ELDOR detected NMR (EDNMR)

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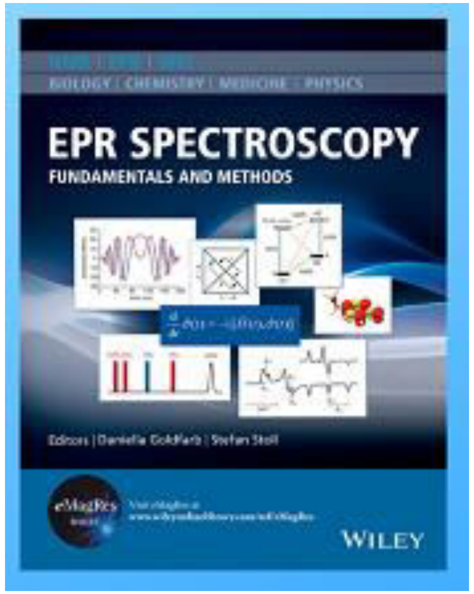
Chapter 17



Literature

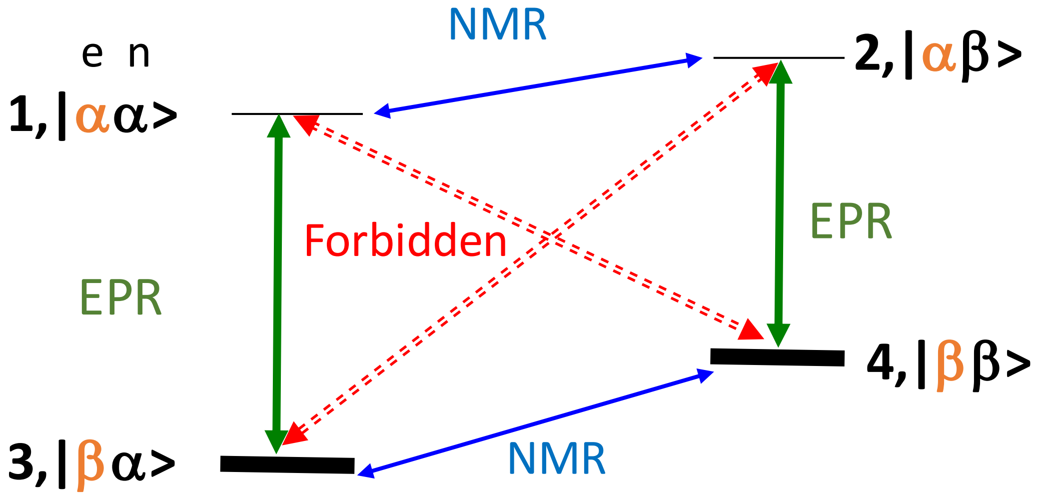
Cox, N.; Nalepa, A.; Lubitz, W.; Savitsky, A.,
ELDOR-detected NMR: A general and robust method for electron-nuclear hyperfine spectroscopy?
J. Magn. Reson. **2017,** *280*, 63-78.

8th EPR school, Brno, Czeck Republic, Nov. 17-25, 2019

How do we measure NMR frequencies ?
Hyperfine spectroscopy

ESEEM	**ENDOR**	**ELDOR detected NMR**
Electron spin echo envelope modulation	Electron-nuclear double resonance	Electron-electron double resonance detected NMR
Single frequency	Double and triple frequencies	Double and triple frequencies
MW	MW RF (one or two)	Two MW or three

The energy level diagram for S=1/2, I=1/2



$\nu_{13} + \nu_{12} = \nu_{23}$

EPR NMR forbidden

$\nu_{\alpha} = \nu_{12} = \nu_{23} - \nu_{13}$

$\nu_{\beta} = \nu_{34} = \nu_{14} - \nu_{24}$

To first order

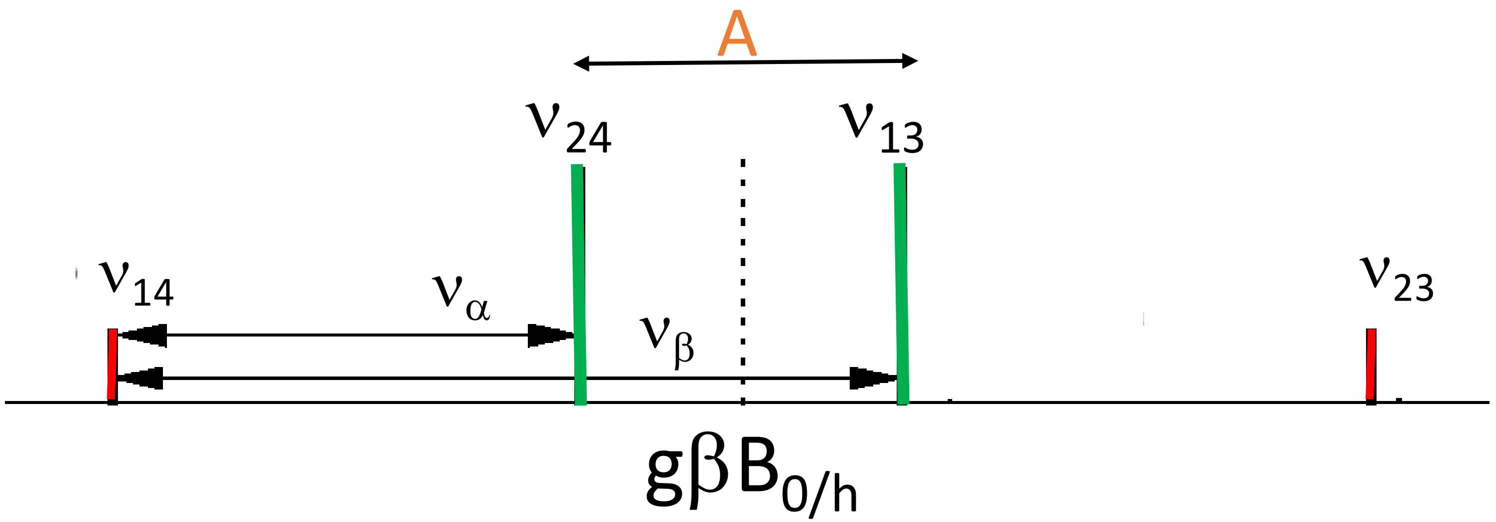
Allowed EPR $\Delta M_S = \pm 1$, $\Delta M_I = 0$

$$\nu_{13} = \nu + A/2$$
$$\nu_{24} = \nu - A/2$$

Forbidden EPR $\Delta MS = \pm 1$, $\Delta M_I = \pm 1$

$$\nu_{14} = \nu - \nu_N$$
$$\nu_{23} = \nu + \nu_N$$

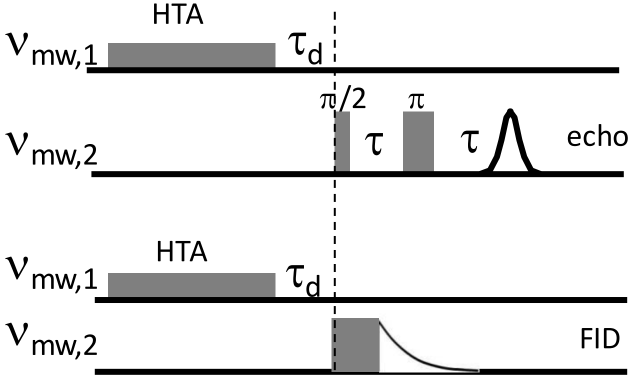
The EPR spectrum



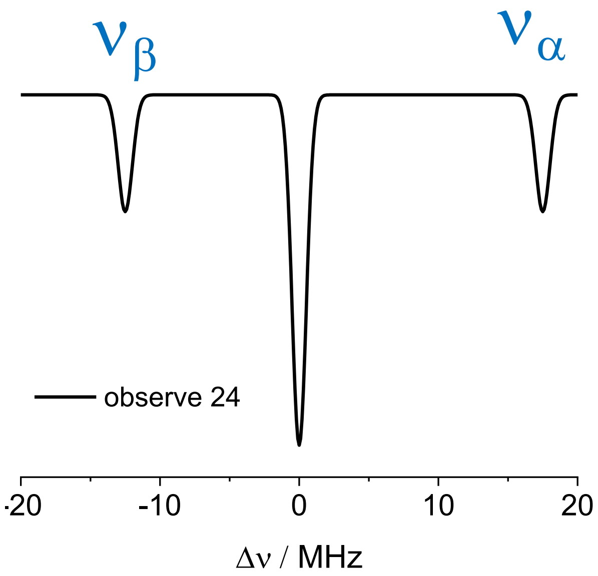
$$\nu_\alpha = \nu_{23} - \nu_{13}$$

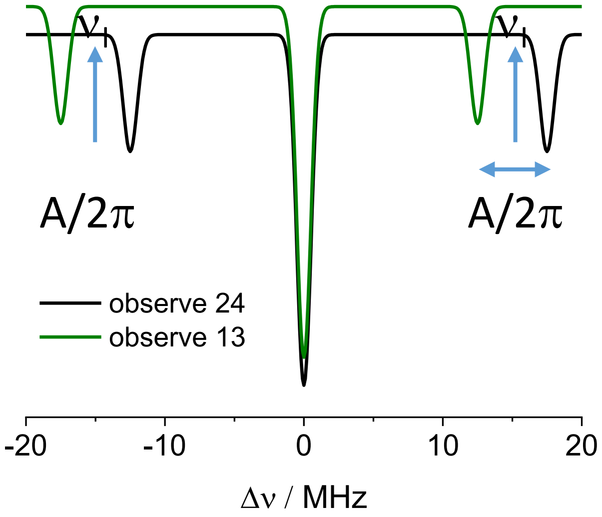
$$\nu_\beta = \nu_{14} - \nu_{24}$$

How can we measure the nuclear frequencies ?



$\Delta\nu=\nu_{mw,2}-\nu_{mw,1}$

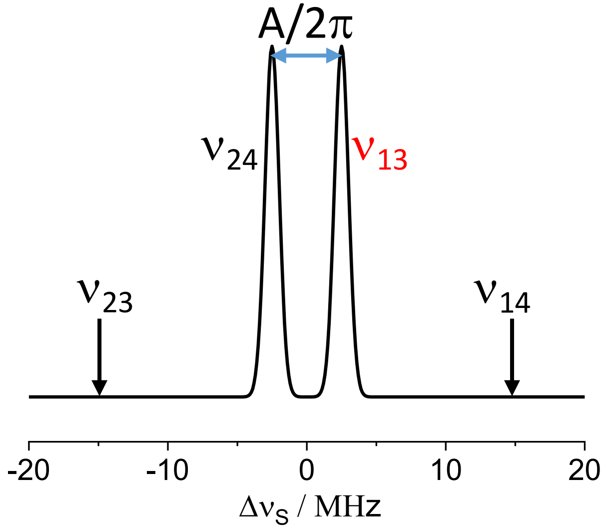


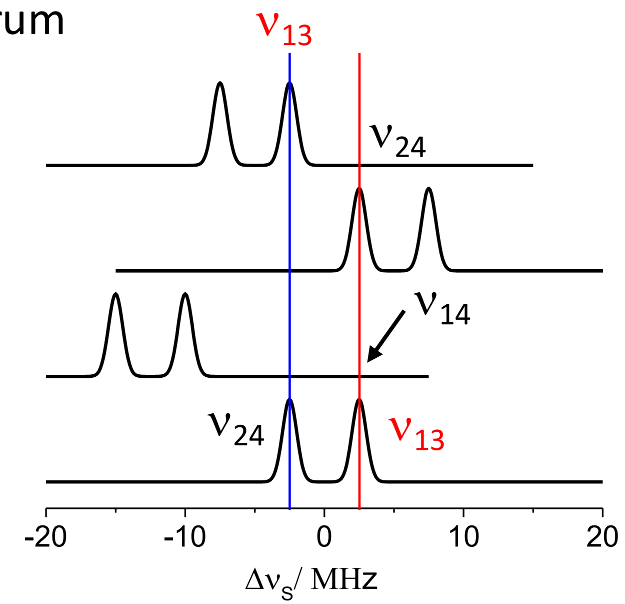


Schosseler, P.; Wacker, T.; Schweiger, A., *Chem. Phys. Lett.* **1994,** *224*, 319-324.

The EDNMR spectrum – inhomogenously broadened EPR spectra, the EPR doublet is not resolved

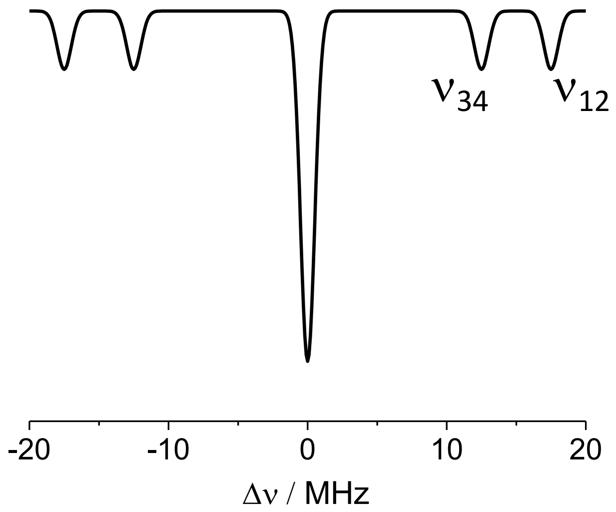
EPR spectrum



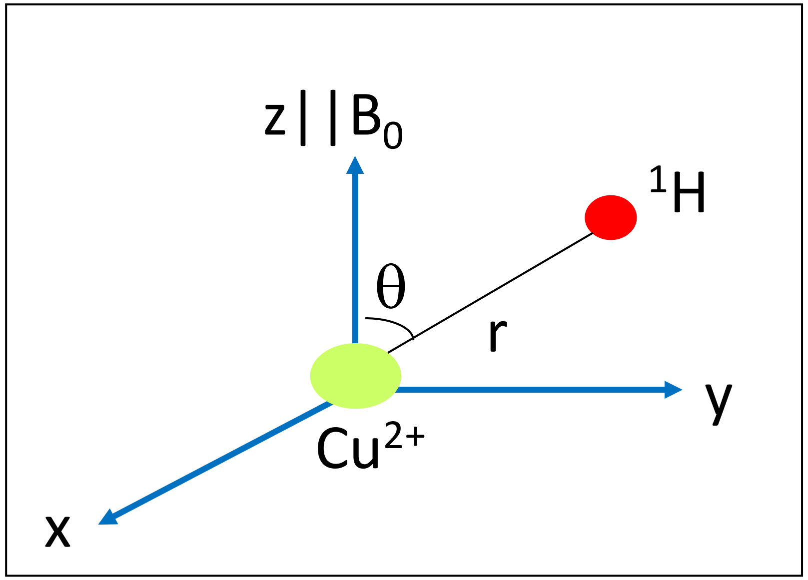


Inhomogeneous broadening
The hyperfine coupling is not resolved

EDNMR spectrum



The spin Hamiltonian



$$\hat{H} = \nu \hat{S}_z - \nu_I \hat{I}_z + A\hat{S}_z\hat{I}_z + B\hat{S}_z\hat{I}_x$$

$$A = A_{||}\cos^2\theta + A_{\perp}\sin^2\theta = A_{iso} + T_{\perp}(3\cos^2\theta - 1)$$

$$B = (A_{||} - A_{\perp})\sin\theta\cos\theta = 3T_{\perp}\sin\theta\cos\theta$$

For the point dipole approximation

$$T_{\perp} = \frac{\mu_0}{4\pi h} g\beta_e \frac{g_n\beta_n}{r^3}$$

$A_{||}$, $\theta = 0^0$ $A_{\perp}$, $\theta = 90^0$

The hyperfine interaction : mixing of Zeeman states

|e,n>	|αα>	|αβ>	|βα>	|ββ>
|αα>	A	B		
|αβ>	B	A		
|βα>			A	B
|ββ>			B	A

$$\nu_{\alpha,\beta} = \left[\left(\pm\frac{1}{2}A + \nu_I\right)^2 + \left(\frac{1}{2}B\right)^2\right]^{1/2}$$

Nuclear frequencies:

$$\nu(m_S) = \sqrt{(\nu_{\mathrm{I}} + m_S A)^2 + (m_S B)^2}$$

$$\nu_{\mathrm{I}} = -g_{\mathrm{n}}\mu_{\mathrm{N}}B_0/h \qquad m_S = \pm 1/2$$

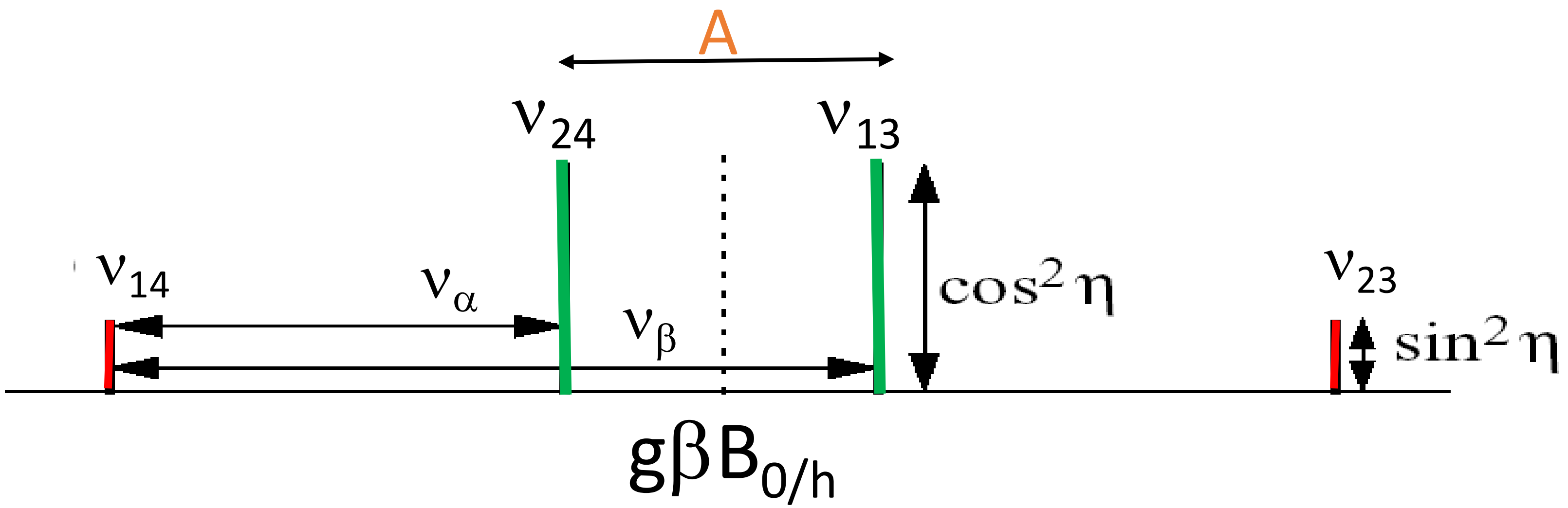
Secular : ENDOR

Pseudo-secular : ESEEM, ELDOR detected NMR

non-secular can be neglected

$\nu_I = \nu_N$ = nuclear Larmor freq

The EPR spectrum



To observed forbidden transitions need :

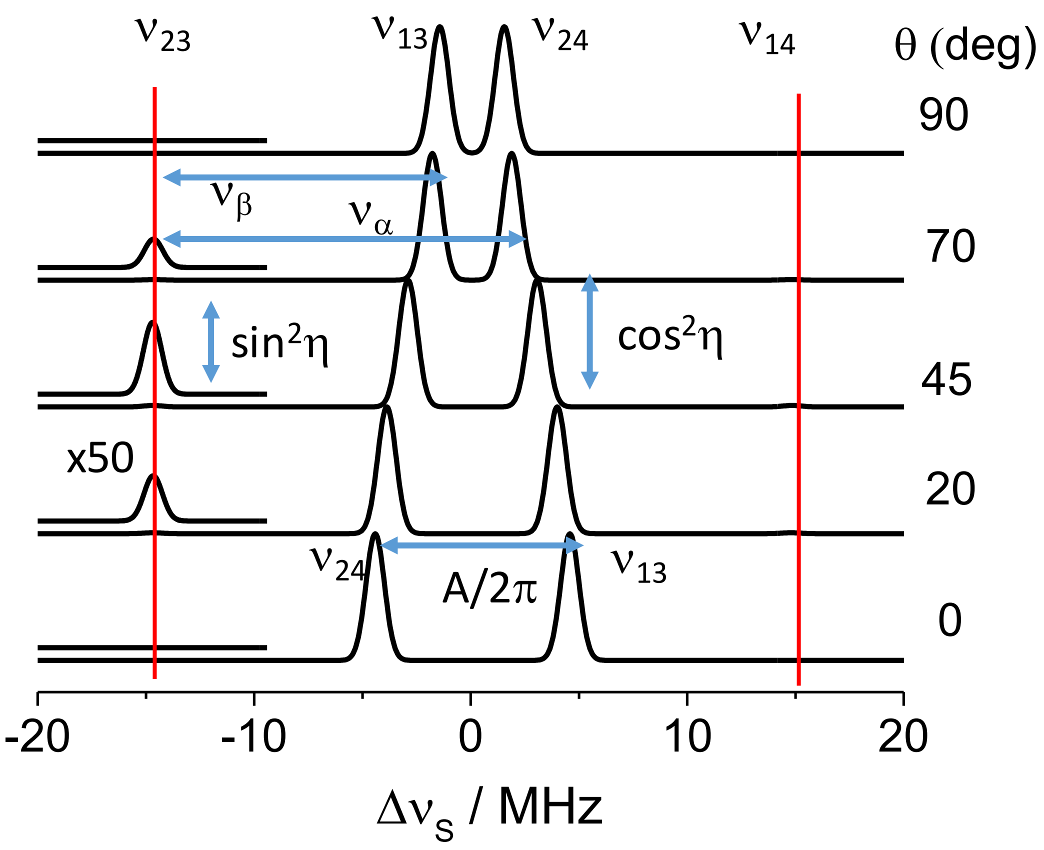
$|B|>0$ and $|A|$ on the order of ν_N

$$\eta_\alpha = \arctan\frac{-B}{A+2\nu_N}$$

$$\eta_\beta = \arctan\frac{-B}{A-2\nu_N}$$

$$\eta = (\eta_\alpha - \eta_\beta)/2$$

Orientation dependence



The intensity of the forbidden transitions are orientation dependent, when B=0 they are 0

Line intensities in EDNMR

The EDNMR experiment creates holes in the broad EPR spectrum.

The signal intensities $\propto$ depth of holes, h.

$$I_f = \sin^2\eta$$

$$I_a = \cos^2\eta$$

$\beta_f = \omega_1 t_{HTA} (I_f)^{1/2} = \beta_0 (I_f)^{1/2}$ the flip angle of the HTA pulse (forbidden transition)

$\omega_1 = g_e \mu_e B_1/\hbar$ The mw amplitude

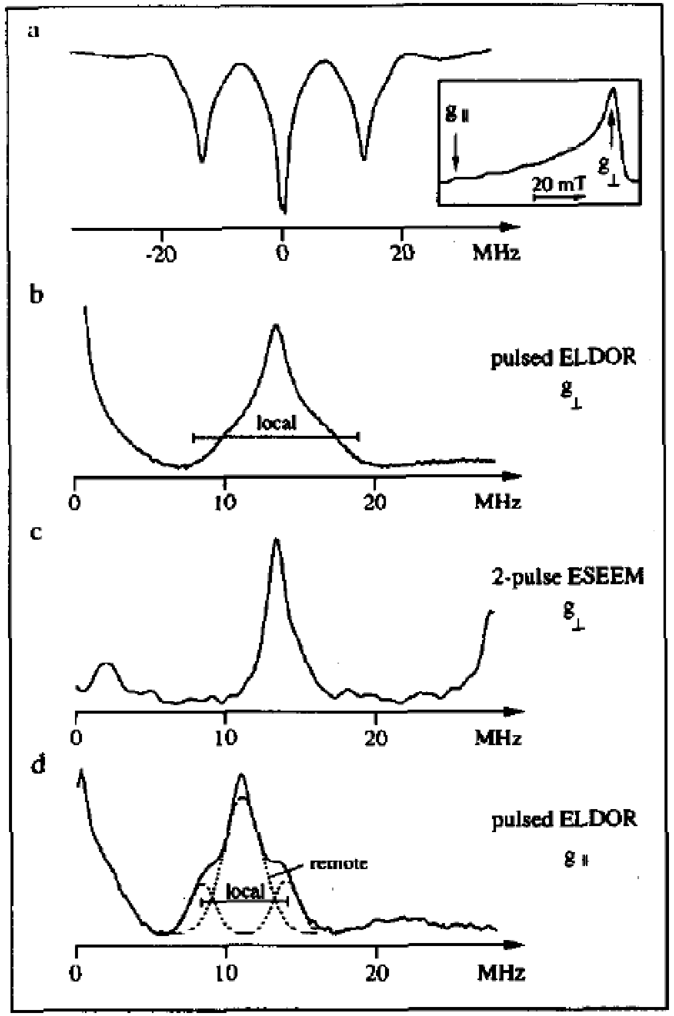
$\beta_0 = \omega_1 t_{HTA}$ The flip HTA flip angle for the allowed transition

$$h = 1 - I_a \cos(\beta_0 (I_f)^{\frac{1}{2}}) - I_f \cos(\beta_0 (I_a)^{\frac{1}{2}})$$

For $I_f/I_a << 1$ and for very small I_f $\beta_0 (I_f)^{\frac{1}{2}} \ll 1$,

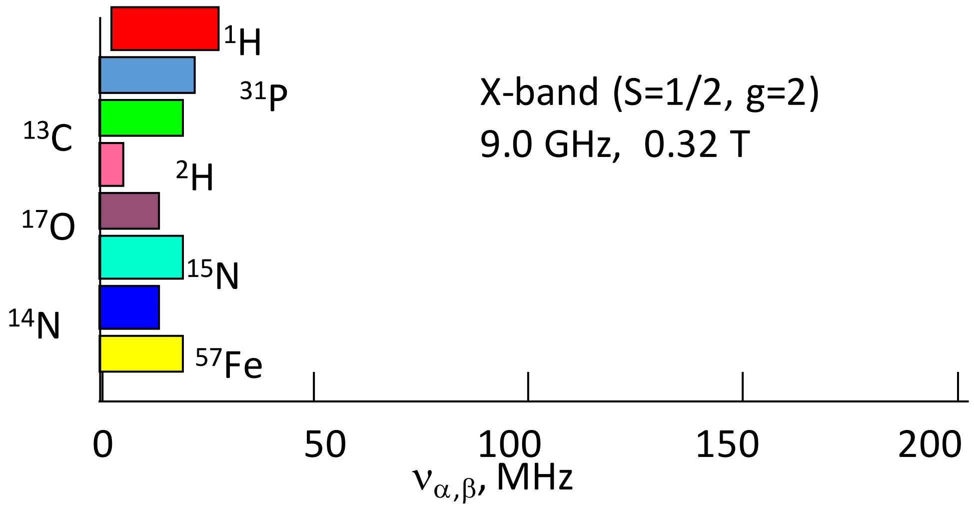
$$h \approx 1 - \cos\left(\beta_0 (I_f)^{\frac{1}{2}}\right) \approx 1 - 1 + \frac{1}{4}\beta_0^2 I_f \propto I_f$$

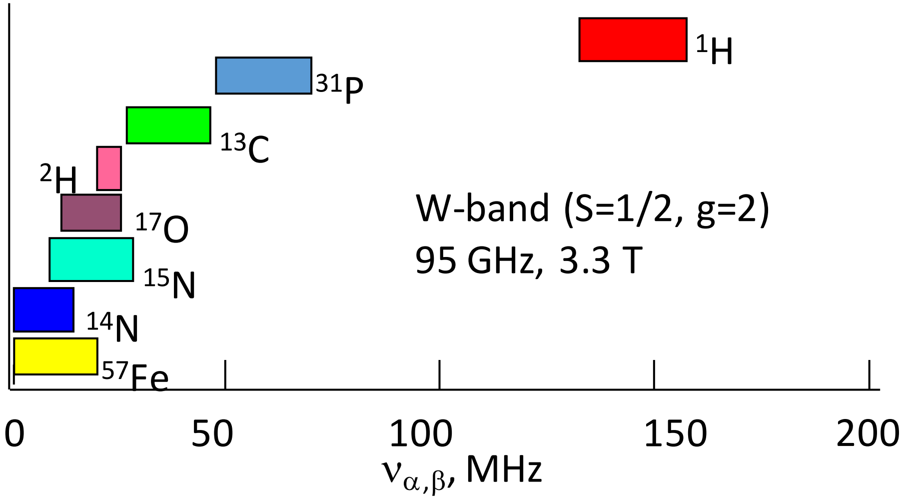
First EDNMR – X band, on 10 mM $Cu(H_2O)_6^{2+}$



Schosseler, P.; Wacker, T.; Schweiger, A., *Chem. Phys. Lett.* **1994,** *224*, 319-324.

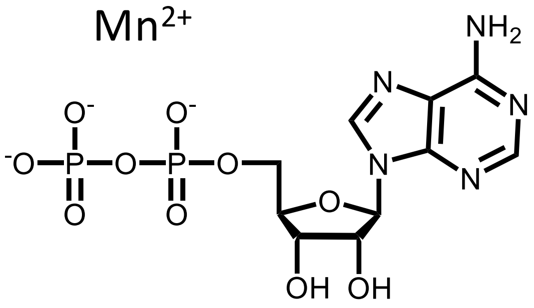
The choice of spectrometer frequency

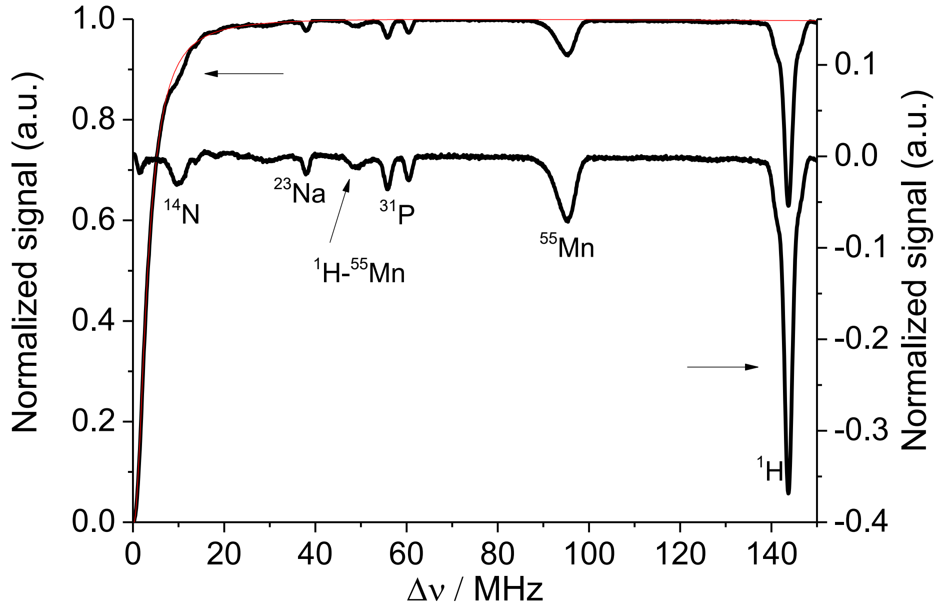


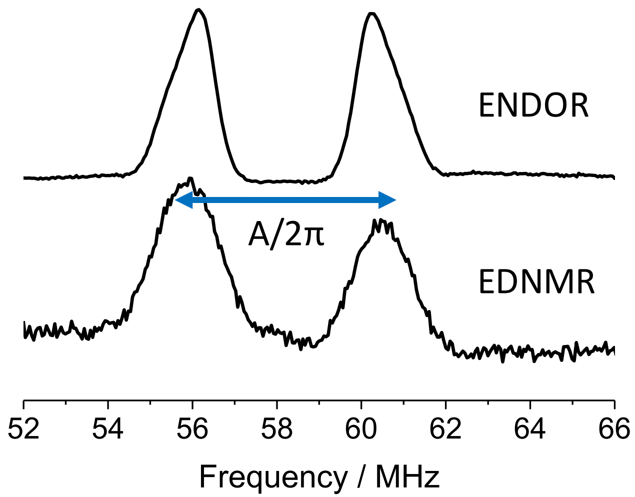


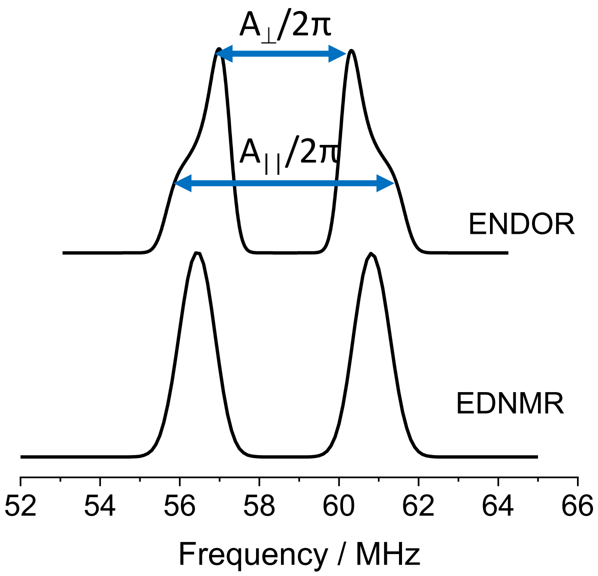
High field – first order expressions

EDNMR at W-band , Mn(II)ADP





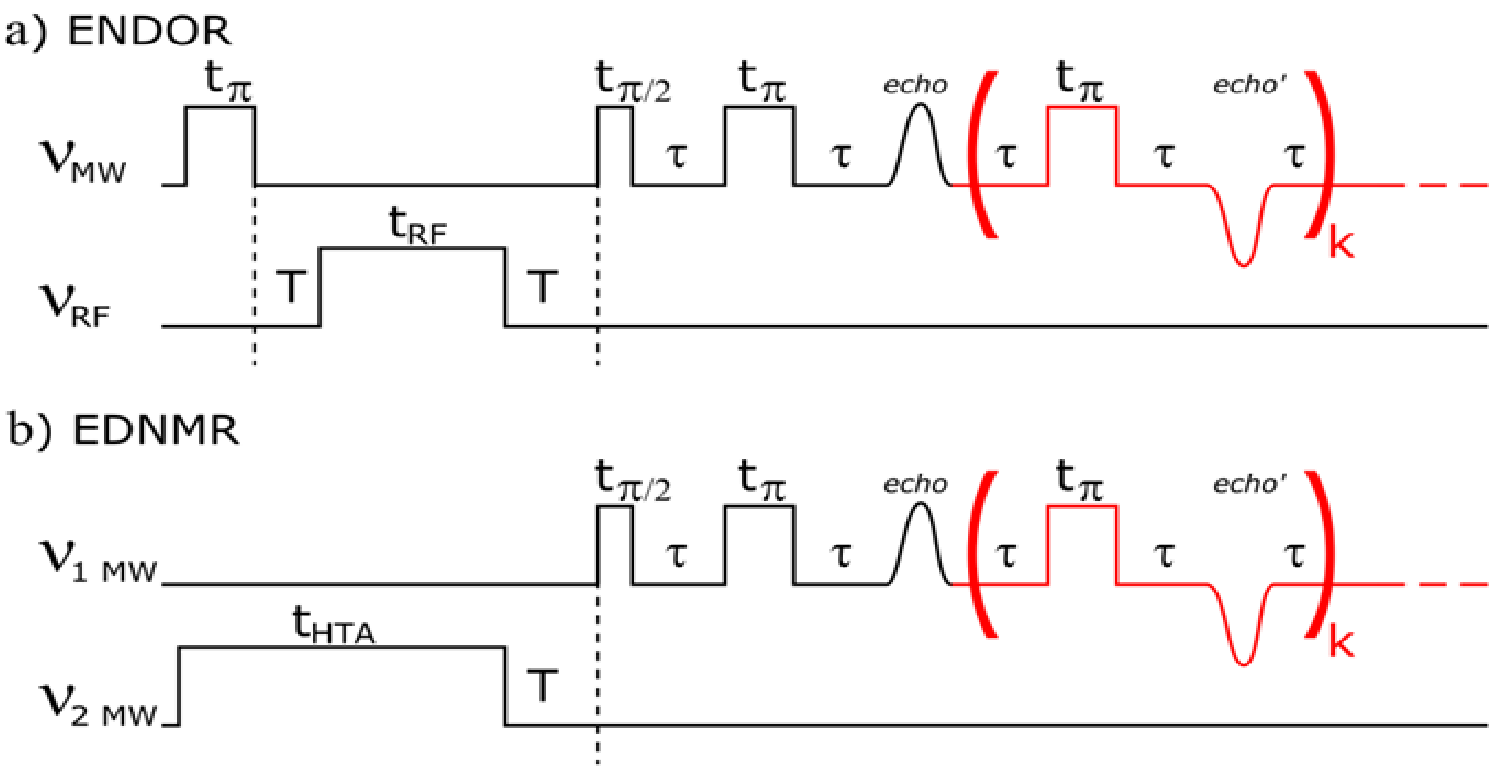




- Narrow central hole can be obtained by applying a weak HTA pulse such that $\omega_1 T_\mathrm{m} \ll 1$
- Same holds for the EDNMR lines (they can be narrower than the central hole)
- Selective detection pulses , with the smallest possible bandwidth are desired (long pulses)
- The wider the integration window, the better the resolution.
- It is recommended to acquire full echo (or FID) transients and carry out the integration post-measurement such that the optimum SNR and resolution can be achieved.

Resolution often comes at the expense of SNR

Improving sensitivity

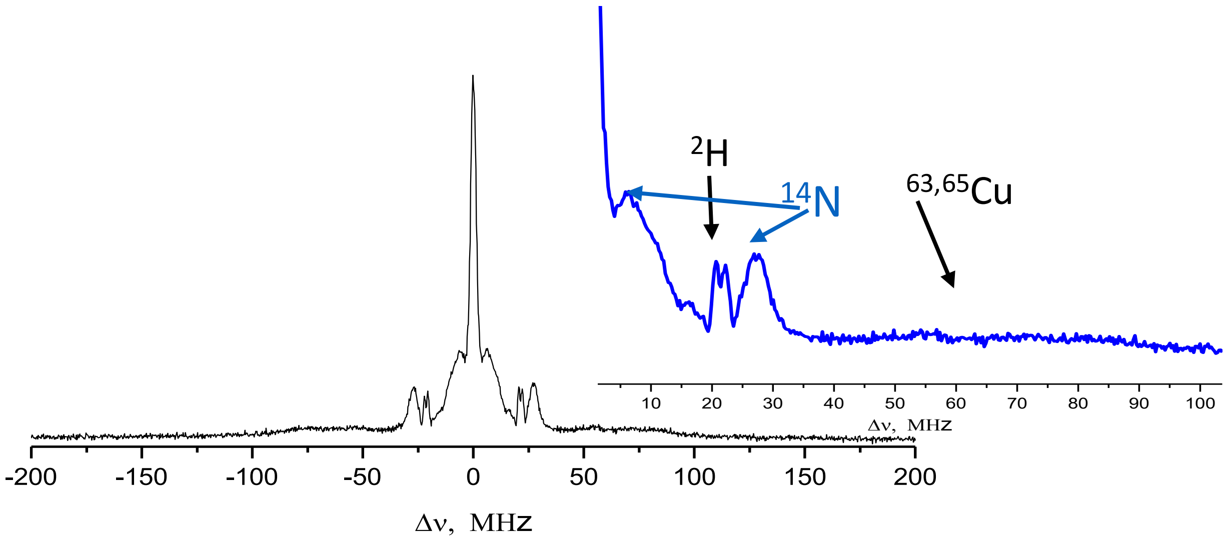


We change the frequency of the HTA pulse randomly

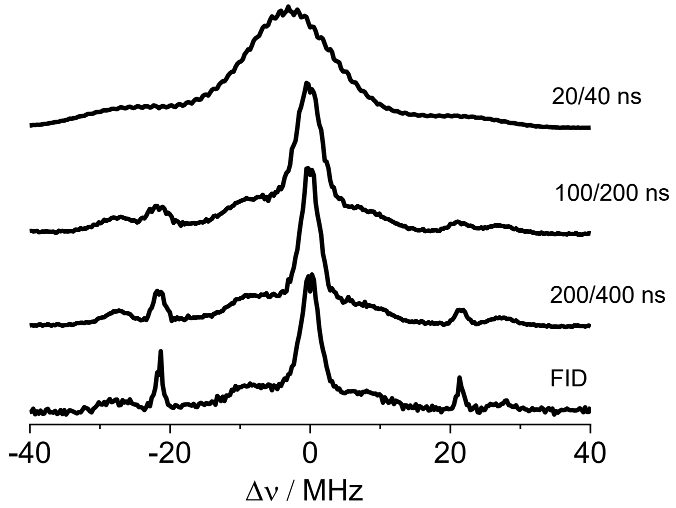
F. Mentink-Vigier, et al, J. Magn. Reson., 236 (2013) 117-125.

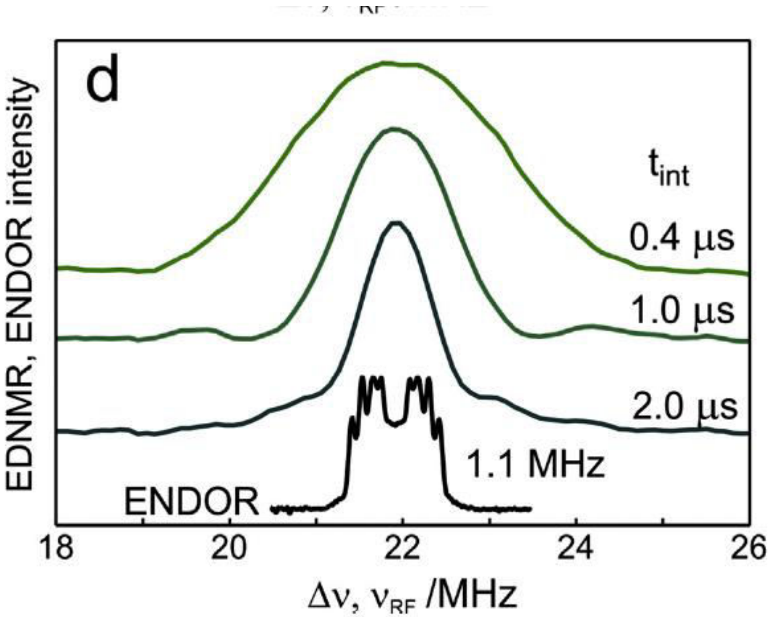
Effect of detection pulses and integration window

Frozen solution of Cu(II)-Histidine in D_2O at 95 GHz



Potapov et al, J. Chem. Phys. **128,** 052320 (2008)

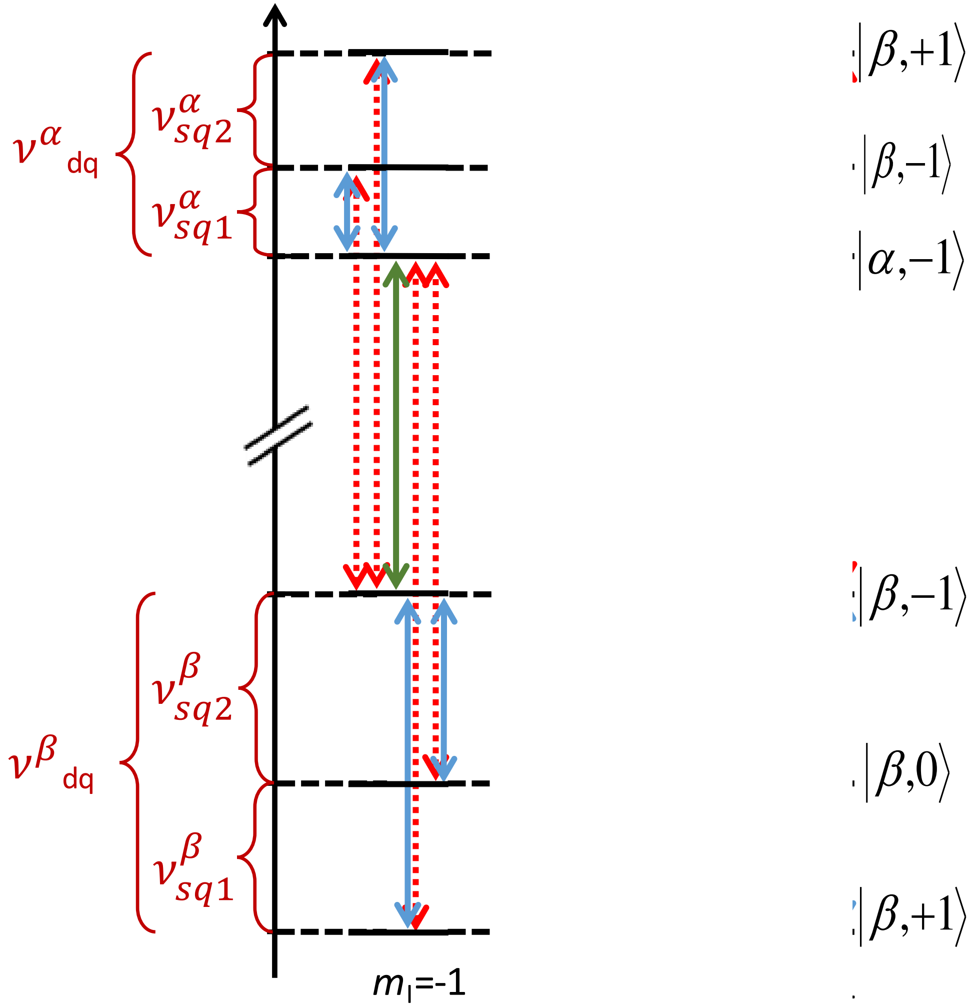




Cox, *J. Magn. Reson.* **2017,** *280*, 63-78.

nitroxide-D_{16} in 2-propanol-D_8

EDNMR for I=1, ^{14}N



The first-order expressions for the ^{14}N nuclear frequencies

for $A > 2\omega_I$, are as follows:

$\omega^{\alpha}_{sq1} = 2\pi\nu^{\alpha}_{sq1} = A/2 - \omega_I - 3P/2$

$\omega^{\alpha}_{sq2} = 2\pi\nu^{\alpha}_{sq2} = A/2 - \omega_I + 3P/2$

$\omega^{\alpha}_{dq} = 2\pi\nu^{\alpha}_{dq} = A - 2\omega_I$

$\omega^{\beta}_{sq1} = 2\pi\nu^{\beta}_{sq1} = A/2 + \omega_I - 3P/2$

$\omega^{\beta}_{sq2} = 2\pi\nu^{\beta}_{sq2} = A/2 + \omega_I + 3P/2$

$\omega^{\beta}_{dq} = 2\pi\nu^{\beta}_{dq} = A + 2\omega_I,$

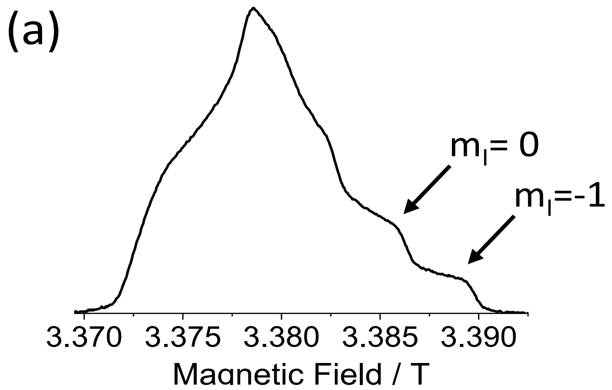
Quadrupole splitting $P = \frac{e^2qQ}{4\hbar}(3cos^2\theta' - 1$

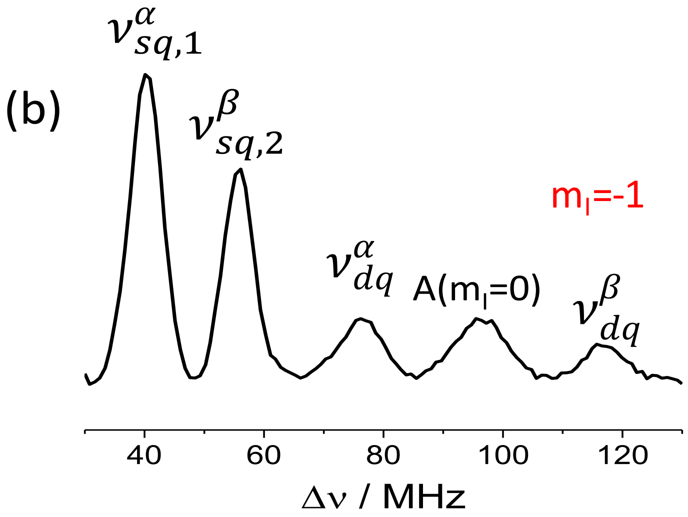
θ' is the angle between the extremal magnetic field and the principal direction of the quadrupole tensor.

W-band EDNMR nitroxide spin probe

Nitroxide labeled polyethylene oxide, PEO-NO, in 3% F127 micelles in D_2O/glycerol-d_8 (7:3)

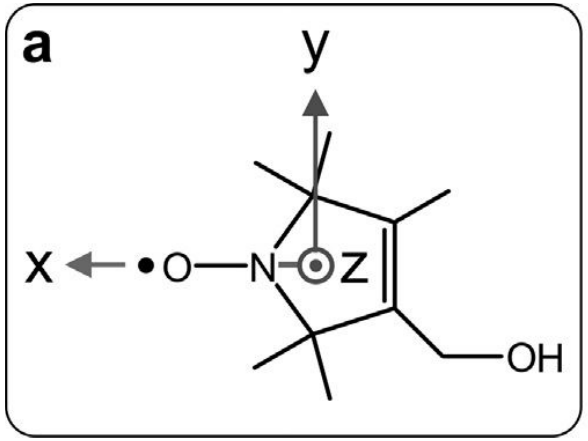
Strong coupling, hyperfine splitting resolved

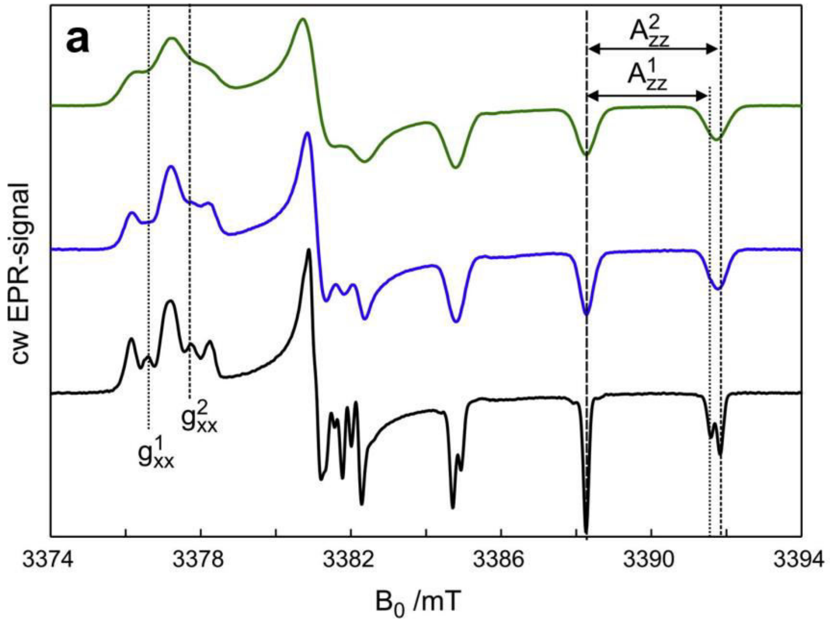




I. Kaminker, T. D. Wilson, M. G. Savelieff, Y. Hovav, H. Zimmermann, Y. Lu and D. Goldfarb, *J. Magn. Reson.*, 2014, **240**, 77-89

More nitroxide W- band EDNMR – high resolution





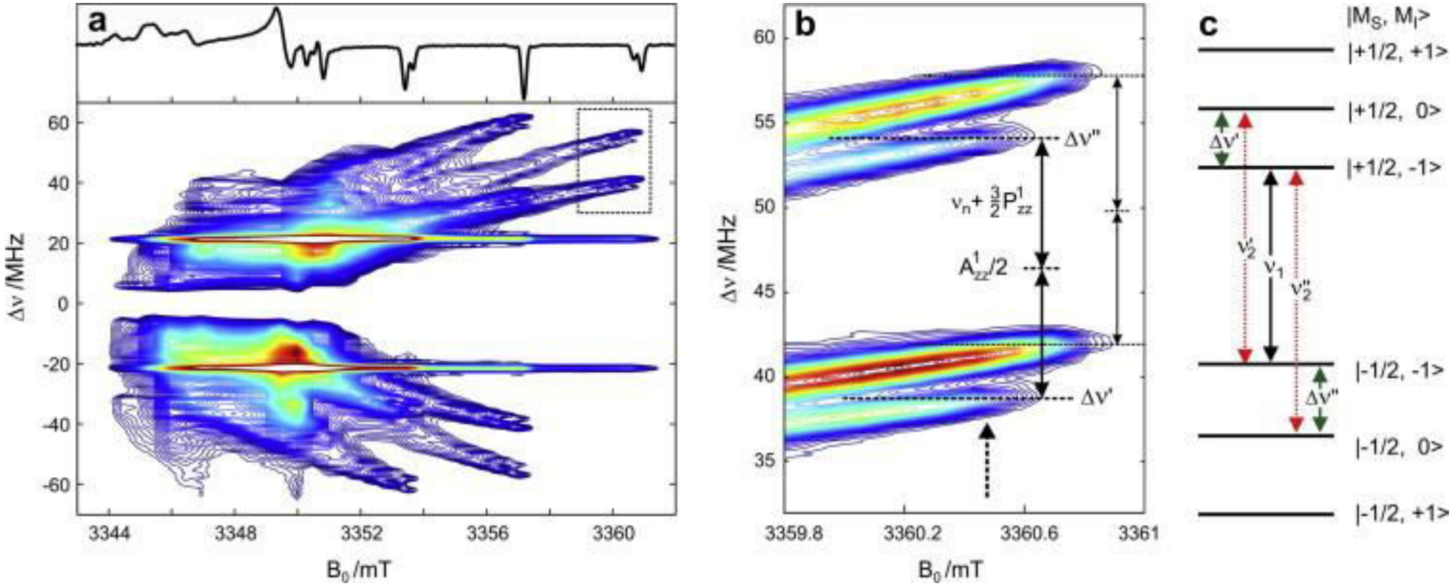
R1-H_{16} in 2-propanol-H_8

R1-D_{16} in 2-propanol-H_8

R1-D_{16} in 2-propanol-D_8

A. Nalepa, K. Moebius, W. Lubitz and A. Savitsky, *J. Magn. Reson.*, 2014, **242**, 203-213

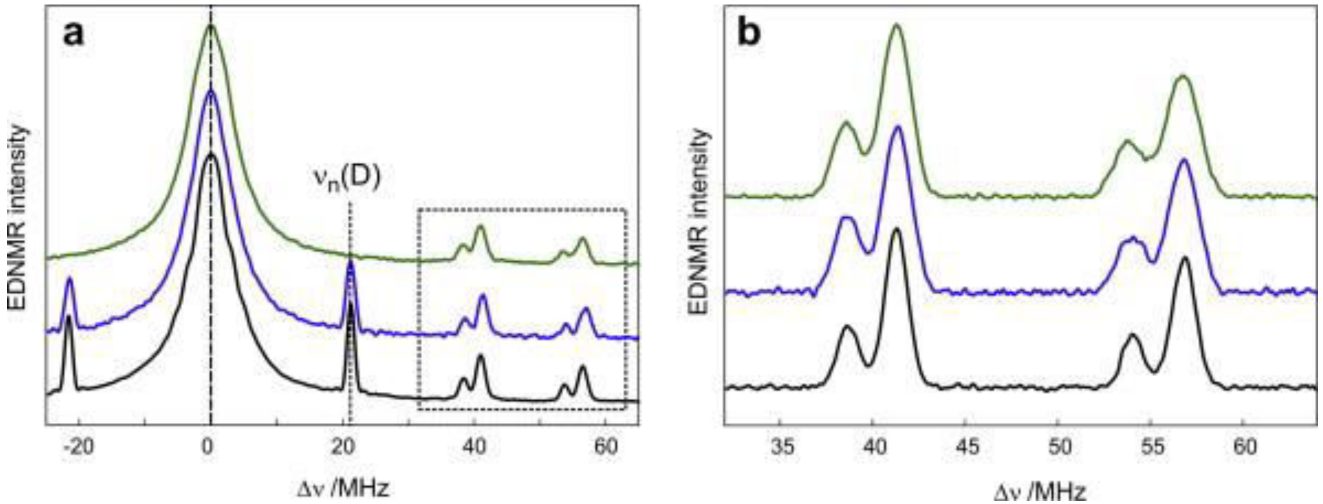
More nitroxide W- band EDNMR – high resolution



$$\omega^{\alpha}_{sq1} = 2\pi\,\nu^{\alpha}_{sq1} = A/2 - \omega_I - 3P/2$$

$$\omega^{\beta}_{sq2} = 2\pi\,\nu^{\beta}_{sq2} = A/2 + \omega_I + 3P/2$$

You can determine P, the quadrupole interaction

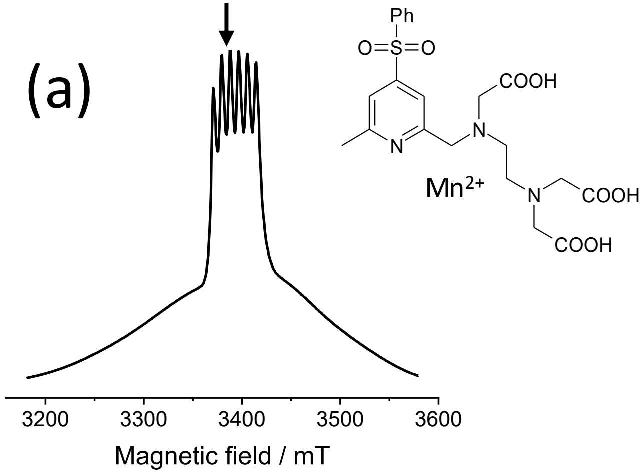


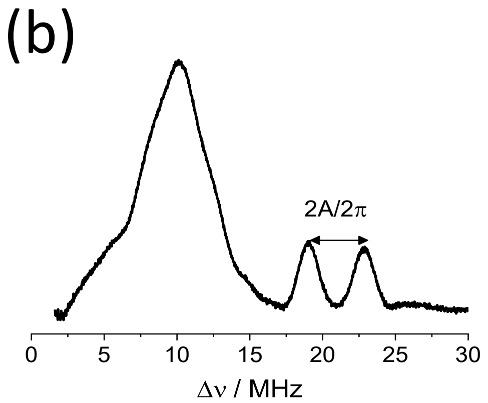
R1-H_{16} in 2-propanol-H_8

R1-D_{16} in 2-propanol-H_8

R1-D_{16} in 2-propanol-D_8

A. Martorana, Y. Yang, Y. Zhao, Q. F. Li, X. C. Su and D. Goldfarb, *Dalton Trans*, 2015, **44**, 20812-20816

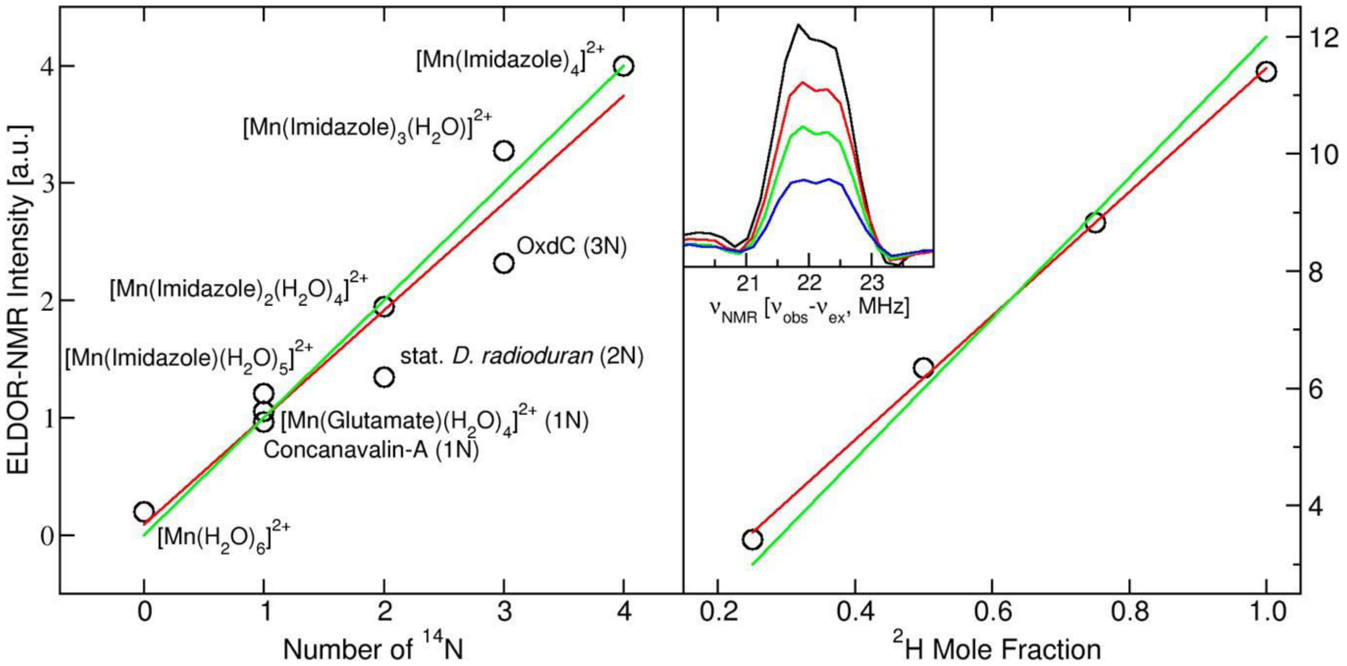




$$\omega^{\beta}_{dq} = 2\pi \nu^{\beta}_{dq} = -A + 2\omega_I,$$

$$\omega^{\alpha}_{dq} = 2\pi \nu^{\alpha}_{dq} = A + 2\omega_I$$

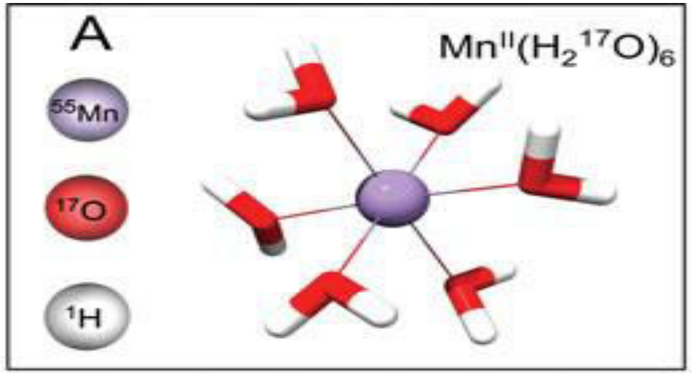
$$\omega^{\beta}_{dq} - \omega^{\alpha}_{dq} = 2A$$

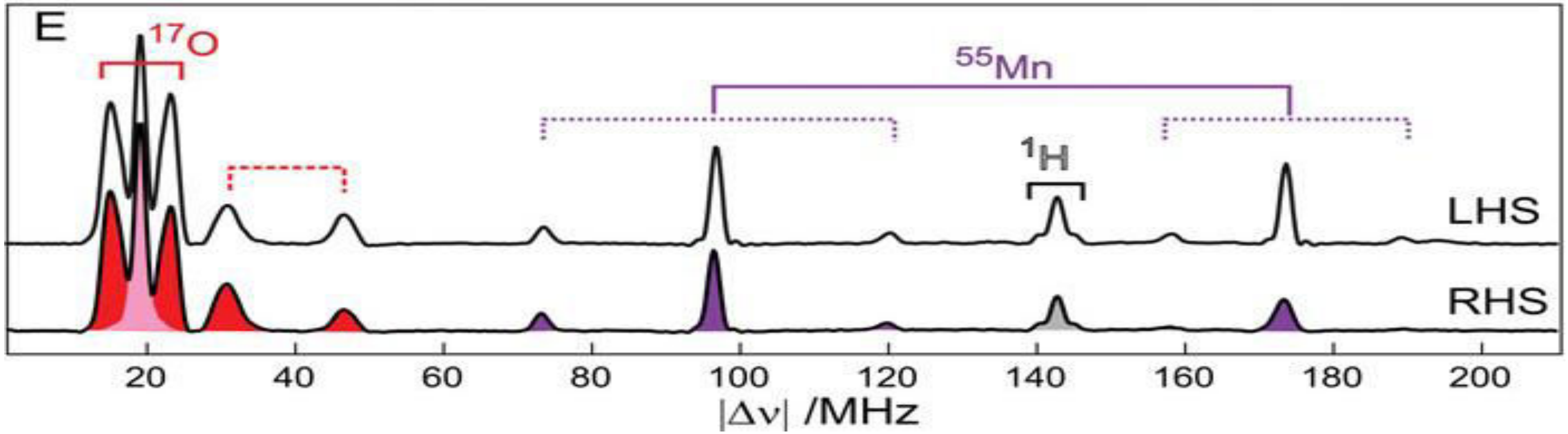


EDNMR is quantitative

E. M. Bruch, M. T. Warner, S. Thomine, L. C. Tabares and S. Un, *J. Phys. Chem. B*, 2015, **119**, 13515-13523.

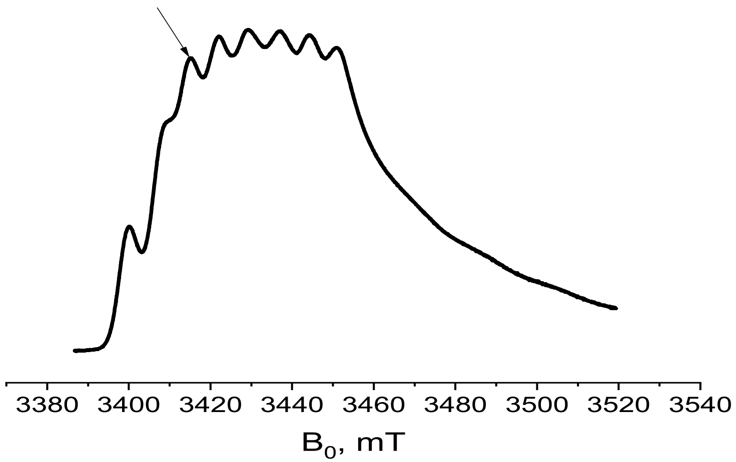
EDNMR : ^{17}O examples

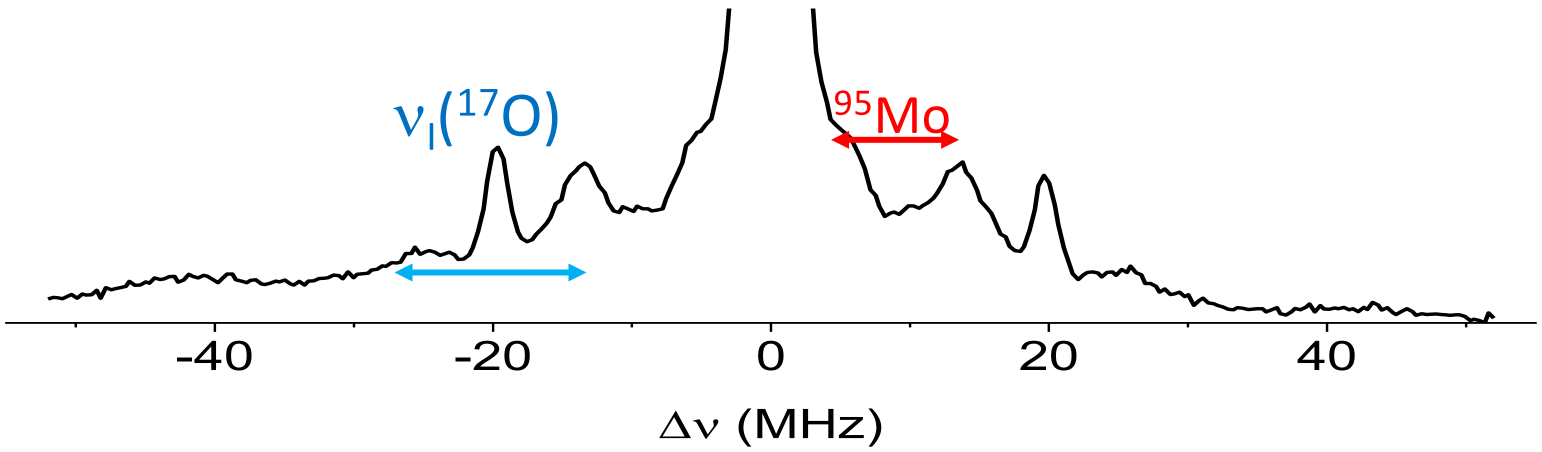




Cox et al, Mol. Phys., 111,2788–2808, 2013

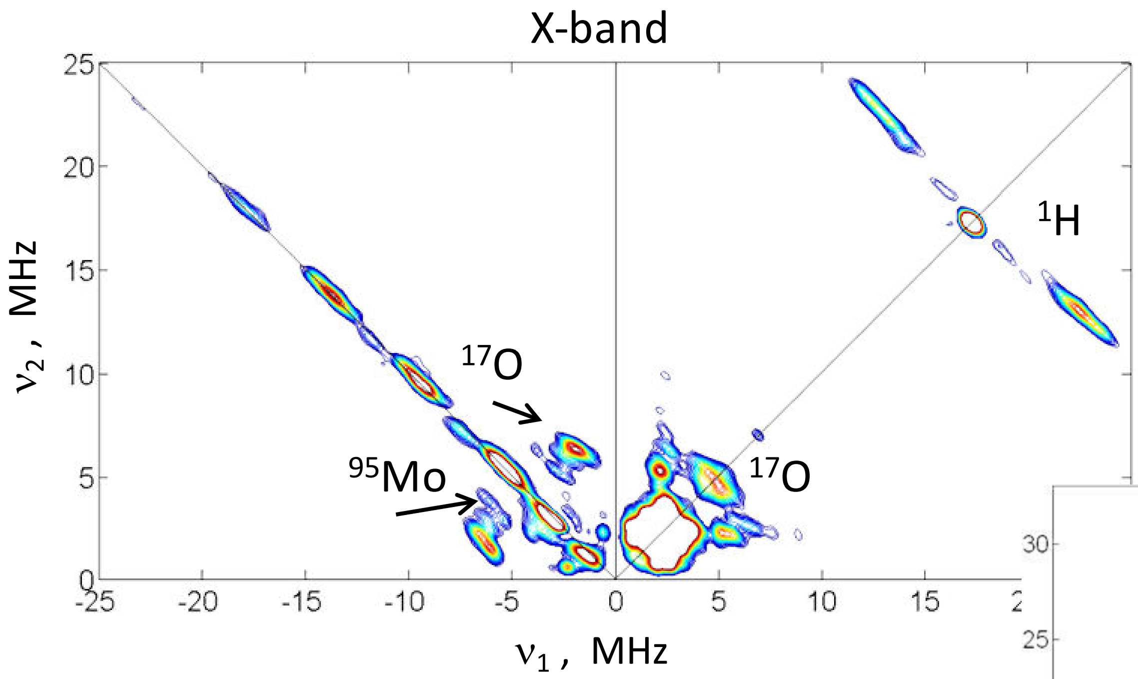
Reduced $H_5PV_2Mo_{10}{}^{17}O_{40}$ Polyoxometalate

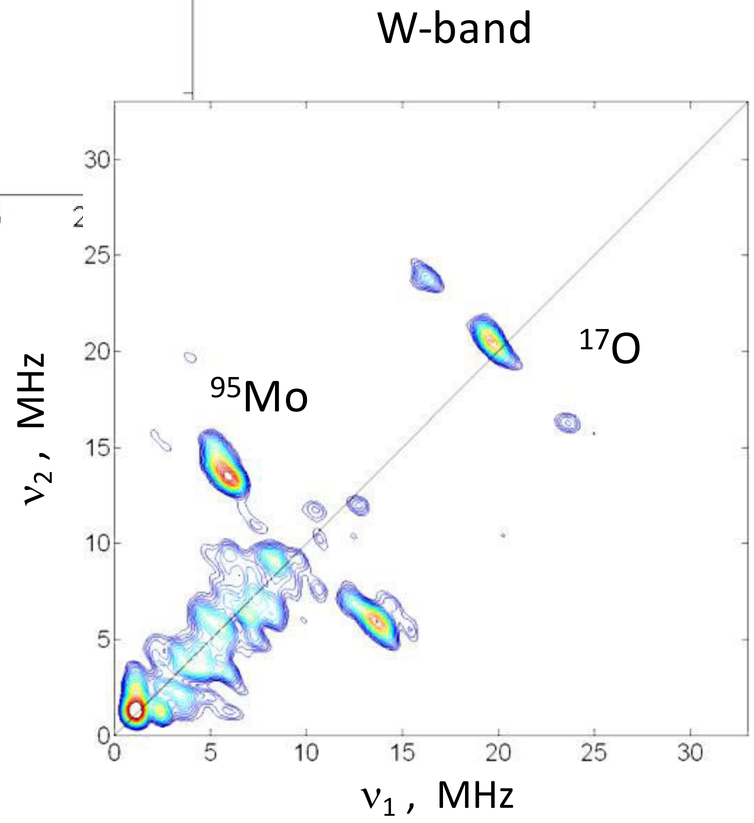




Kaminker, et al Chemistry – a European Journal. 16 ,10014-10020 (2010).

HYSCORE of $[PV(V)V(IV)\ Mo_{10}{}^{17}O_{40}]^{6-}$

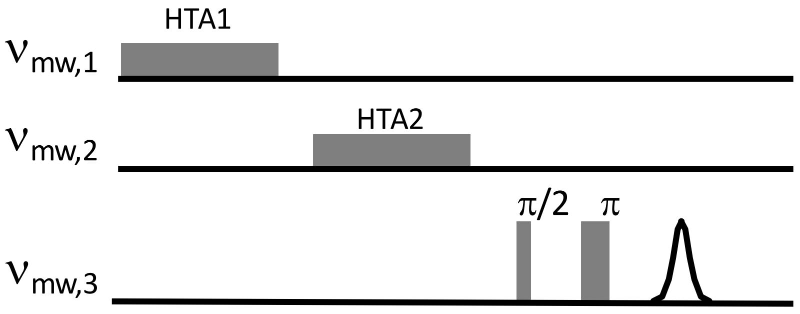




Triple resonance experiments - providing correlations

The 2D EDNMR pulse sequence

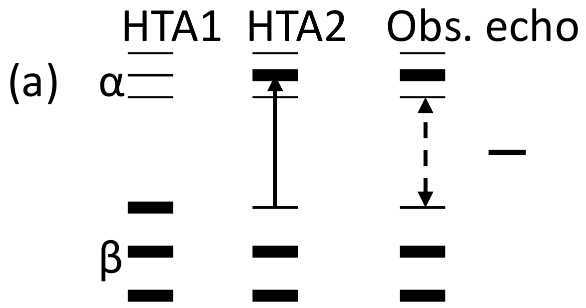
(a)



correlate nuclear frequencies that belong to different m_s manifolds and tells is different nuclei are coupled to the same paramagnetic center

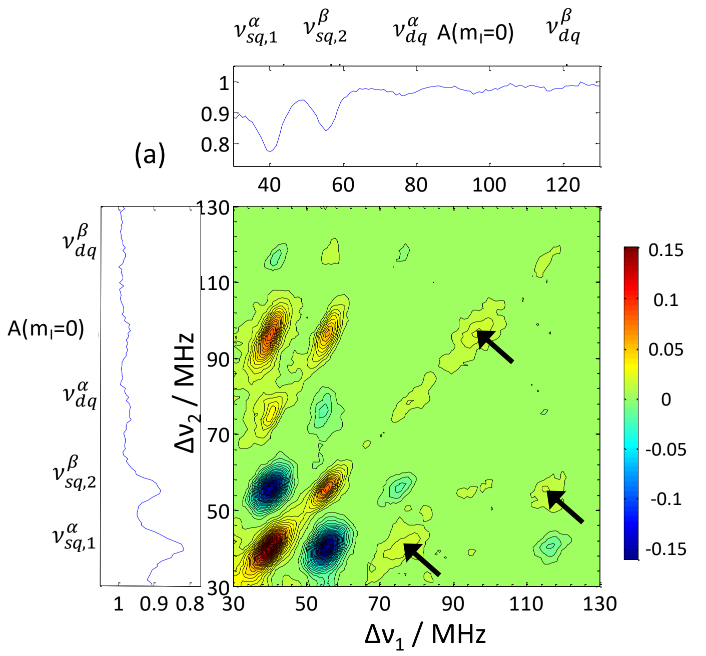
Kaminker, et al, *J. Magn. Reson.*, 2014, **240**, 77-89 ; A. Potapov et al , *J. Chem. Phys.* , 2008, **128**

2D ELDOR for nitroxide

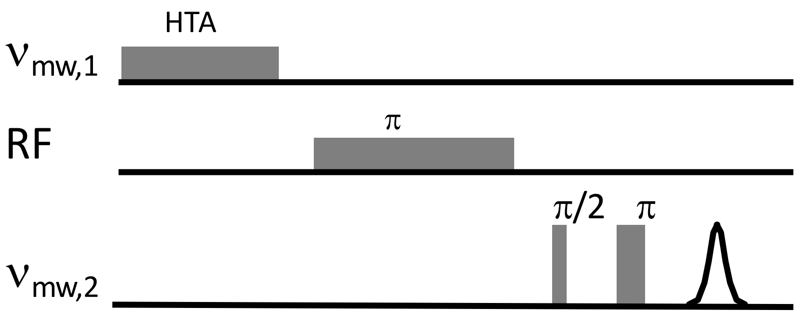


HTA2 = $^{\alpha}$sq

HTA1 – off resonance

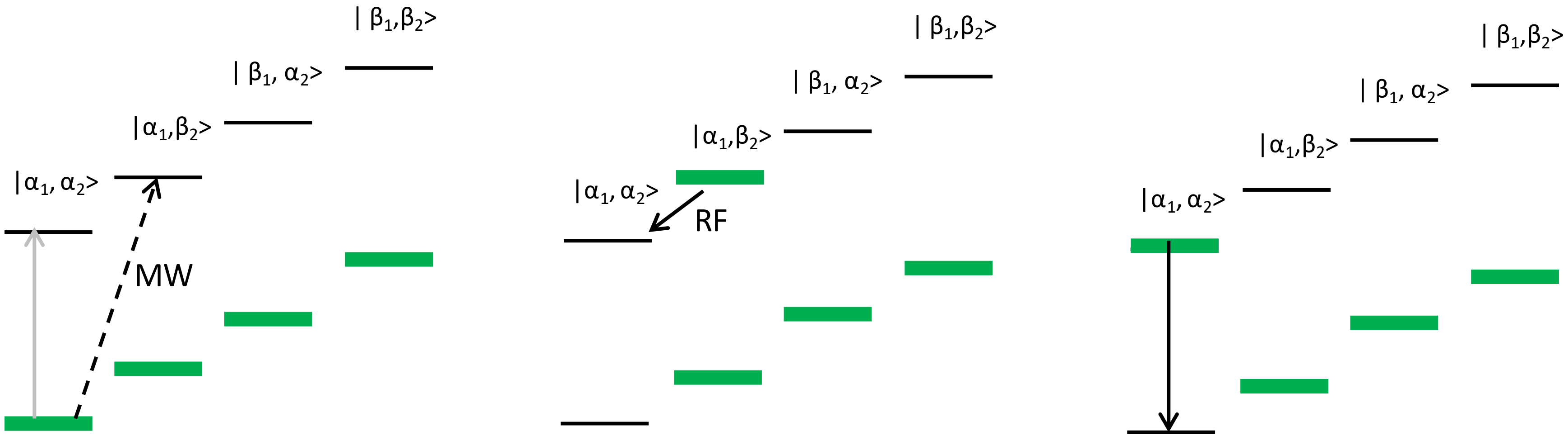


The THYCOS
(Triple resonance HYperfine Sublevel COrrelation Spectroscopy)

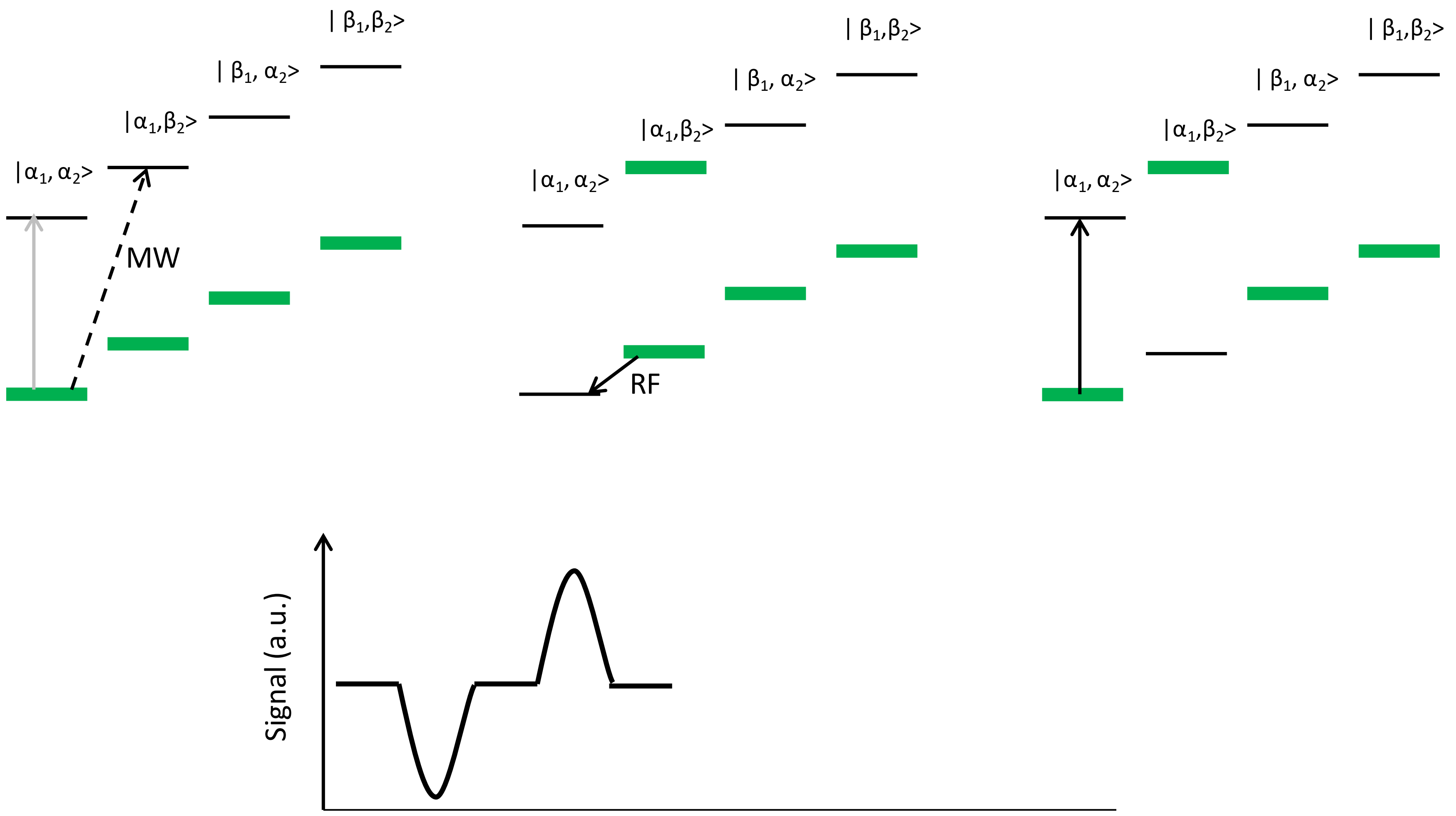


Potapov, et al , *J. Chem. Phys.* **2008,** *128* (5).

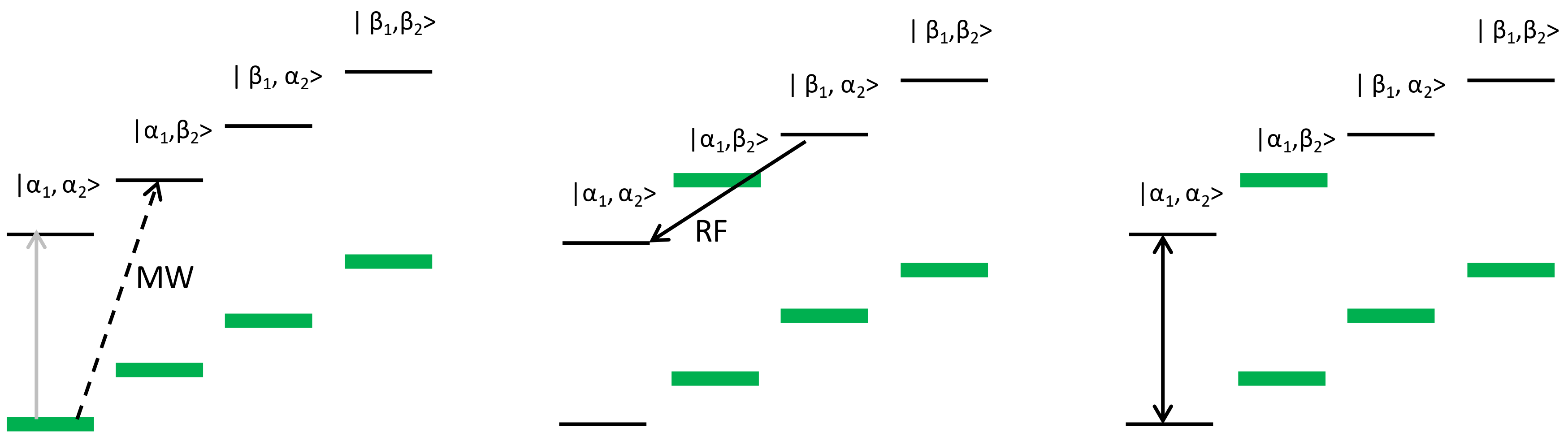
THYCOS – how it works ?

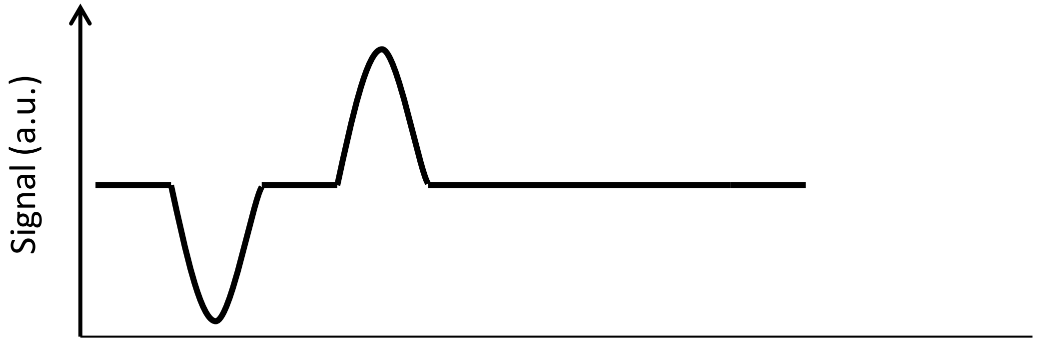


THYCOS – how it works ?

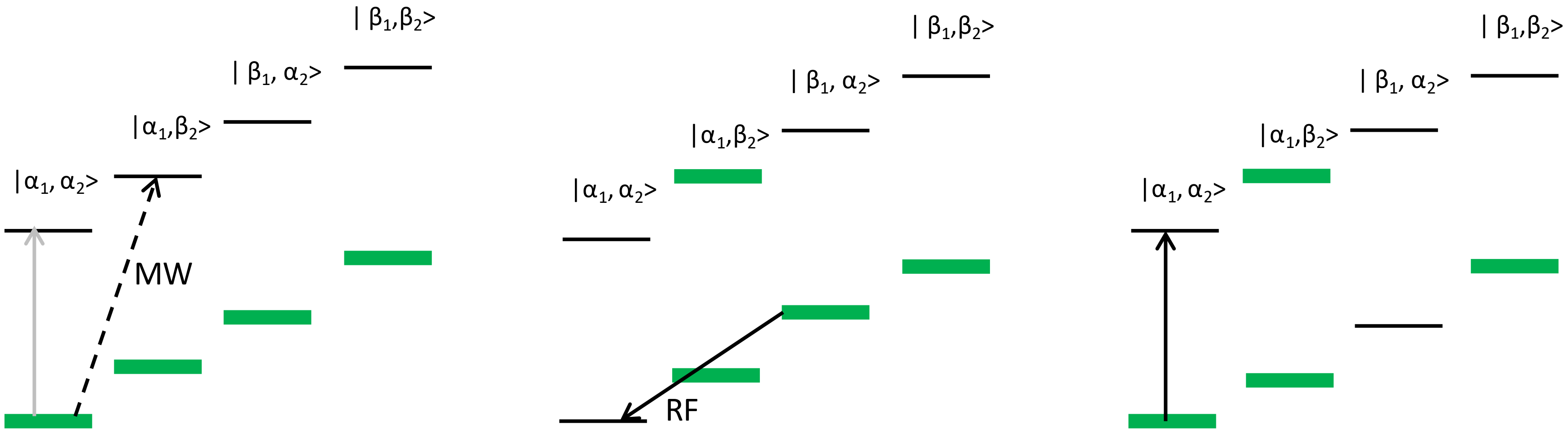


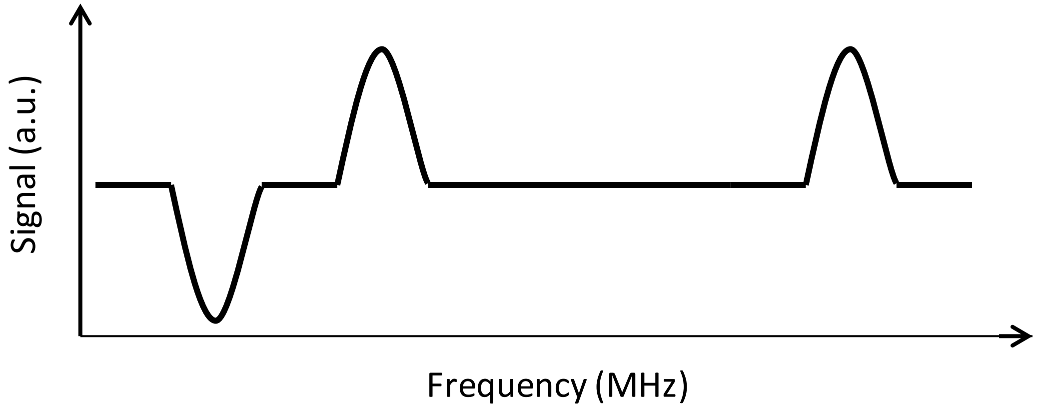
THYCOS – how it works ?





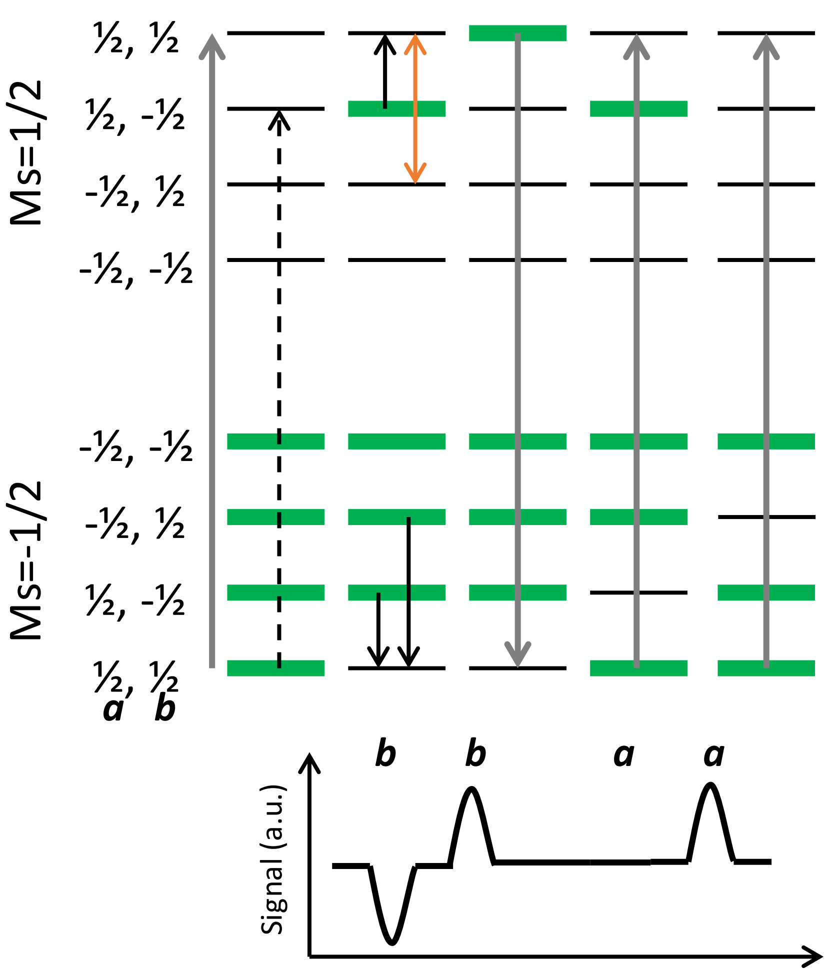
THYCOS – how it works ?



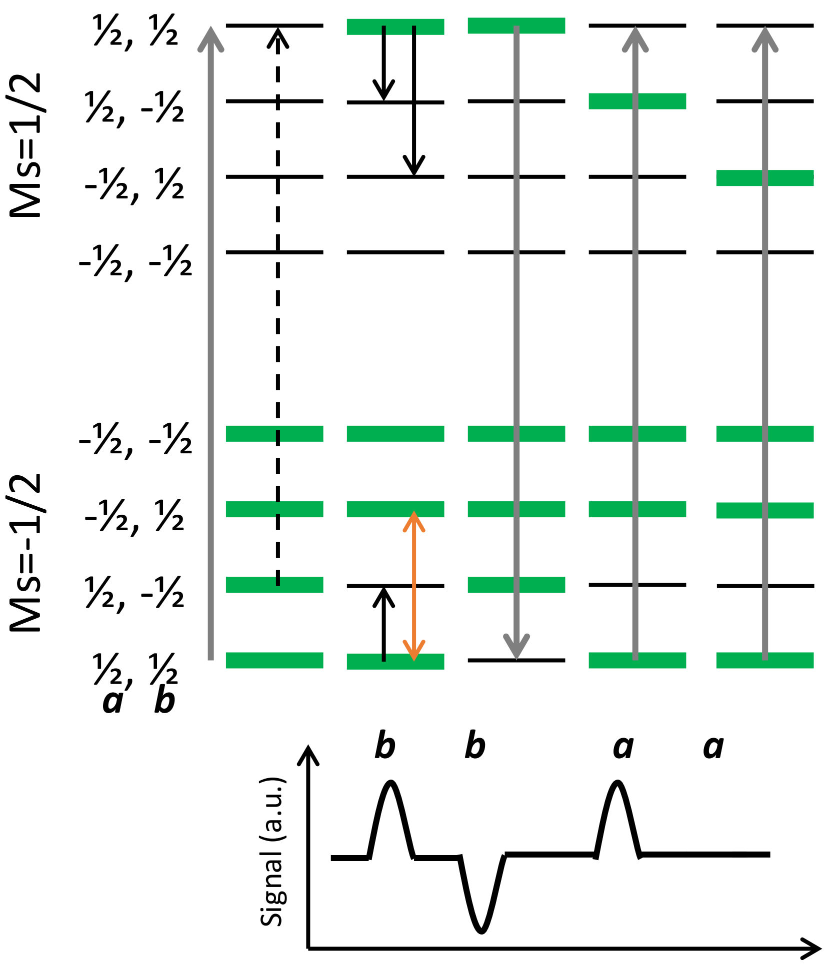


THYCOS – how it works ?

HTA pulse on nucleus ***a***

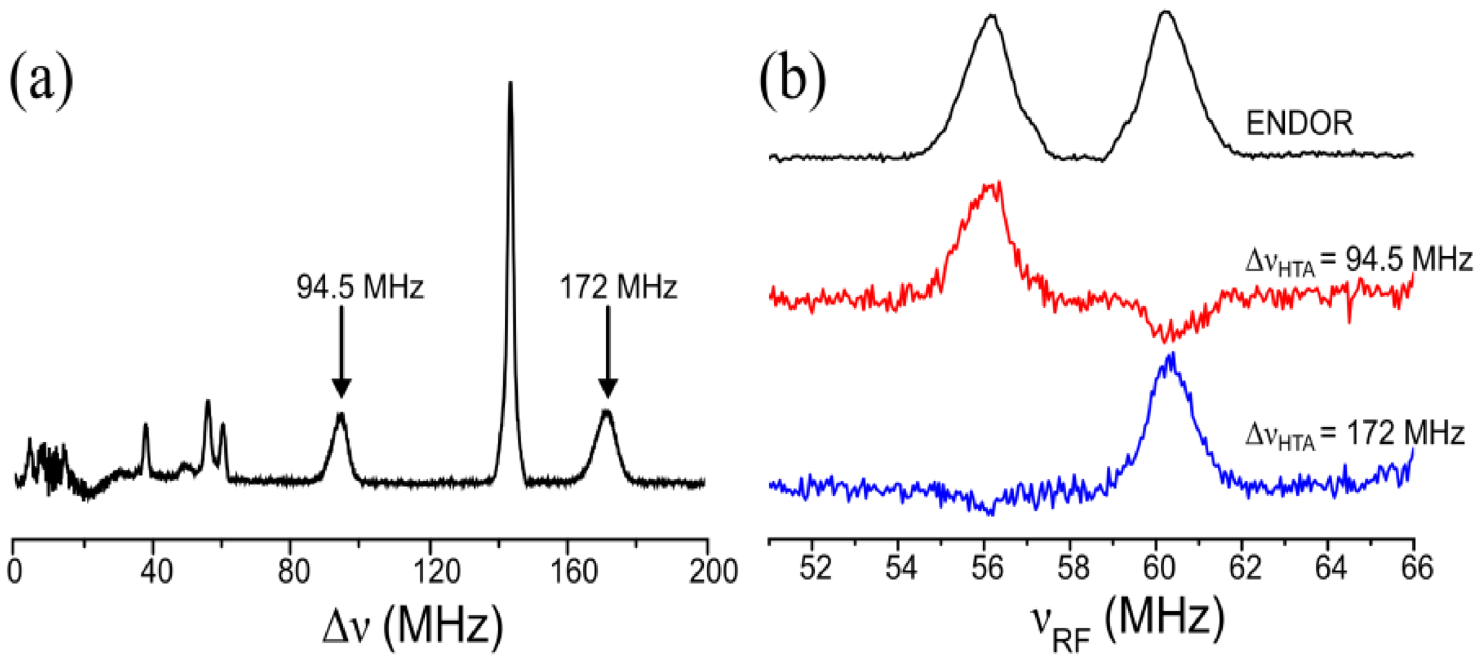


HTA pulse on nucleus **b**



THYCOS of the Mn-$^{15}N_5$-ATP sample

EDNMR　　　　　　　　EDNMR



Litvinov et al, JMR 2018

Q-band

W-band

X-band

ENDOR

ELDOR detected NMR

ESEEM