



**SECOND WINTERSCHOOL
ON BIOMOLECULAR SOLID-STATE NMR**

Floquet theory in solid state NMR
theory and applications

Homonuclear Decoupling

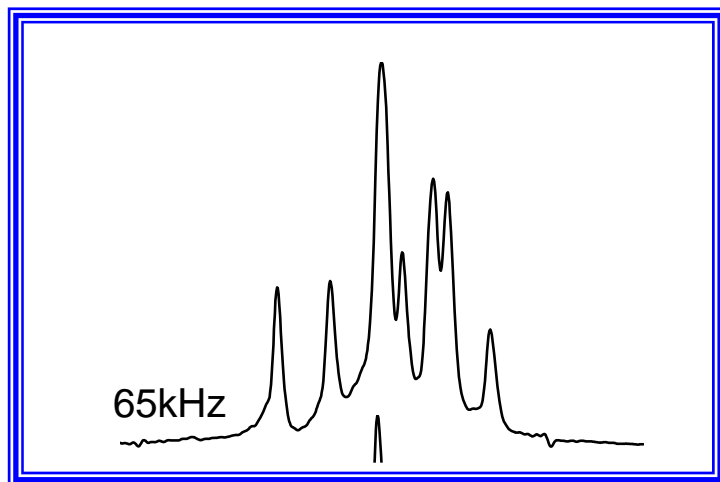
Shimon Vega
Weizmann Institute of Science
with

Michal Leskes and P.K. Madhu

Stowe Vermont

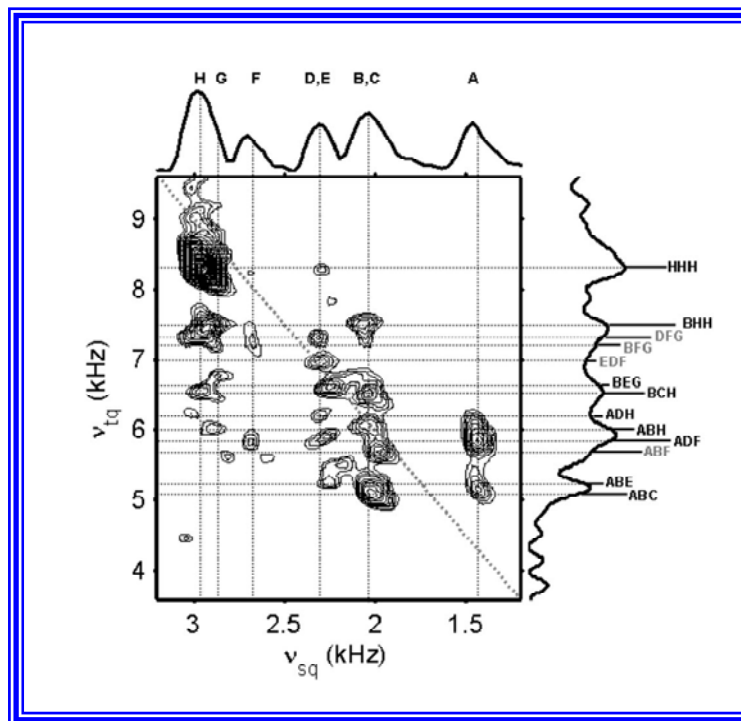
January 24-29, 2010

Homonuclear decoupling and Proton MAS NMR



homonuclear decoupling
at ultra-fast MAS

CPL (2008) 466, 95
JMR (2009)



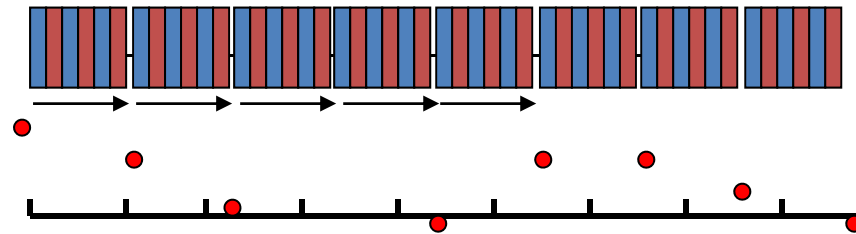
a pulse sequence for
SQ-TQ auto-correlation
JCP (2009) 130, 124506



What happens when

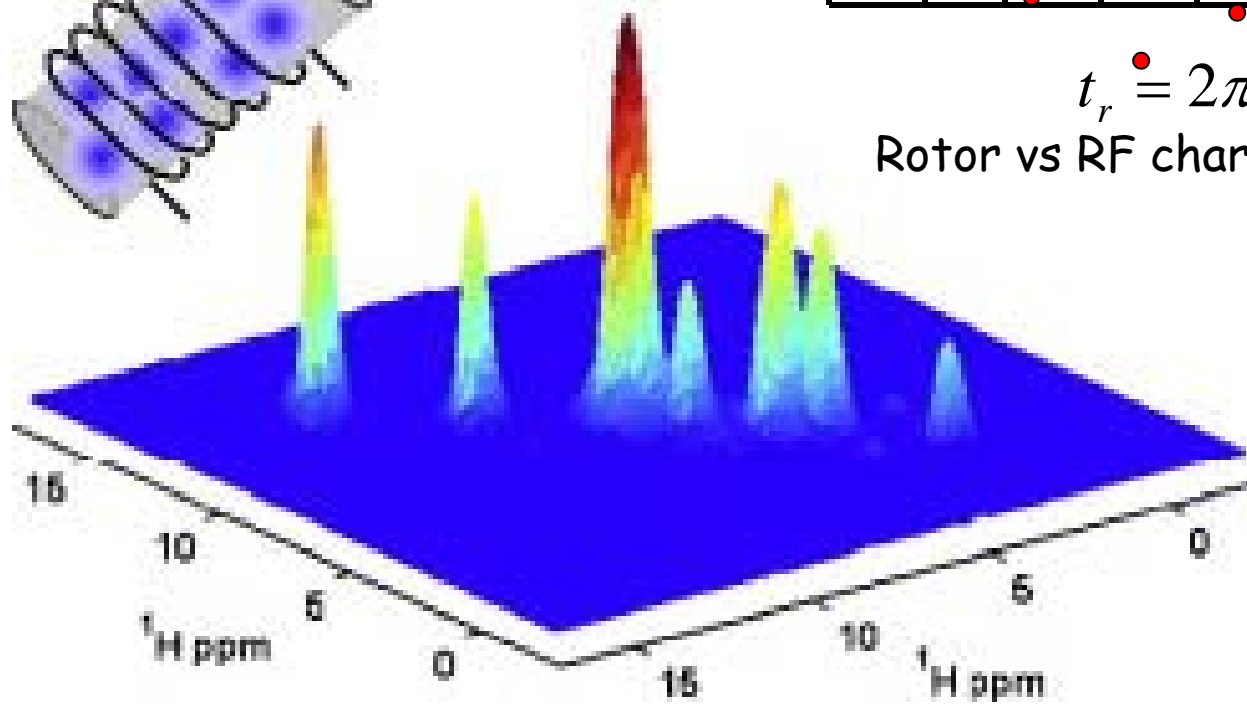
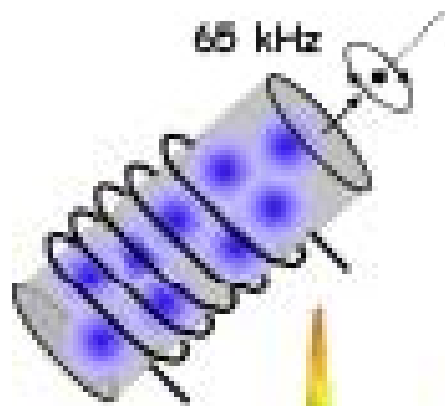
$$\boxed{\omega_r} > \boxed{\omega_c}$$

$$t_c = 2\pi / \omega_c$$



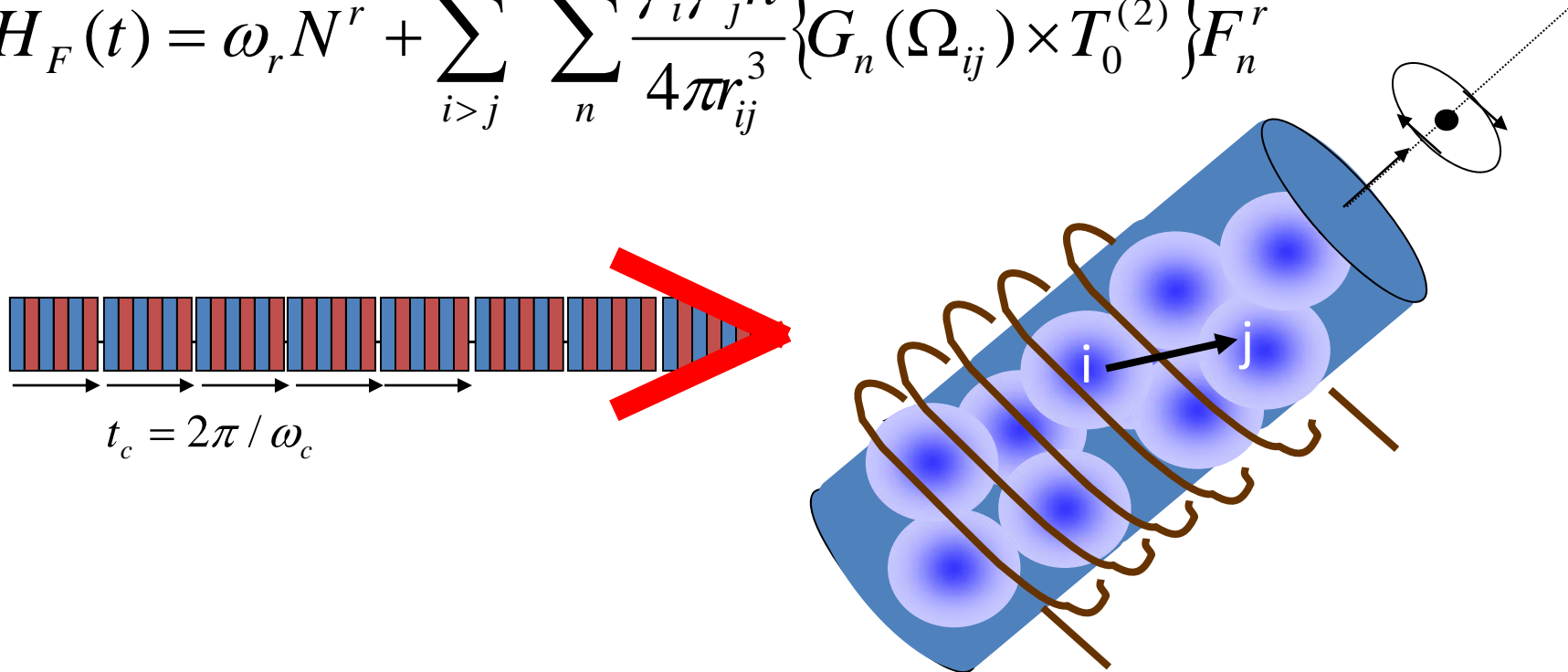
$$t_r = 2\pi / \omega_r$$

Rotor vs RF characteristic times



The homonuclear dipole-dipole interaction:

$$H_F(t) = \omega_r N^r + \sum_{i>j} \sum_n \frac{\gamma_i \gamma_j \hbar}{4\pi r_{ij}^3} \{G_n(\Omega_{ij}) \times T_0^{(2)}\} F_n^r$$



$$H_{\text{int}}(t) = \omega_r N^r + \omega_c N^c + \sum_{i<j} \sum_{n,k} \Delta_{ij} \{G_n(\Omega_{ij}) \times d_{mk}^{(2)} T_m^{(2)}\} F_n^r F_k^c$$

$$T_0^{(2)} = \frac{1}{\sqrt{6}} (3I_z^2 - I(I+1)) \quad T_{\pm 1}^{(2)} = \mp \frac{1}{2} (I^\pm I_z + I_z I^\pm) \quad T_{\pm 2}^{(2)} = \frac{1}{2} (I^\pm)^2$$

MP – CRAMPS History

'65

'70

'75

'80

'85

'90

'95

LG Lee,Goldburg

WHH4 Haeberlen,Huber,Waugh; Mehring

MREV8 Vaughan et al.,Mansfield

CRAMPS Gerstein et al**

BR24 Burum,Rhim

BLEW12 Burum,Linder,Ernst

FSLG Bielecki,Kolbert,Levitt

CORY24 Cory

'95

'00

'05

WHH4 Demco,Hafner,Spiess

MSHOT-3 Nielsen et al.

PMLG Vinogradov, Madhu

DUMBO Emsley et al.

R-symmetry Levitt et al.

w-PMLG5 Vinogradov, Madhu

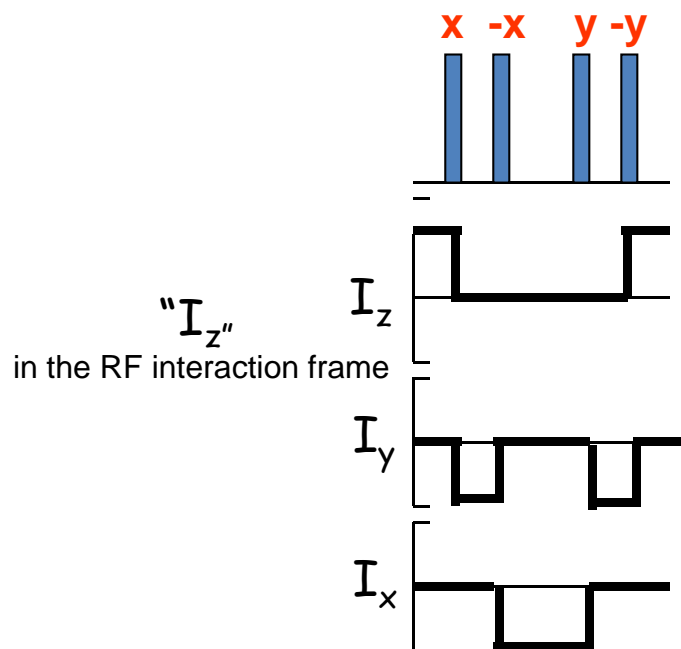
w-eDUMBO Elena et al.

w-PMLG3 Leskes, Madhu

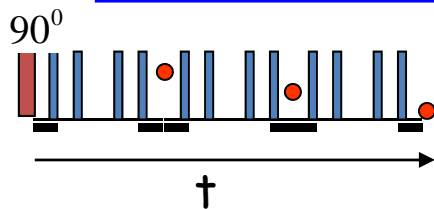
SAM Amoureux

The basic sequences

WAHUHA (1967)



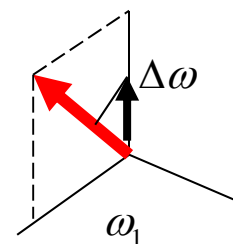
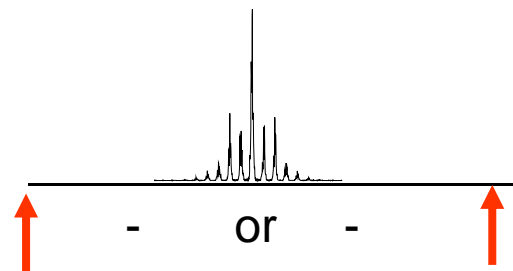
$$H^{(0)}_{CS} = \sqrt{\frac{1}{3}} \Delta\omega \left(\frac{I_z - I_x - I_y}{\sqrt{3}} \right)$$



$$d_{m0}^{(2)}(\theta_m) D_{00}^{(2)} T_m^{(2)} = d_{00}^{(2)}(\theta_m) D_{00}^{(2)} T_0^{(2)} + \dots$$

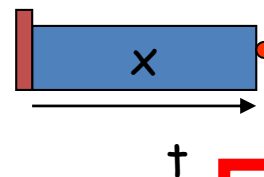
$$H^{(0)}_{DD} = 0$$

Lee-Godburg (1965)



Truncation of
 I_z

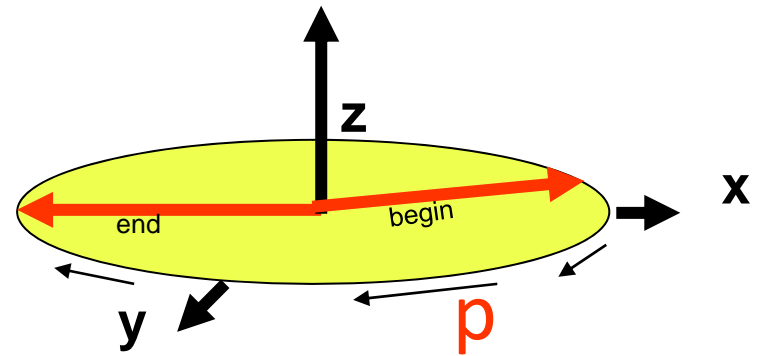
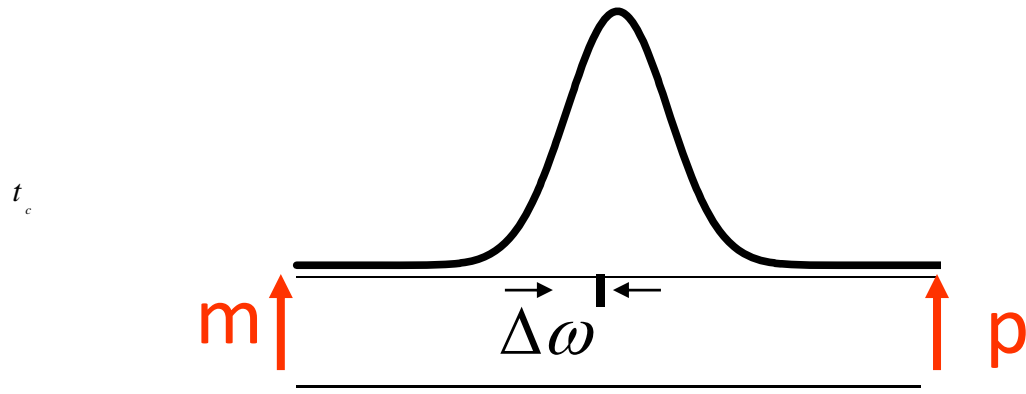
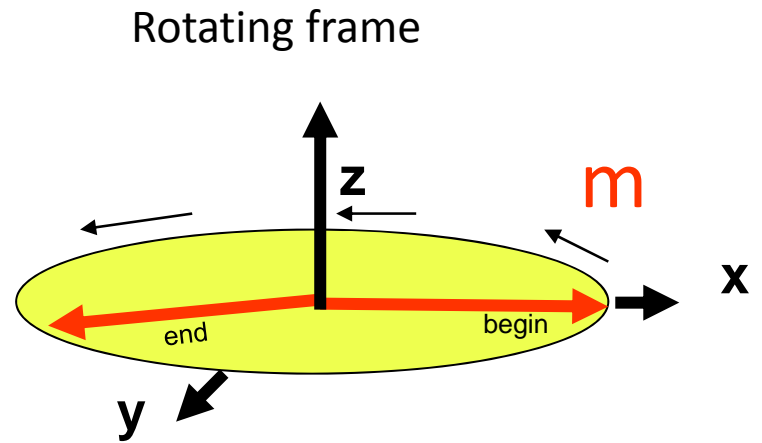
$$H^{(0)}_{CS} = \Delta\omega \cos \theta_m \left(\frac{I_z \pm I_x}{\sqrt{2}} \right)$$



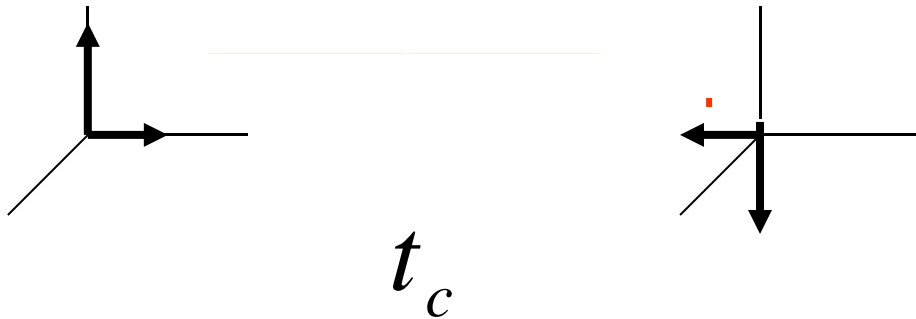
$$H^{(0)}_{DD} = 0$$

Homonuclear proton decoupling

Bielecki, Kolbert, Levitt

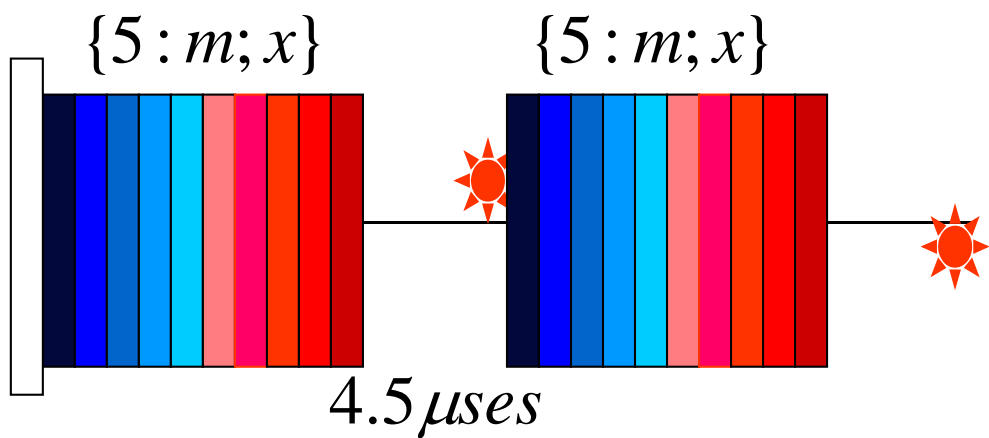


1972's field switching, Mehring
 1991's frequency switching, Bielecki, Kolbert, Levitt

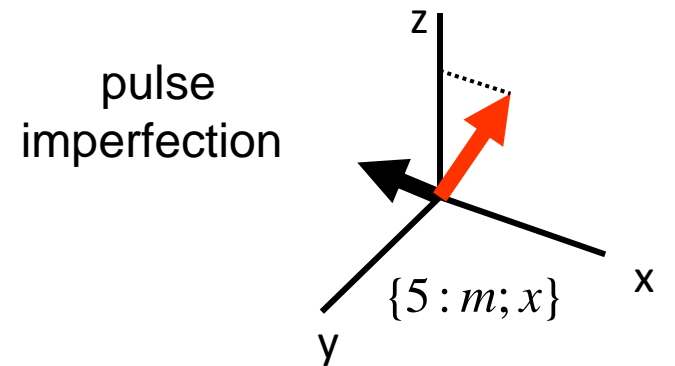


WPMLG5

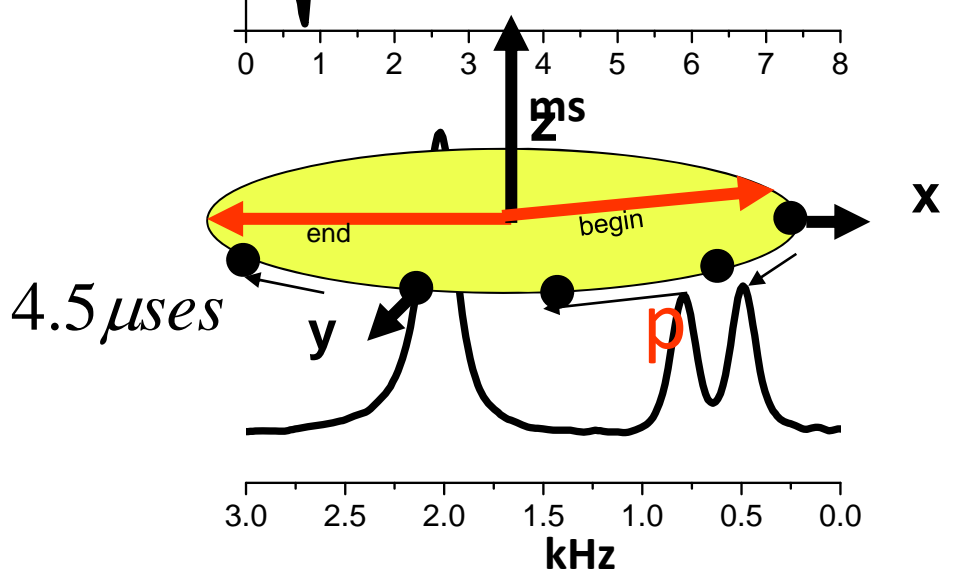
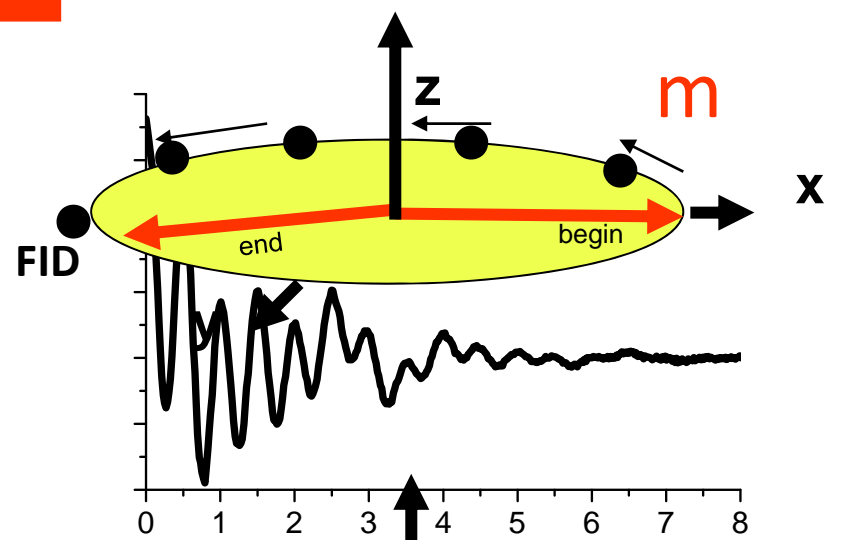
x
m



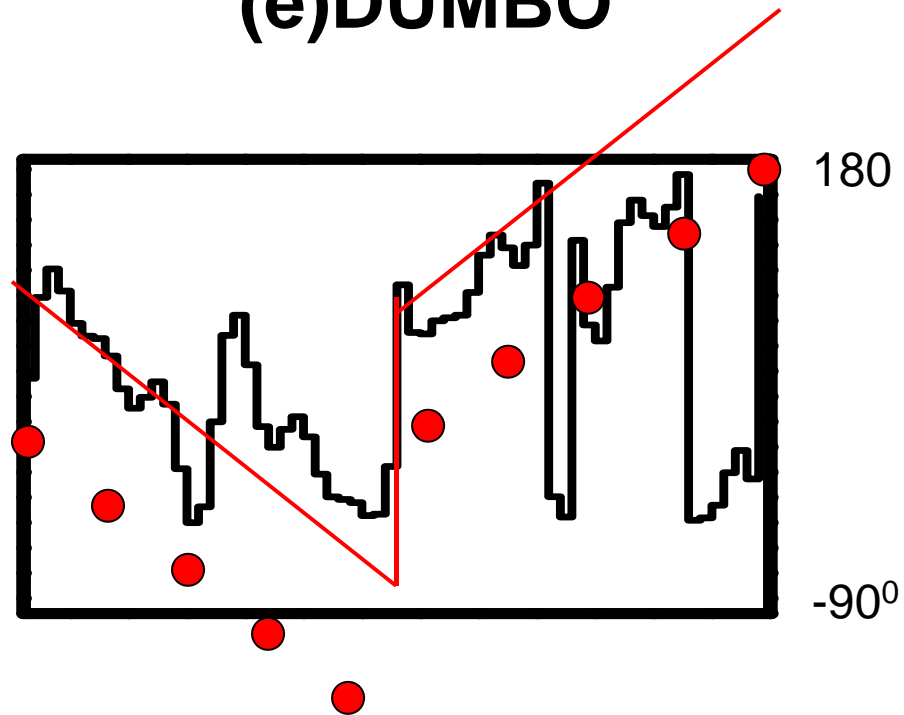
20.78, 62.34, 103.9, 145.46, 187.02
7.02, 325.46, 283.39, 242.34, 200.78



Rotating frame

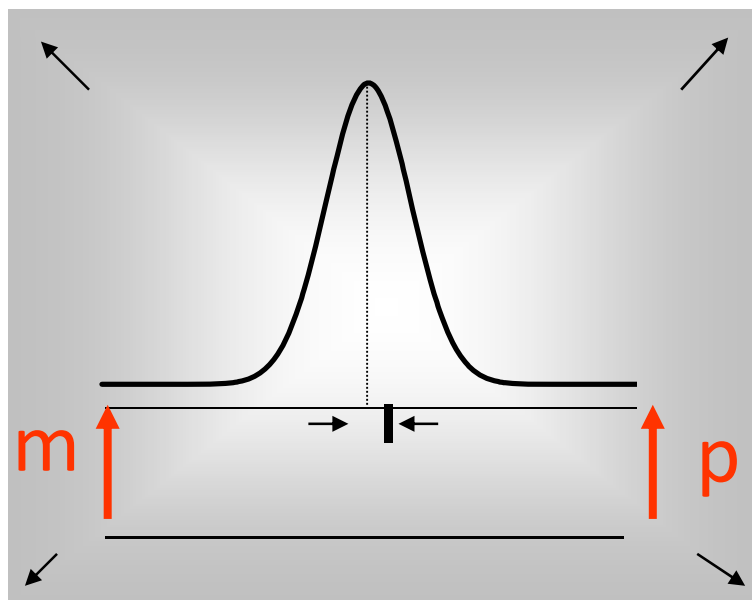
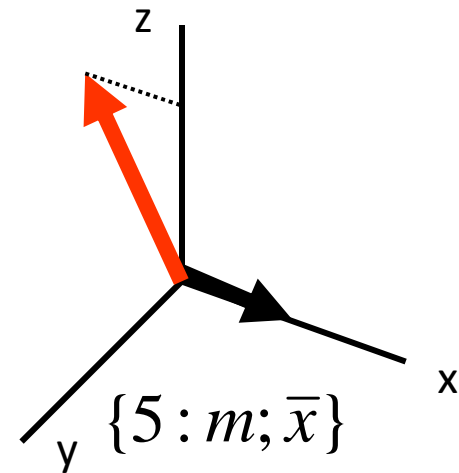
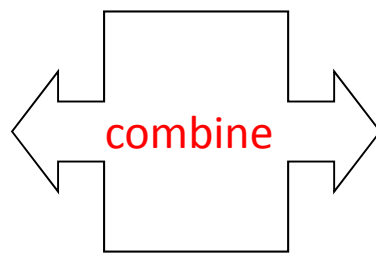
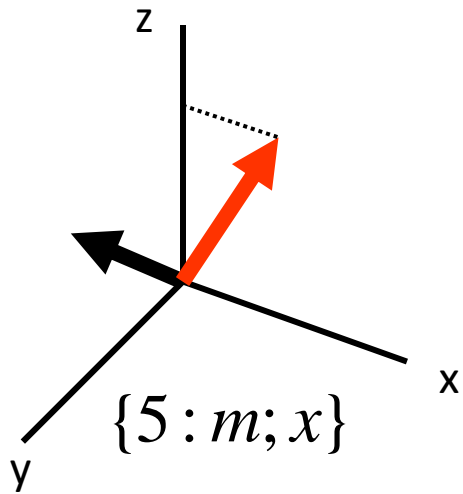


(e)DUMBO

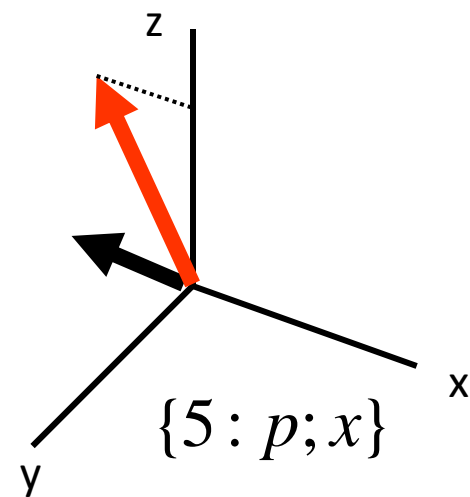
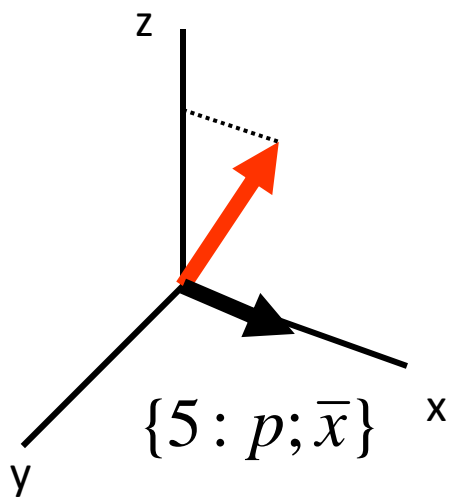


optimized 7 Fourier components in 64 pulses

A. Lesage, D. Sakellariou, S. Hedier, B. Elena,
P. Charmont, S. Steuernigel, L. Emsley,
J. Magn. Reson. 163 (2003) 105.



$$\Delta\omega > 0$$



wPMLG5 x \bar{x} m m supercycle

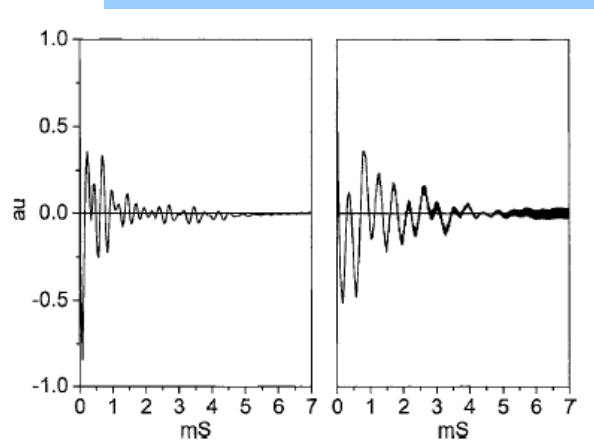
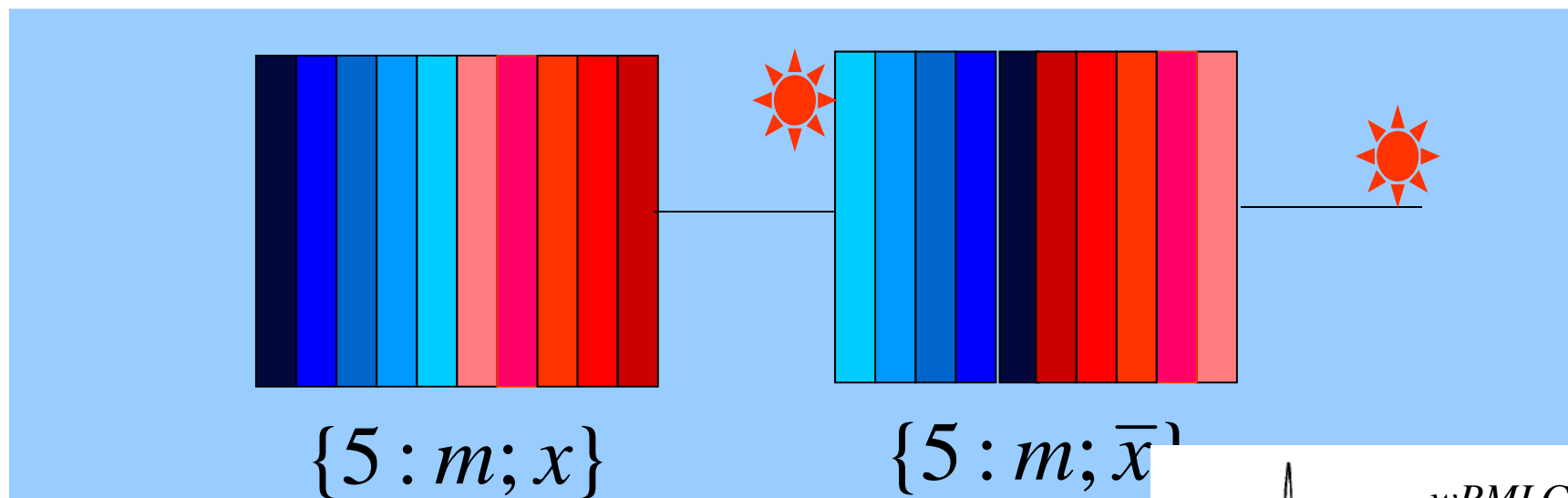


FIG. 7. The glycine time-domain signals acquired with $wPMLG5_{mm}^{\bar{x}x}$, when detected at every $\tau_c^{\bar{x}}$ (left) and τ_c^x (right). Different off-resonance values were used to emphasize the effect of nonsynchronized detection.

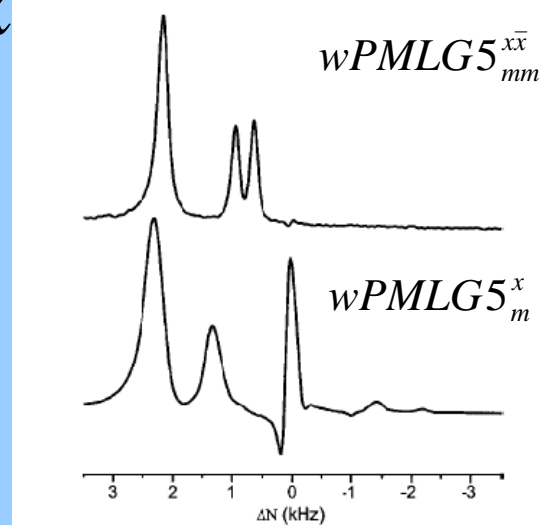


FIG. 6. Experimental glycine spectra obtained at 10 kHz spinning with $wPMLG5_{mm}^{\bar{x}x}$ (top) and $wPMLG5_m^x$ (bottom). A pulse length of 1.4 μs , window of 4.35 μs , and a rf power of 95 kHz, optimized for the best performance of the $\bar{x}x$ scheme, were chosen.

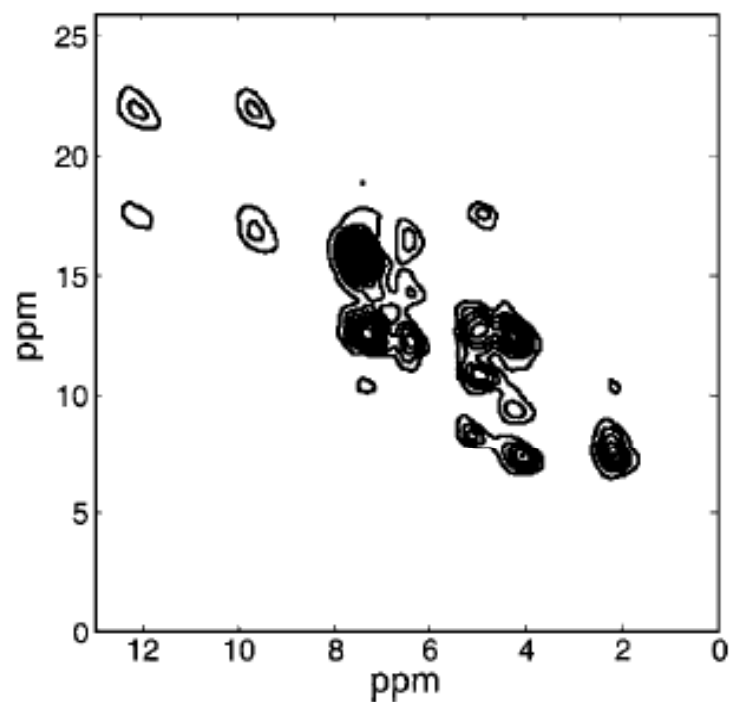
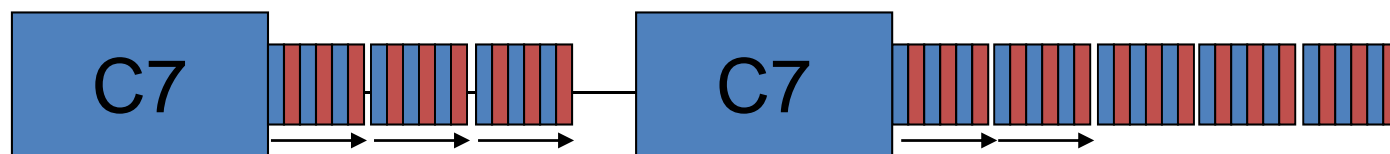
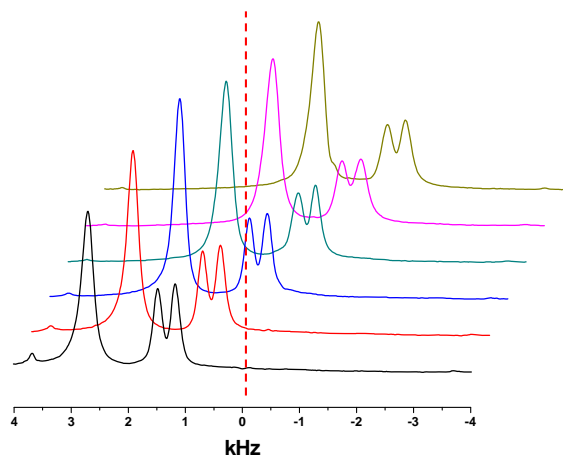


FIG. 10. DQ-SQ correlation spectrum of tyrosine HCl obtained using a one rotor period of $C7_1^3$ as the DQ excitation and reconversion pulse sequence and a data acquisition at a spinning frequency of 20 kHz using $wPMLG5_{mm}^{\bar{x}\bar{x}}$ in both the time dimensions. DQ filter phase cycling and TPPI detection were used to select the desired DQ pathway and obtain frequency discrimination in the indirect dimension.



Experimental parameters.

Pulse scheme	$\omega_r/2\pi$ (kHz)	35	45	55	65
wPMLG5 xx _{mm}	τ_{rf} (μ s)	15.4	11.6	12	9.6
	$\omega_1/2\pi$ (kHz)	131	180	190	216
	$\omega_c/2\pi$ (kHz)	26.32	34.97	34.01	40.65
	s	0.44	0.45	0.43	0.48
wDUMBO $^{\phi\bar{\phi}}$	τ_{rf} (μ s)	15.4	12	12	9.6
	$\omega_1/2\pi$ (kHz)	196	232	226	254
	$\omega_c/2\pi$ (kHz)	26.32	34.01	34.01	40.65
	s	0.54	0.55	0.56	0.56
wSAM	τ_{rf} (μ s)	20	22.2	36.4	15.4
	τ_m (μ s)	6.67	7.41	5.2	5.13
	$\omega_1/2\pi$ (kHz)	124	137	183	194
	$\omega_c/2\pi$ (kHz)	42.37	40.1	25.6	55.3
	s	0.88	0.78	0.75	0.73
	w (μ s)	3.6	2.7	2.7	2.7

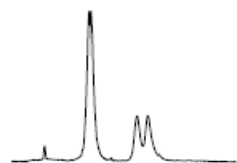
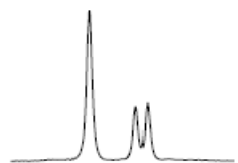
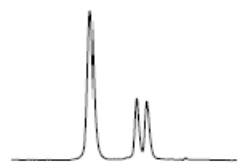
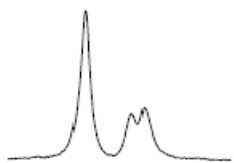
MAS

wPMLG5 xx _{mm}

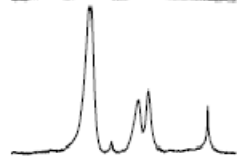
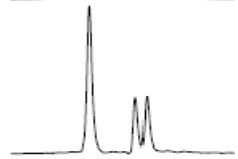
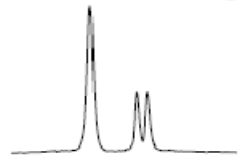
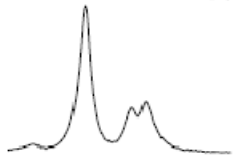
wDUMBO $^{\phi\bar{\phi}}$

SAM

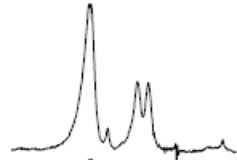
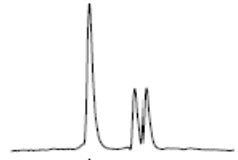
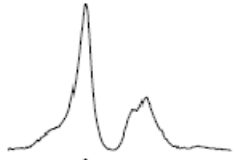
35kHz



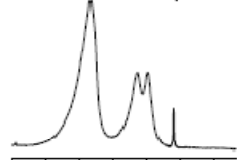
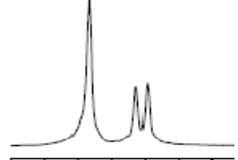
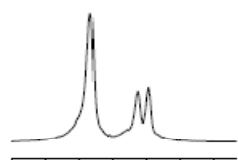
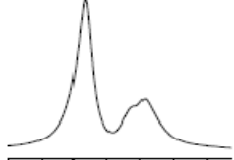
45kHz



55kHz



65kHz



12 6 0 ppm

12 6 0 ppm

12 6 0 ppm

12 6 0 ppm

Glycine, 600 MHz

DUMBO:

D. Sakellariou, A. Lesage,
P. Hodgkinson, L. Emsley,
Chem. Phys. Lett. 319
(2000) 253.

SAM:

J.P. Amoureux, B. Hu, J. Trebosc,
J. Magn. Reson. 193 (2008) 305.

The effective dipolar Hamiltonian

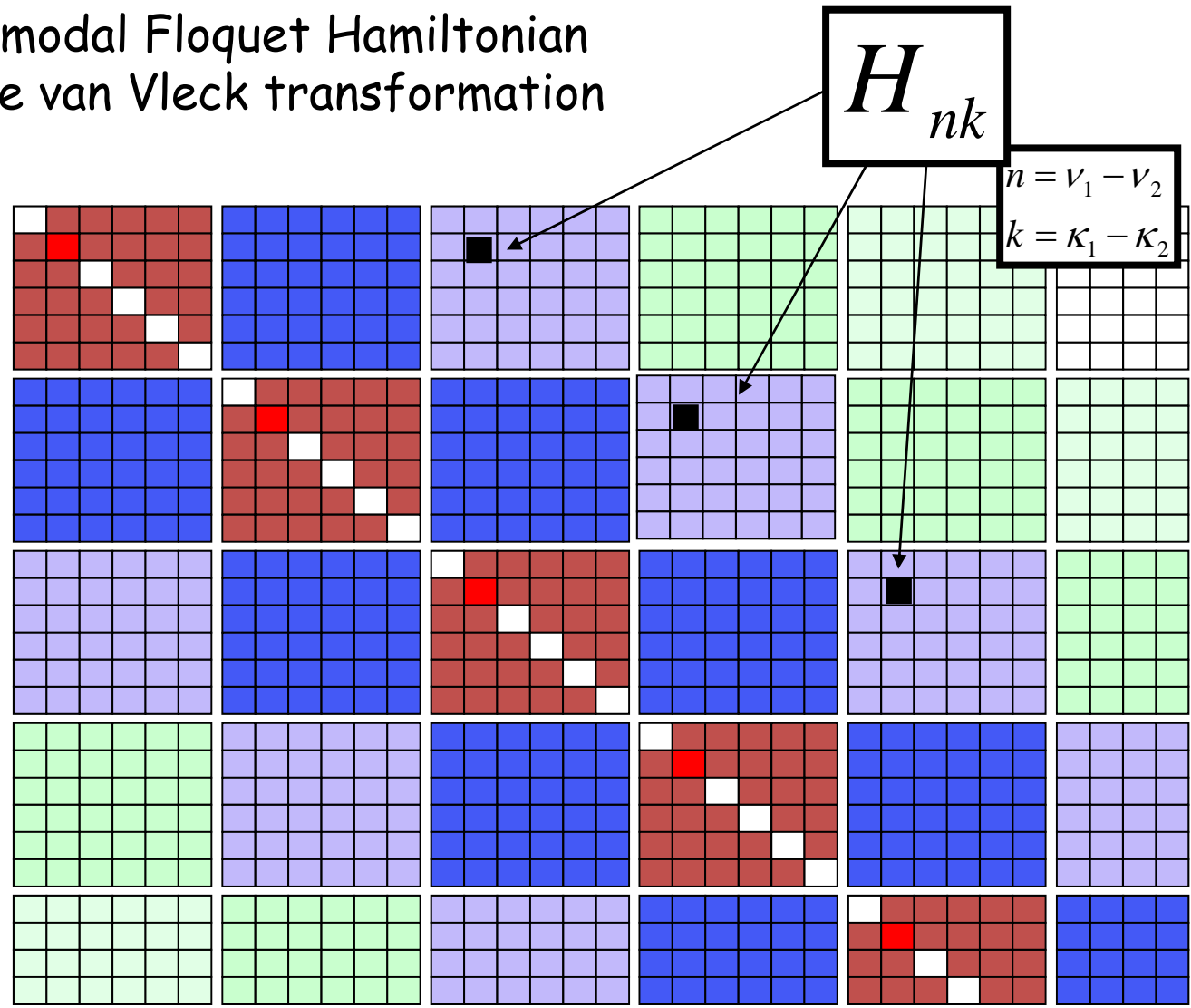
$$\tilde{H}_{00} F_0^r F_0^c \cong \left\{ H_{00} - \frac{1}{2} \sum_{k,n;\neq 0,0} \frac{[H_{n,k}, H_{-n,-k}]}{n\omega_r + k\omega_c} \right\} F_0^r F_0^c$$

the degenerate resonance case

$$n\omega_r + k\omega_c = 0$$

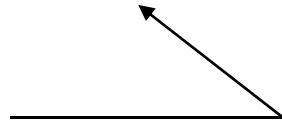
$$H_F = \tilde{H}_{0,0} F_0^r F_0^c + H_{n,k} F_n^r F_k^c - \frac{1}{2} \sum_{\substack{n',n'' \\ k',k''}} \frac{[H_{n',k'}, H_{n'',k''}]}{n'\omega_r + k'\omega_c} F_{n'+n''}^r F_{k'+k''}^c + \omega_r N^r + \omega_c N^c$$

The Bimodal Floquet Hamiltonian and the van Vleck transformation



$$n\omega_r + k\omega_c = 0 \text{ !!!!!}$$

$$H_{00} + \nu\omega_r + \kappa\omega_c$$



Minimize
Dipolar broadening

$$\sum_{n,k} \frac{[H_{nk}, H_{-n-k}]}{n\omega_r + k\omega_c} \propto \sum_{n,k} \frac{d_{nk}^{(2)} d_{-n-k}^{(2)}}{n\omega_r + k\omega_c}$$



$$\chi^2 \equiv \frac{\sum_{n,m,m'} \left(\sum_k \frac{d_{mk}^{(2)} d_{m'-k}^{(2)}}{n\omega_r + k\omega_c} \right)^2}{\sum_m \left(\sum_k d_{mk}^{(1)} \right)^2}$$



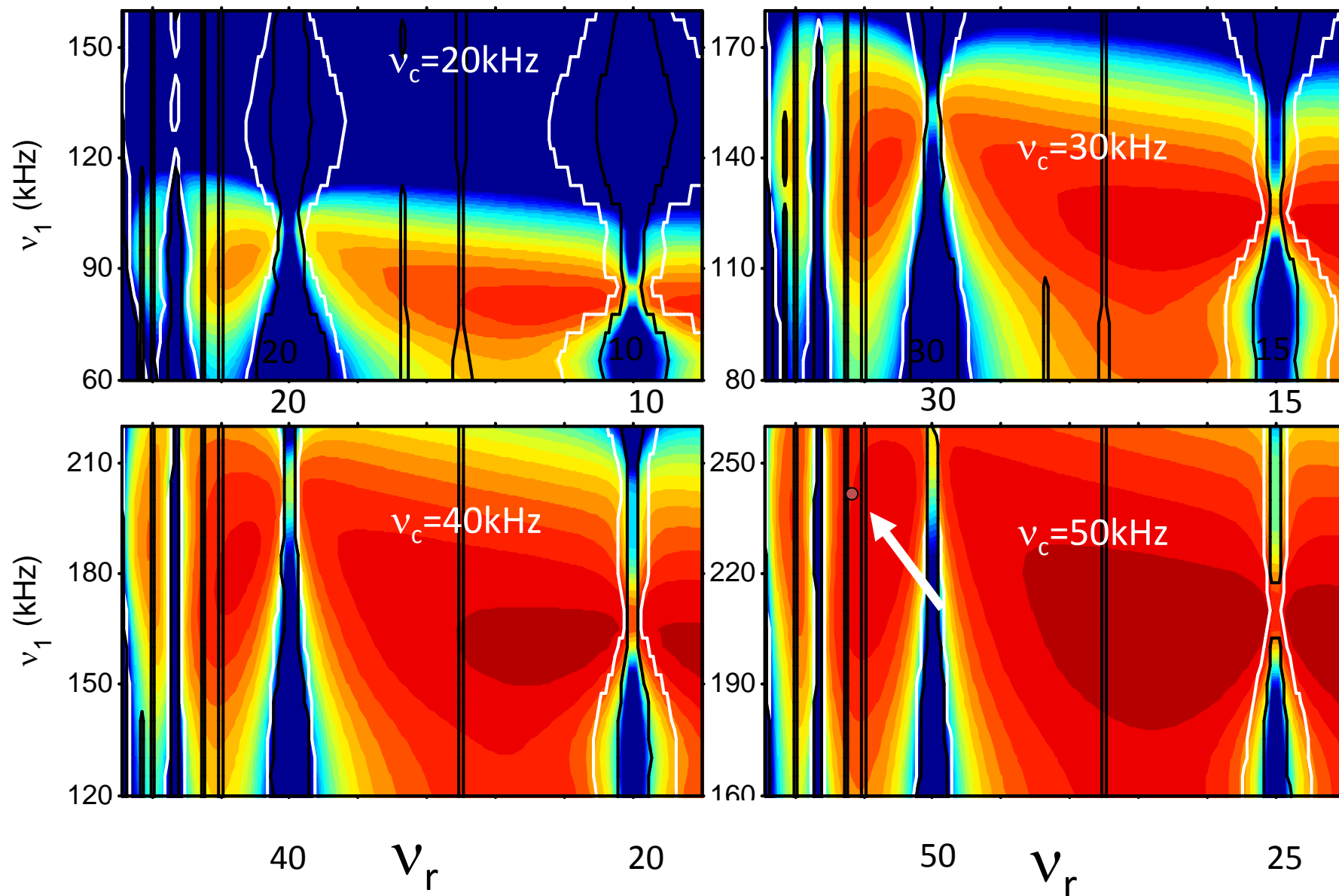
Maximize
Chemical shift

$$H_{00} \propto \sum_k d_{mk}^{(1)}$$

A measure for the linewidth of a
five-proton spin system

WP M L G5

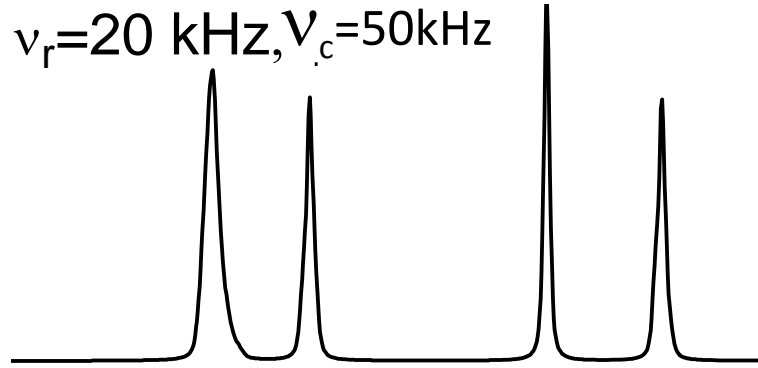
xx
mm



$\nu_r=65$ kHz $\nu_c=50$ kHz



$\nu_r=20$ kHz, $\nu_c=50$ kHz



$\nu_r=20$ kHz, $\nu_c=15$ kHz

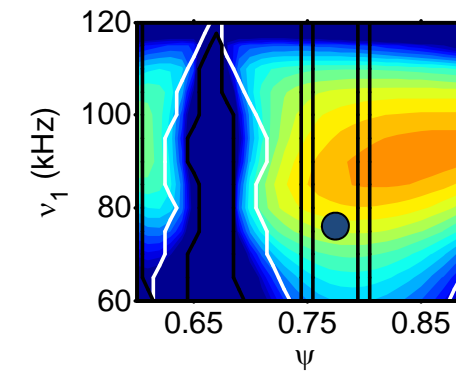
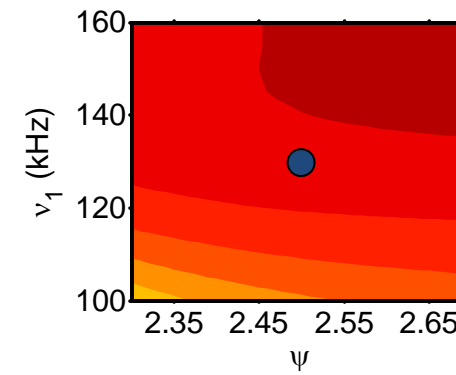
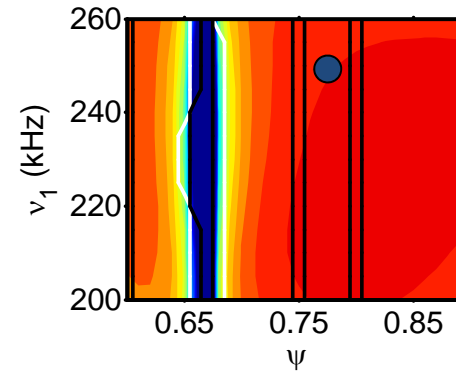
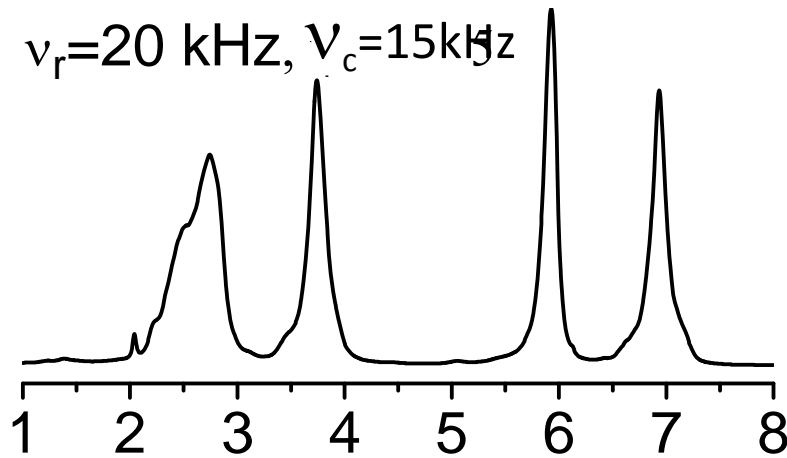


Figure 4

kHz

Tyrosine.HCl

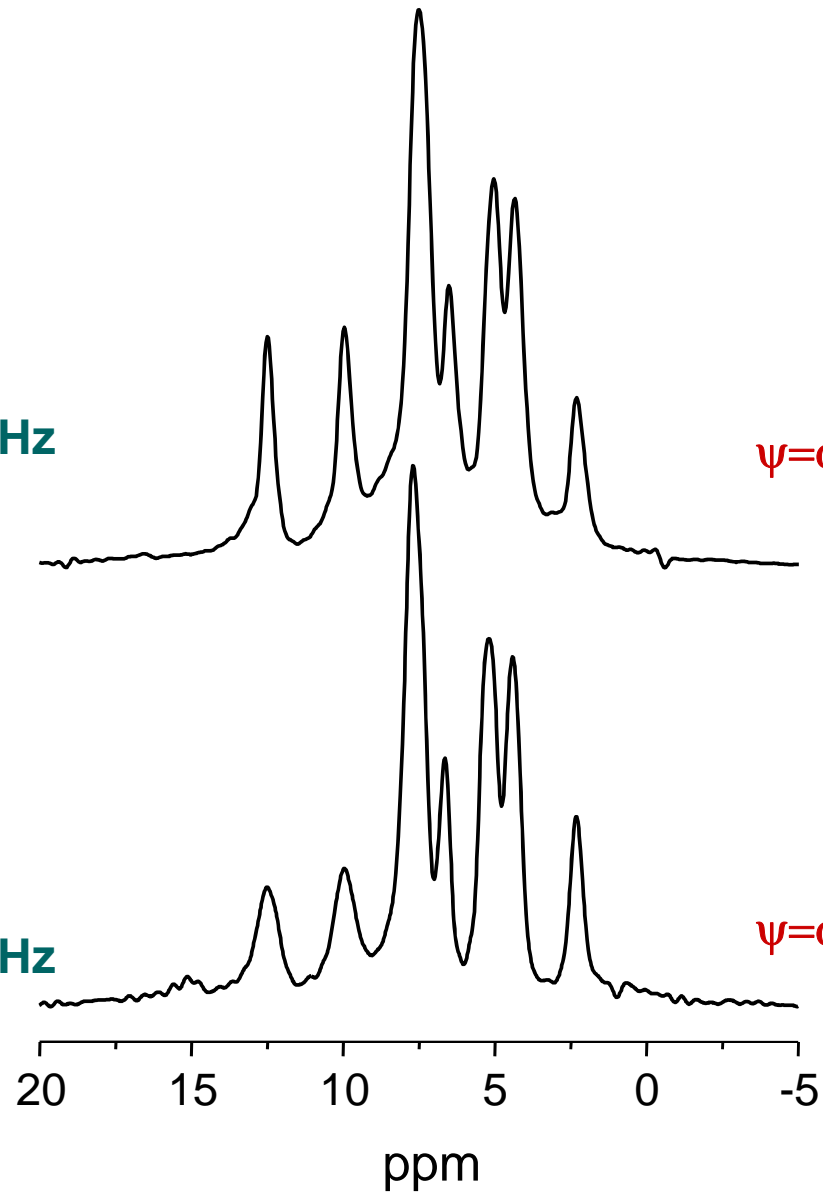
600 MHz

MAS at 65 kHz

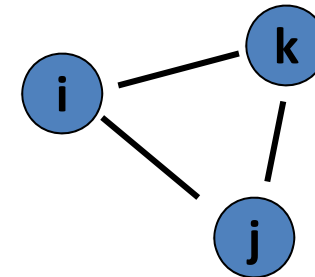
$\psi = \omega_c / \omega_r = 0.63$, $\nu_{\text{nut}} = 216$ kHz

MAS at 10 kHz

$\psi = \omega_c / \omega_r = 2.75$, $\nu_{\text{nut}} = 96$ kHz



A pulse sequence for:
SQ-TQ auto-correlation
 experiments



By considering the first order off diagonal BMF term of the dipolar interaction

$$\omega_{ij} \omega_{jk} \sum_{n,k} G_n(\Omega_{ij}) G_{-n}(\Omega_{jk}) \frac{d_{nk}^{(2)} d_{-n-k}^{(2)}}{n\omega_r + k\omega_c} [T_{m,ij}^{(2)}, T_{m',jk}^{(2)}]$$

$$m, m' = \pm 1, \pm 2$$

$$[I_i^+ I_j^+, I_{zj} I_k^+]$$

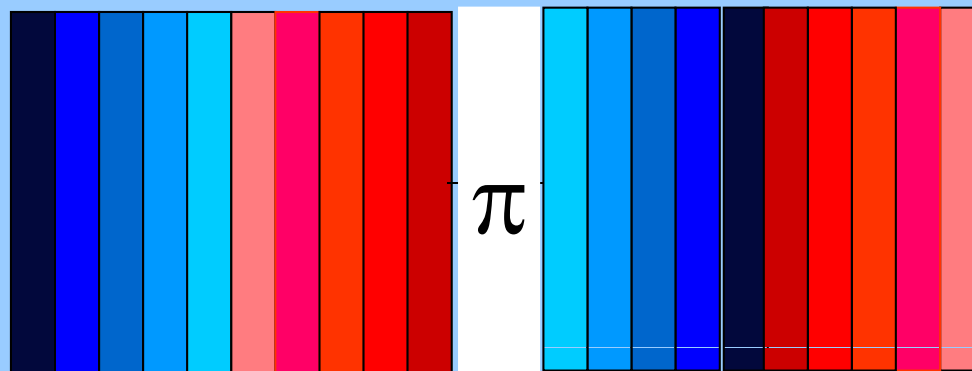
$$I_p^+ I_q^+ I_r^+ + I_p^- I_q^- I_r^-$$

$$T_0^{(2)} = \frac{1}{\sqrt{6}} (3I_z^2 - I(I+1)) \quad T_{\pm 1}^{(2)} = \mp \frac{1}{2} (I^\pm I_z + I_z I^\pm) \quad T_{\pm 2}^{(2)} = \frac{1}{2} (I^\pm)^2$$

wP M L G5 π

\bar{x}

mm



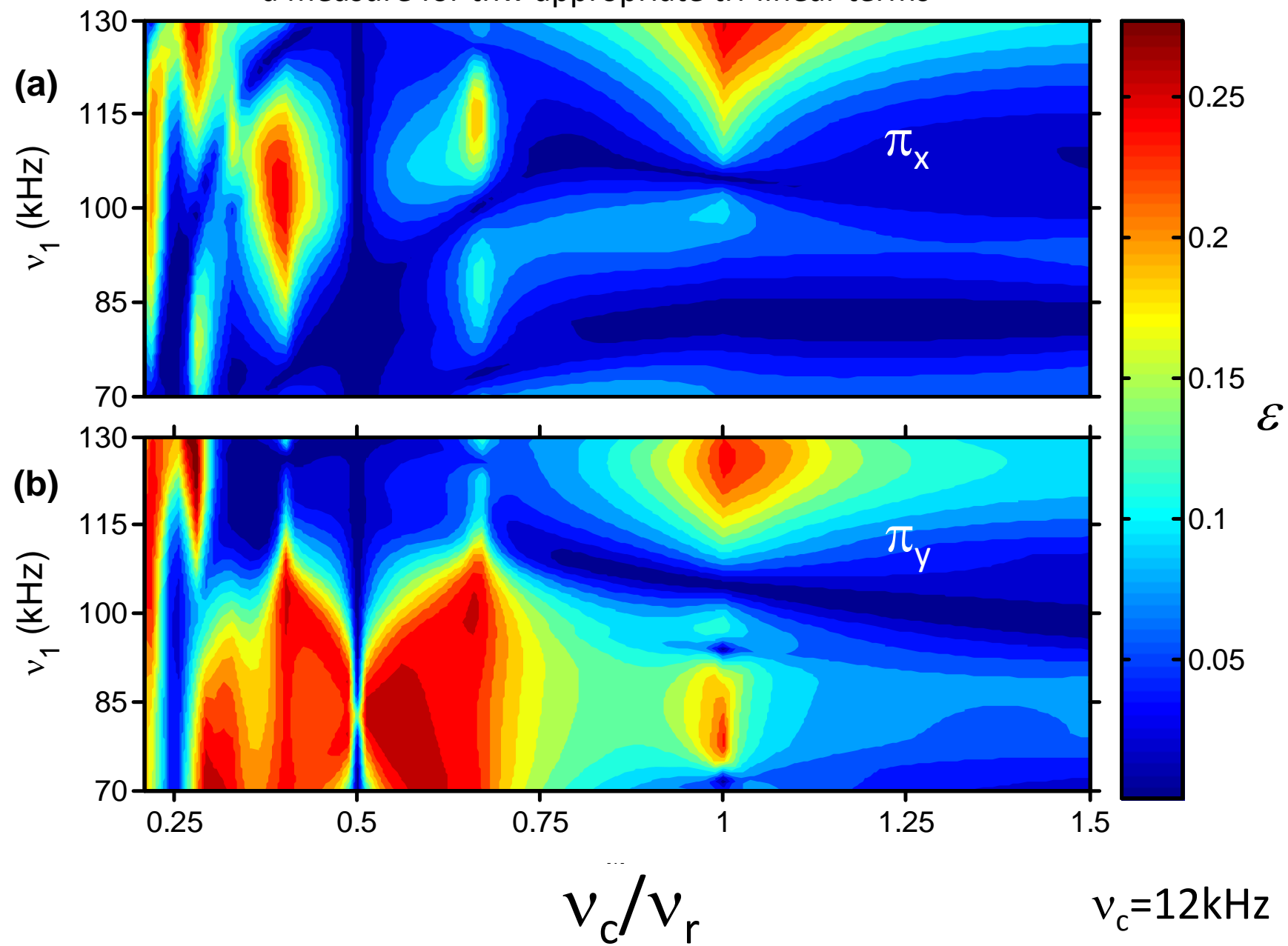
$\{5 : m; x\}$

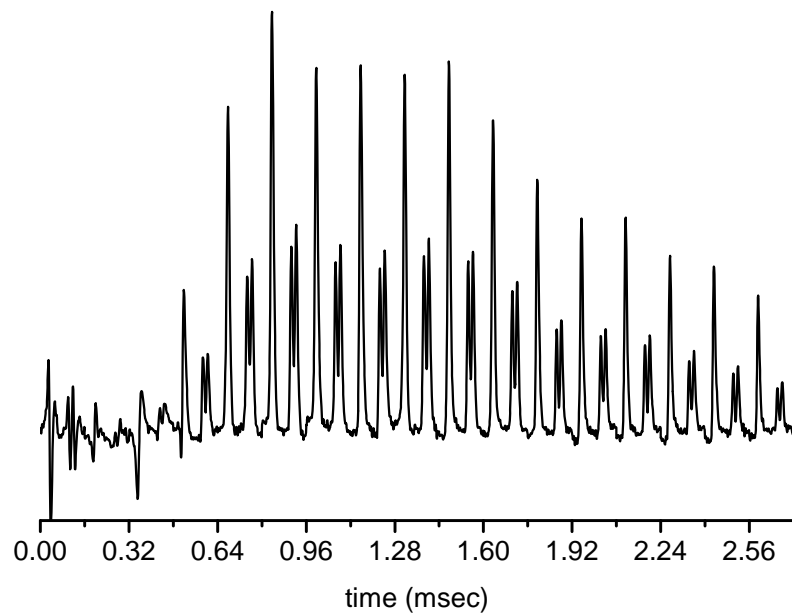
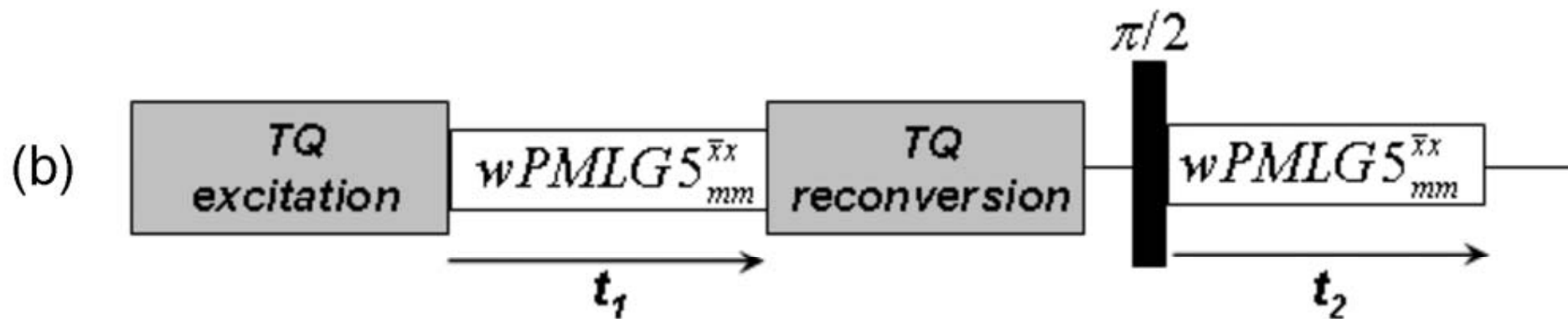
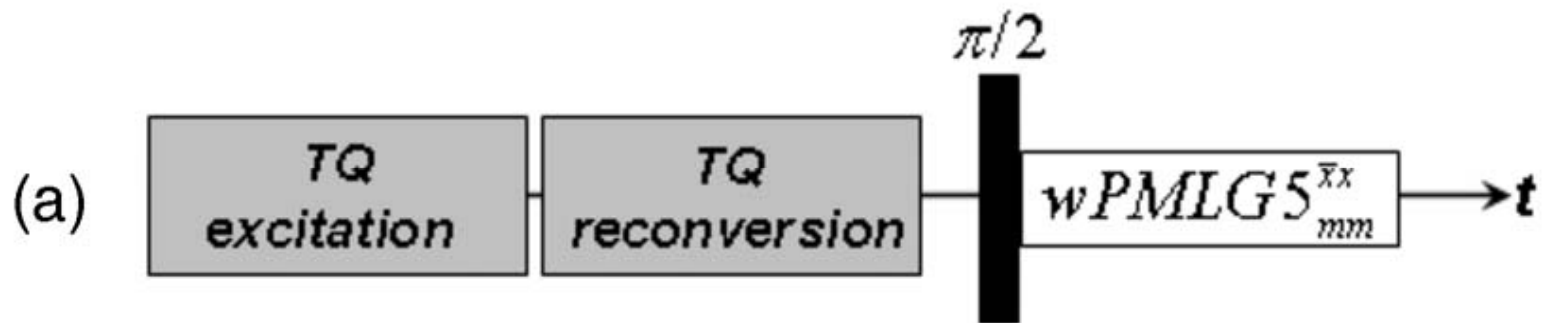
$\{5 : m; \bar{x}\}$

Some earlier examples of DQ : BABA, HORROR, C7, DRAWS : "SQ to TQ"

Eden suggested to use higher order Average Hamiltonian Theory

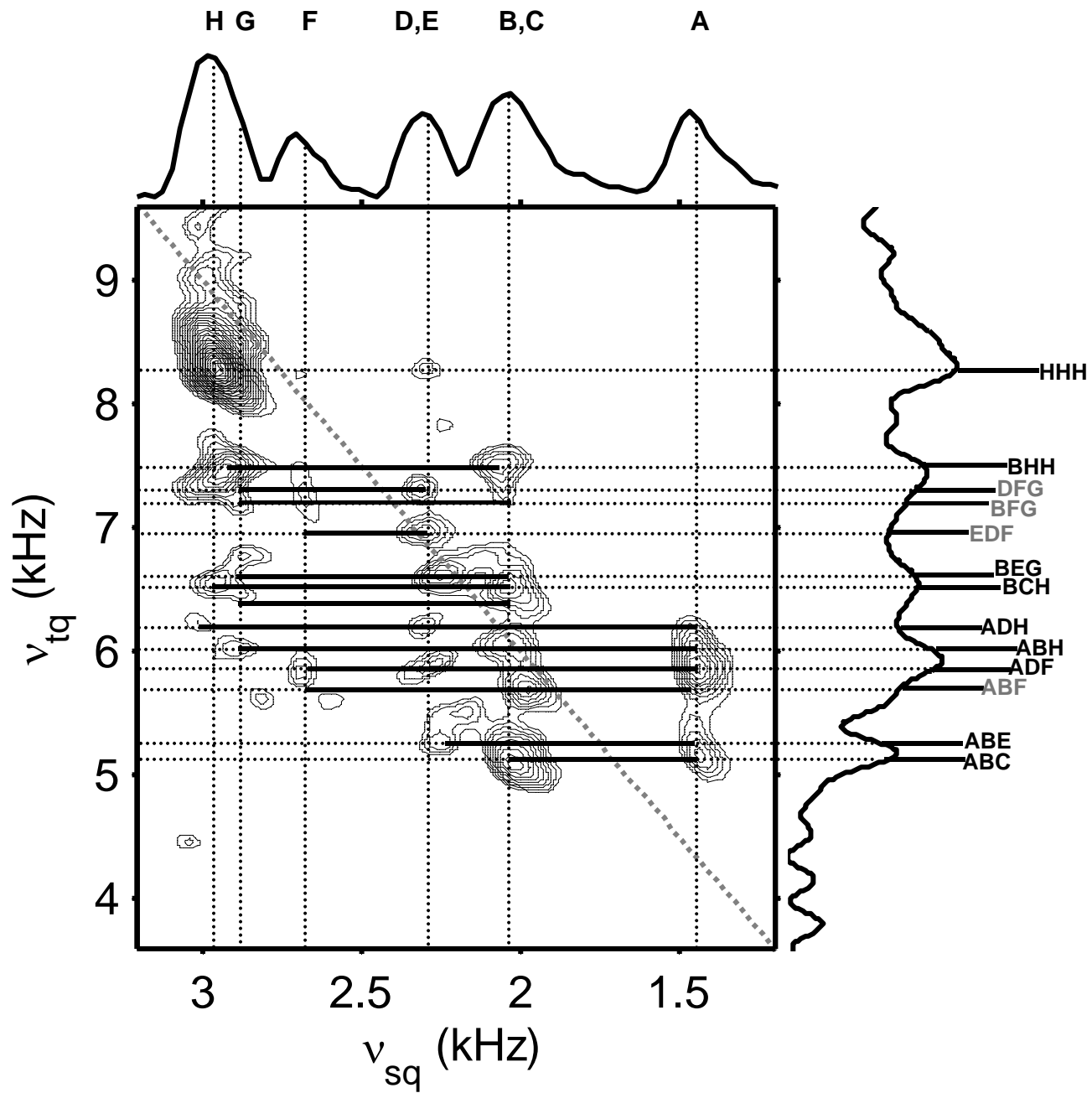
a measure for thw appropriate tri-linear terms

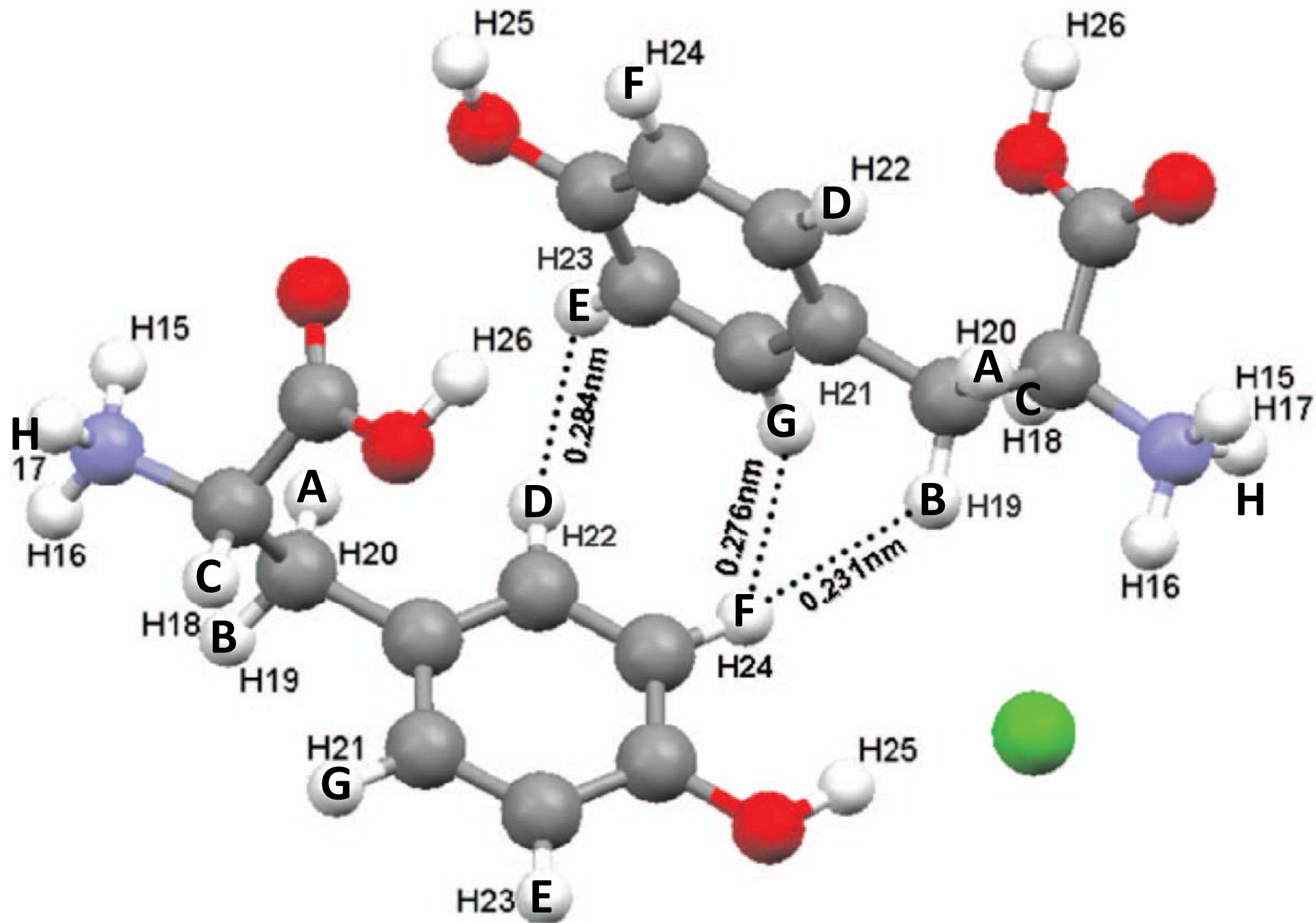




Michal Leskes'
assignment:

tyrosine





Thanks for listening

