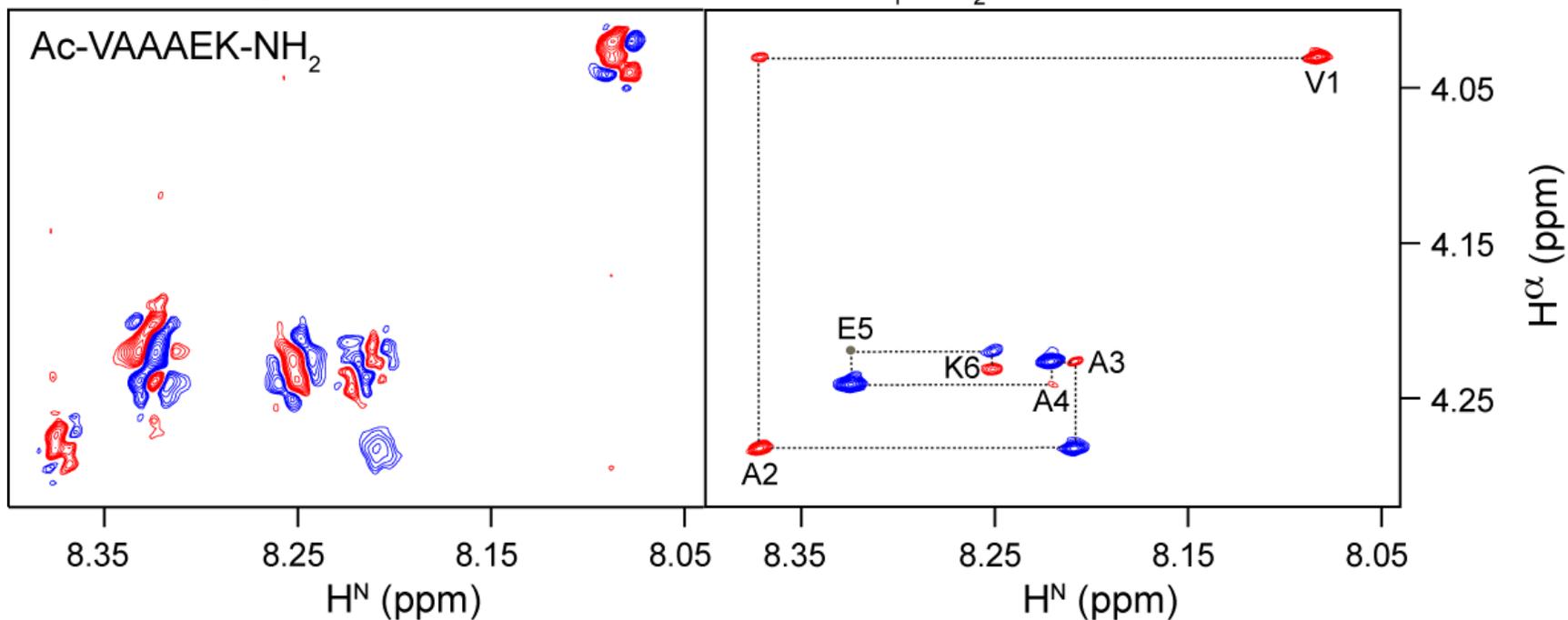


BASHD Application: 2D NOESY

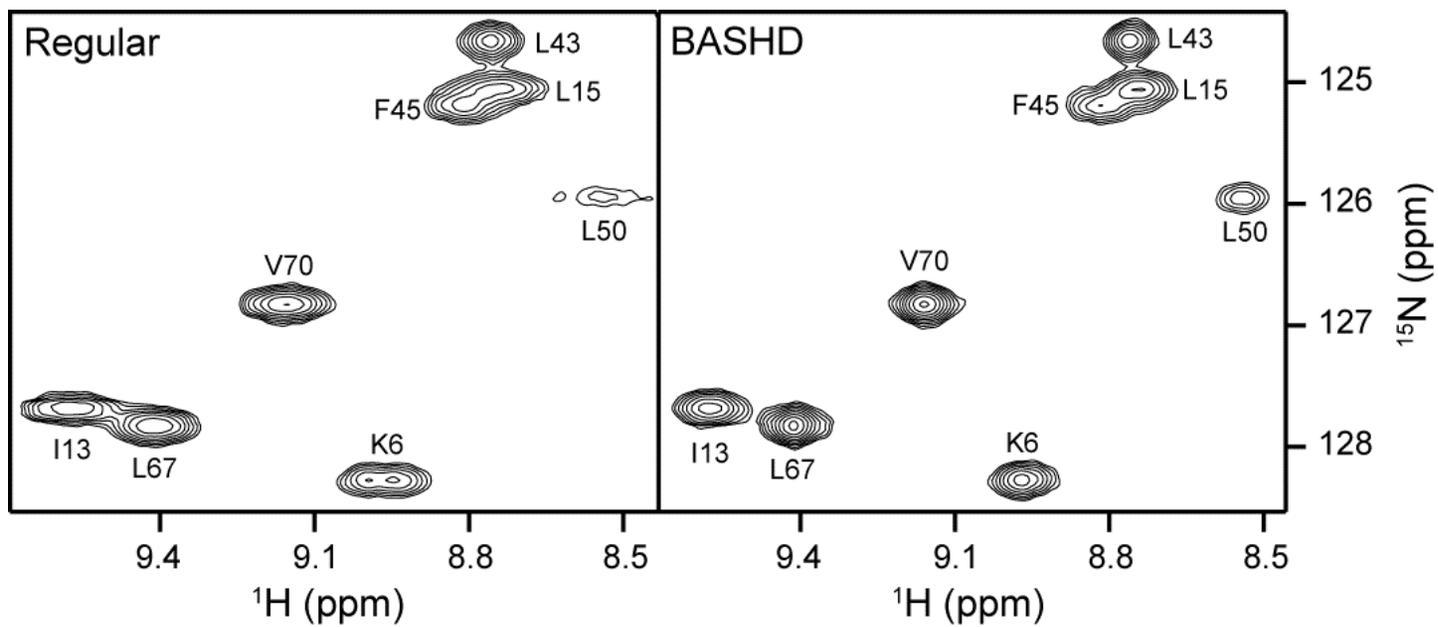
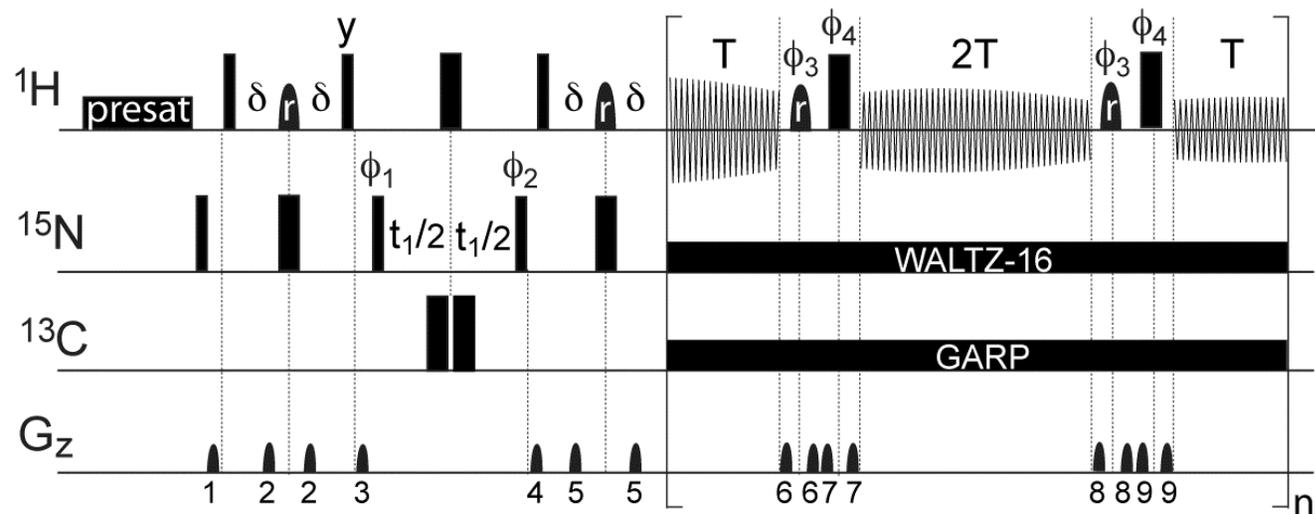


Regular NOESY

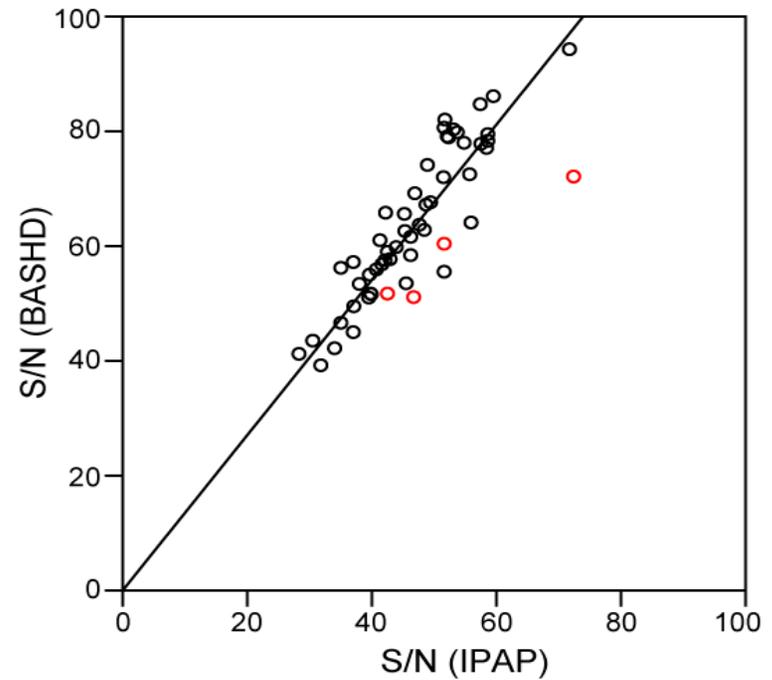
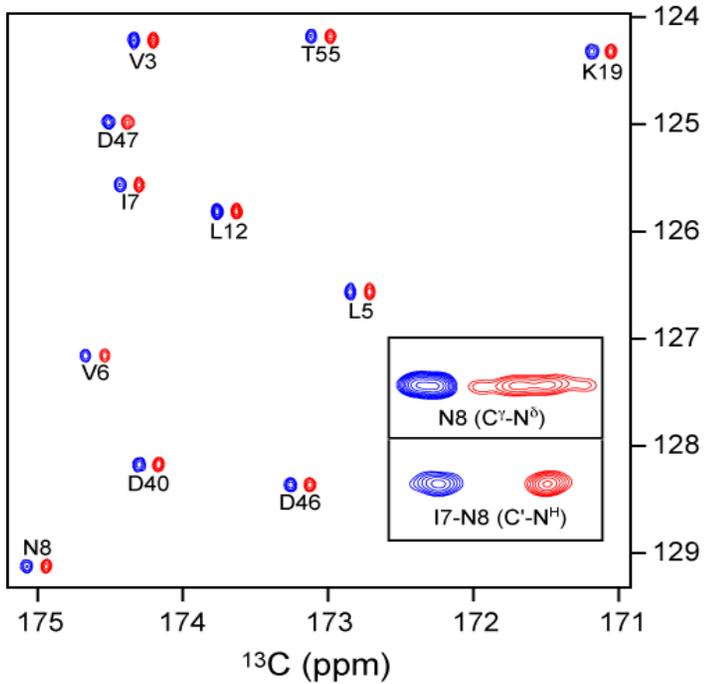
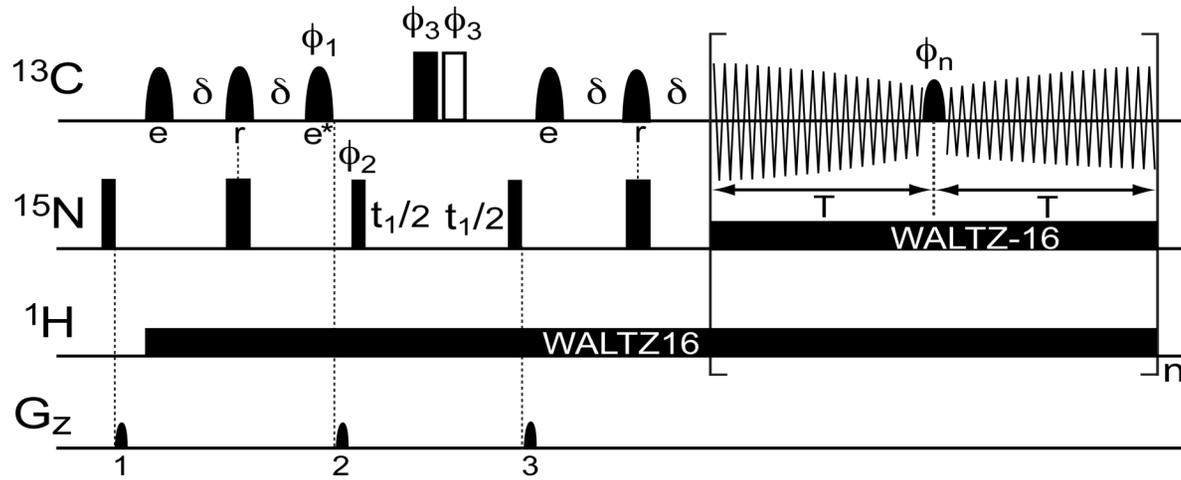
F_1 & F_2 -BASHD NOESY



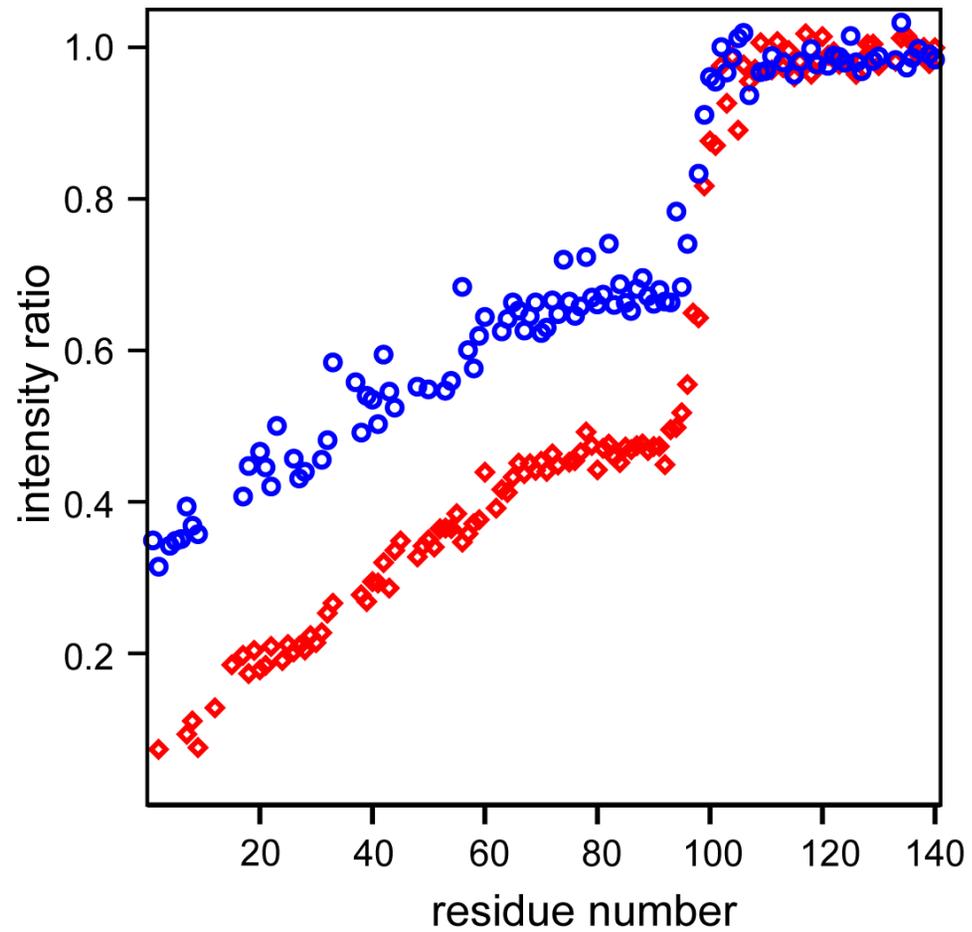
BASHD Application: HSQC for RDCs



BASHD Application to ^{13}C Detection: 2D N-CO



^{13}C BASHD for Studying α -Synuclein/Lipid Interaction



Alternative to “go=2”

Analog Mode

```
define loopcounter tdCount
“tdCount=td/2+2”
“d28=dw*2-4u”
“anavpt=2048”
...
1 ze
2 30m
...
ACQ_START(ph30,ph31)
  3u REC_UNBLK
  4 4u DWL_CLK_ON
    d28 DWL_CLK_OFF
  lo to 4 times tdCount
  3u REC_BLK
rcyc = 2
50m wr #0
...
```

Digital Mode

```
“d28 = aq”
dwellmode explicit
...
1 ze
2 30m
...
ACQ_START(ph30,ph31)
  0.05u DWL_CLK_ON
  0.1u REC_UNBLK
  d28
  0.1u REC_BLK
  0.05u DWL_CLK_OFF
rcyc = 2
50m wr #0
...
```

Pulse Interrupted Data Acquisition in Analog Mode

<pre> ACQ_START(ph30,ph31) 3u REC_UNBLK 3u ;syrec 4 4u DWL_CLK_ON d28 DWL_CLK_OFF lo to 4 times tdcoun1 3u 3u ;sytra 3u REC_BLK p21:gp1 45u pl0:f1 (p10:sp0 ph2):f1 2u p21:gp1 52u p22:gp2 54u pl1:f1 (p1*2 ph4):f1 5u p22:gp2 43u 3u REC_UNBLK 3u ;syrec 5 4u DWL_CLK_ON advdel DWL_CLK_OFF lo to 5 times tdcoun1 </pre>	<pre> 6 4u DWL_CLK_ON advdel DWL_CLK_OFF lo to 6 times tdcoun1 3u 3u ;sytra 3u REC_BLK p21:gp3 45u pl0:f1 (p10:sp0 ph2):f1 2u p21:gp3 52u p22:gp4 54u pl1:f1 (p1*2 ph4):f1 5u p22:gp4 43u ip2*2 ip4*2 3u REC_UNBLK 3u ;syrec 7 4u DWL_CLK_ON advdel DWL_CLK_OFF lo to 7 times tdcoun1 lo to 4 times tdcoun2 6u rp2 rp4 rcyc = 2 50m wr #0 </pre>
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Pulse Interrupted Data Acquisition in Digital Mode

<pre> ACQ_START(ph30,ph31) 0.05u DWL_CLK_ON 0.1u REC_UNBLK 77 d28 0.1u REC_BLK 0.05u DWL_CLK_OFF if "I24%8==0 I24%8==5" { "cnst22=0" "cnst24=0" } if "I24%8==1 I24%8==4" { "cnst22=180" "cnst24=180" } if "I24%8==3 I24%8==6" { "cnst22=0" "cnst24=180" } if "I24%8==2 I24%8==7" { "cnst22=180" "cnst24=0" } </pre>	<pre> 5u p21:gp1 20u ip2+cnst22 23u ip4+cnst22 3u pl0:f1 (p10:sp0 ph2):f1 6u p21:gp1 45u p22:gp2 40u 60u pl1:f1 (p1*2 ph4):f1 5u p22:gp2 95u 0.05u DWL_CLK_ON 0.1u REC_UNBLK d29 0.1u REC_BLK 0.05u DWL_CLK_OFF </pre>	<pre> 5u p21:gp3 20u ip2+cnst24 20u ip4+cnst24 5u pl0:f1 (p10:sp0 ph2):f1 5u p21:gp3 45u p22:gp4 100u pl1:f1 (p1*2 ph4):f1 5u p22:gp4 95u iu24 0.05u DWL_CLK_ON 0.1u REC_UNBLK d28 lo to 77 times tdCount 0.1u REC_BLK 0.05u DWL_CLK_OFF 6u ru24 rcyc = 2 50m wr #0 </pre>
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BASHD Experimental Setup in Topspin

Pars **AcquPars** Title PulseProg Peaks Integrals S

↓ 1,2... ▾ Installed probe: 5 mm QXI 1H/

▼ Experiment

PULPROG	homodec1D.jfy	...	E
AQ_mod	qsim	▾	
TD	4096		
NS	4		
DS	2		
TDO	1		

▼ Width

SW [ppm]	9.9973
SWH [Hz]	5000.000
AQ [s]	0.4096500
FIDRES [Hz]	1.220703
FW [Hz]	125000.00

▼ Receiver

RG	128	
DW [μs]	100.000	
DWOV [μs]	0.025	
DECIM	1	
DSPFIRM	sharp(standard)	▾
DIGTYP	DRU	▾
DIGMOD	analog	▾

Pars **AcquPars** Title PulseProg Peaks Integrals S

↓ 1,2... ▾ Installed probe: 5 mm QXI 1H/

▼ Experiment

PULPROG	homodec1D_dqd_mlev.jfy	...	E
AQ_mod	DQD	▾	
TD	4096		
NS	4		
DS	2		
TDO	1		

▼ Width

SW [ppm]	9.9973
SWH [Hz]	5000.000
AQ [s]	0.4096500
FIDRES [Hz]	1.220703
FW [Hz]	125000.00

▼ Receiver

RG	128	
DW [μs]	100.000	
DWOV [μs]	0.025	
DECIM	4000	
DSPFIRM	sharp(standard)	▾
DIGTYP	DRU	▾
DIGMOD	digital	▾

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