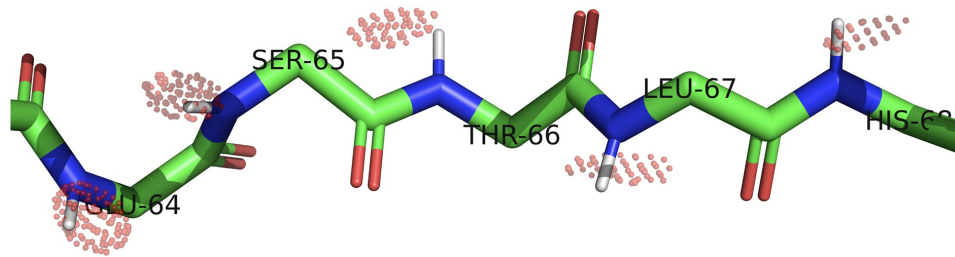


paramagnetism in NMR



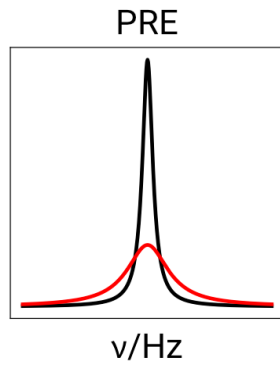
Paramagnetism: a compound that becomes magnetic in a magnetic field and, in an inhomogeneous magnetic field, is pulled into the region of higher magnetic field. Paramagnetism arises from unpaired electrons.

Diamagnetism: a compound that becomes magnetic in a magnetic field and, in an inhomogeneous magnetic field, tries to move away from the region of higher magnetic field.

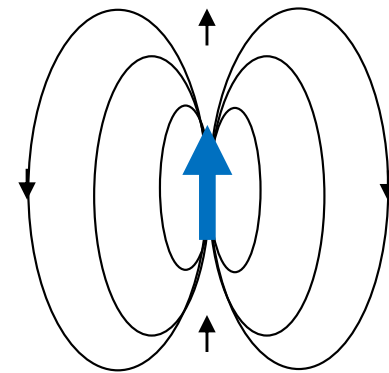
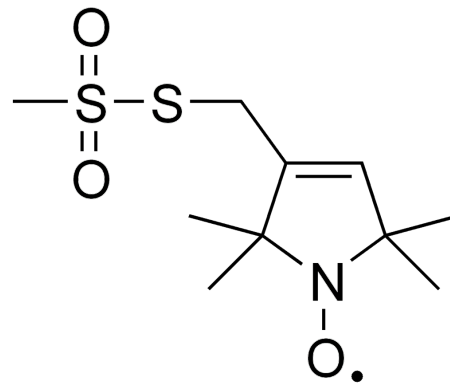
diamagnetism

<https://www.youtube.com/watch?v=KlJsVqc0ywM&t=34s>

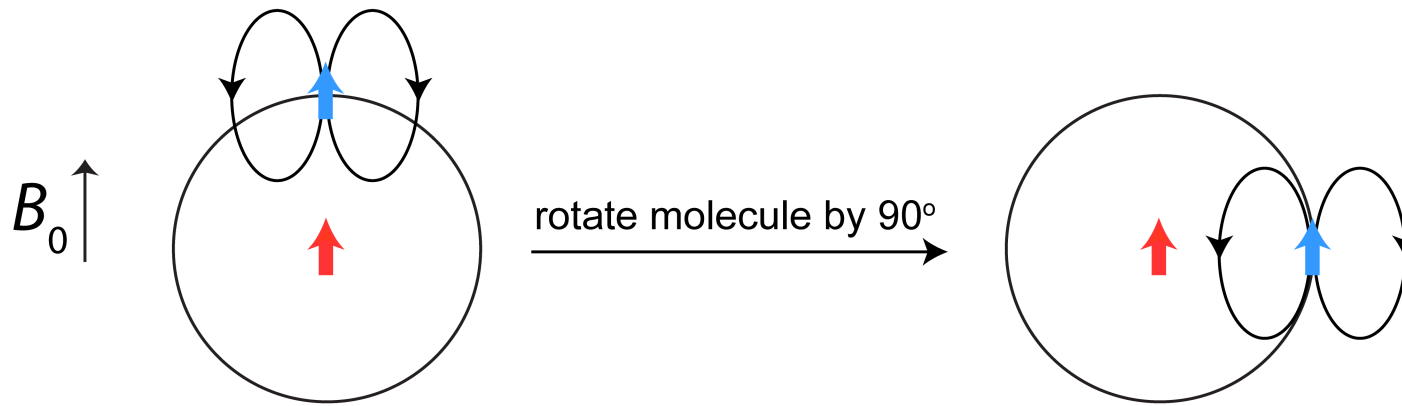
paramagnetic relaxation enhancement



MTSL



dipole-dipole interaction



paramagnetic relaxation enhancement, PRE

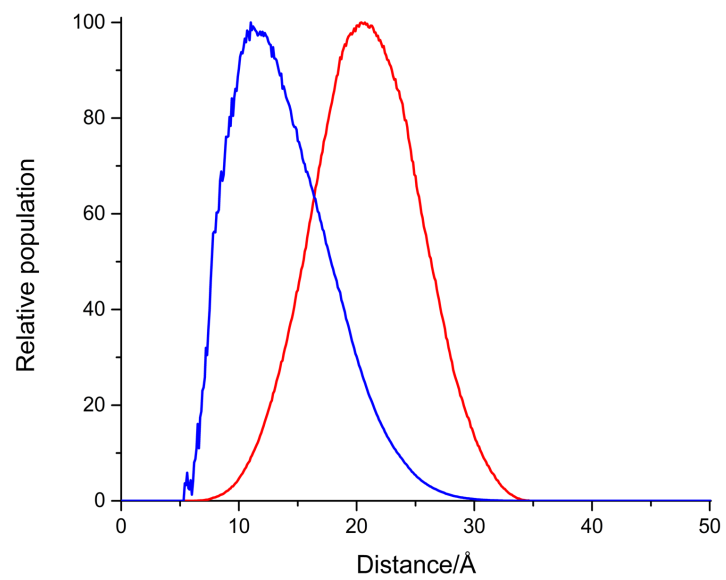
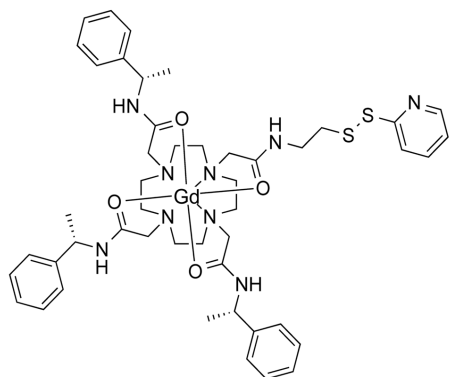
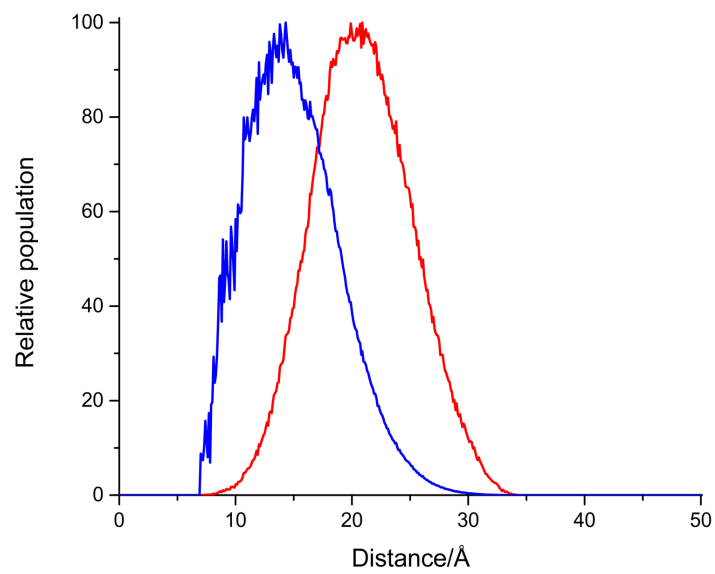
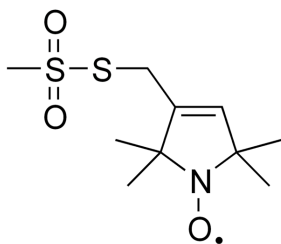
$$R_2^{\text{SBM}} = \frac{1}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_I^2 g_e^2 \mu_B^2 S(S+1)}{r_{\text{IS}}^6} \left(4\tau_c + \frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{13\tau_c}{1 + \omega_S^2 \tau_c^2} \right)$$

$$R_2^{\text{SBM}} = C \times S(S+1)\tau_c / r^6$$

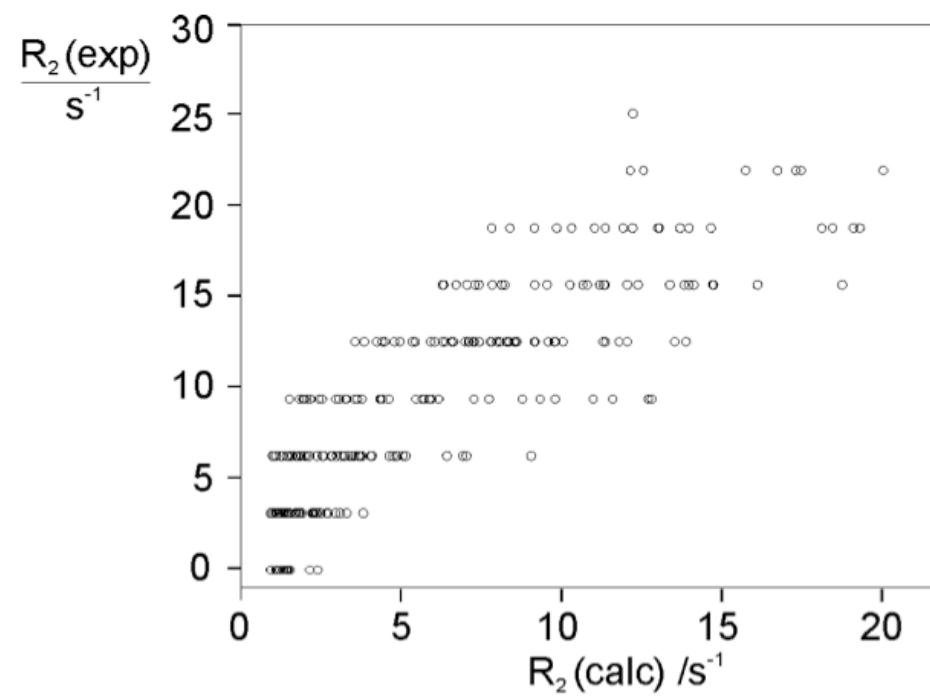
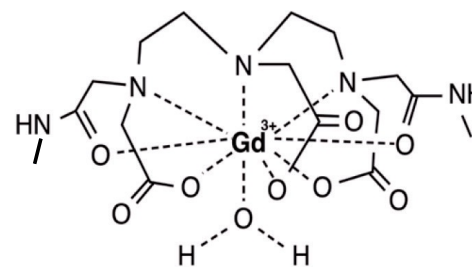
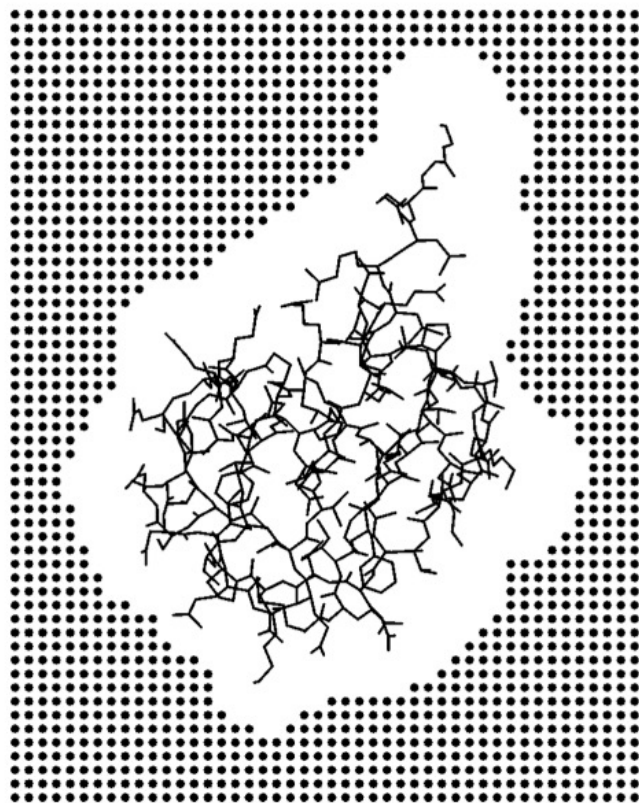
$$C = 6.5 \times 10^{16} \text{ \AA}^6 \text{ s}^{-2}$$

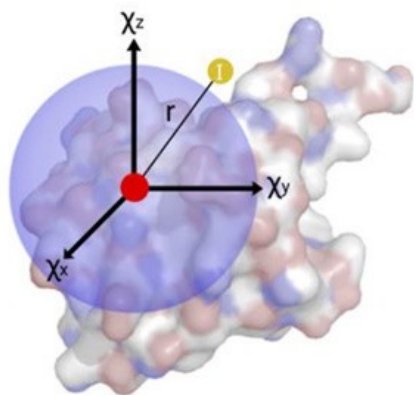
$$\tau_c^{-1} = \tau_r^{-1} + \tau_s^{-1}$$

Battiste & Wagner, Biochemistry 2000, 39, 5355-5365
Clare & Iwahara, Chem. Rev. 2009, 109, 4108-4139

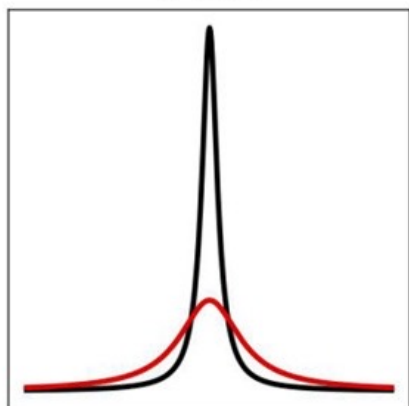


Intermolecular PRE

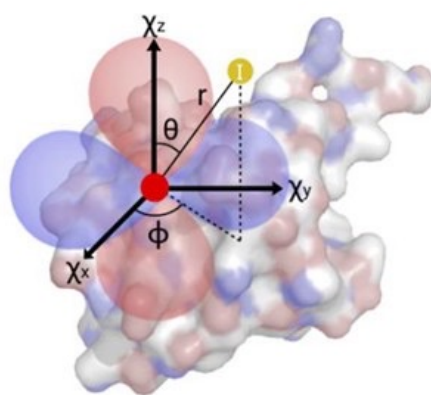




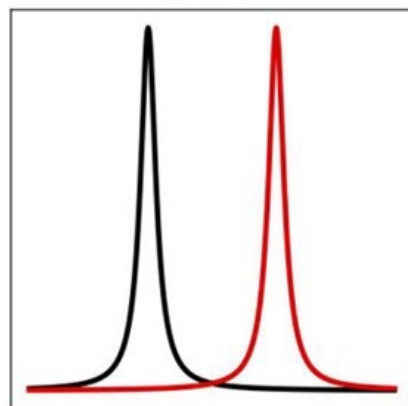
PRE



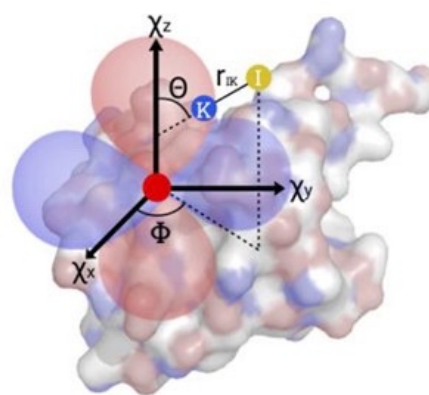
v/Hz



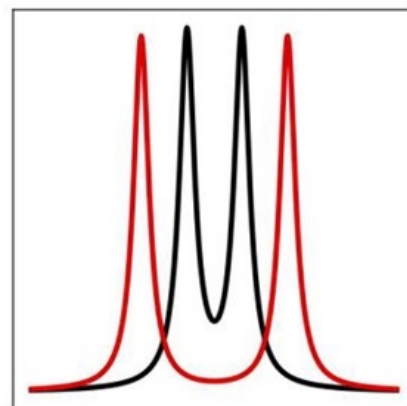
PCS



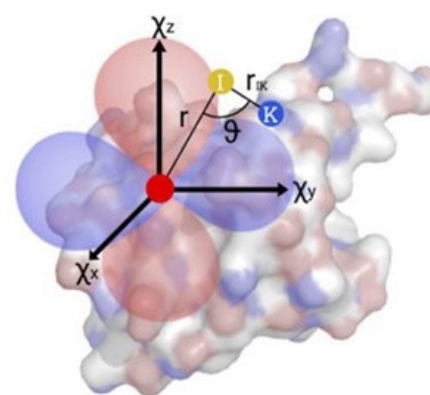
δ /ppm



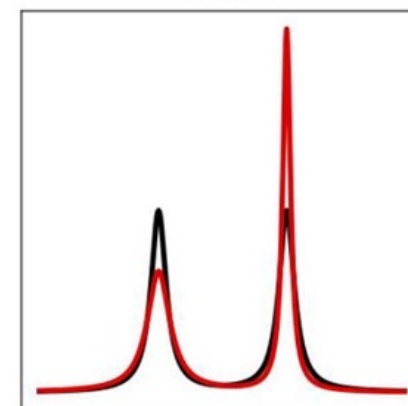
RDC



v/Hz



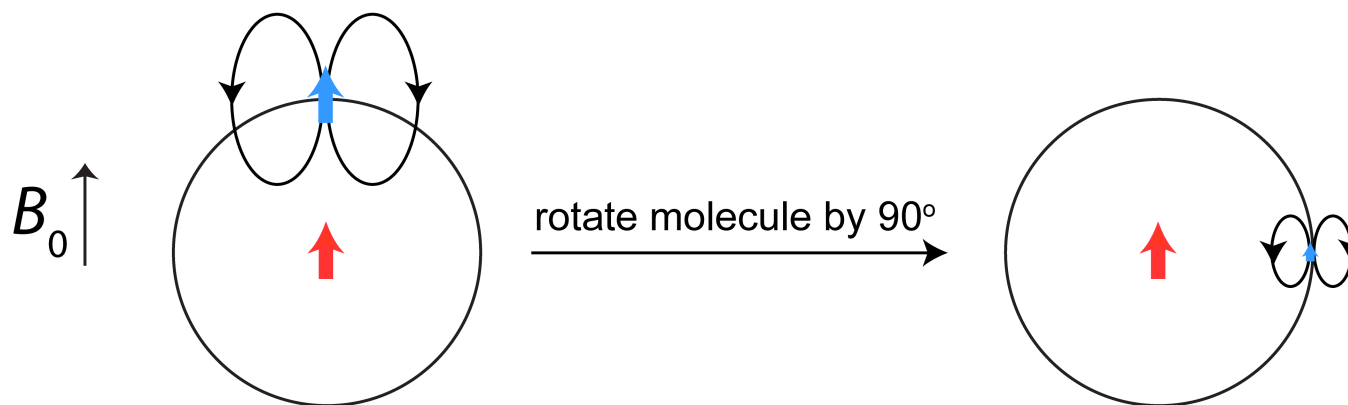
CCR



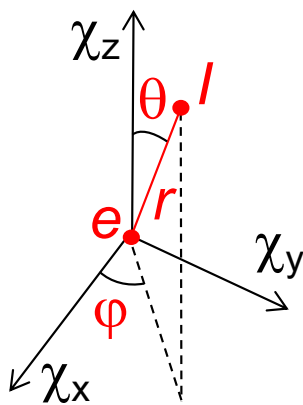
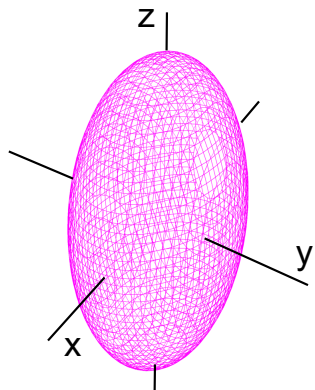
v/Hz

pseudocontact shifts

an orbital (f_{xz^2})



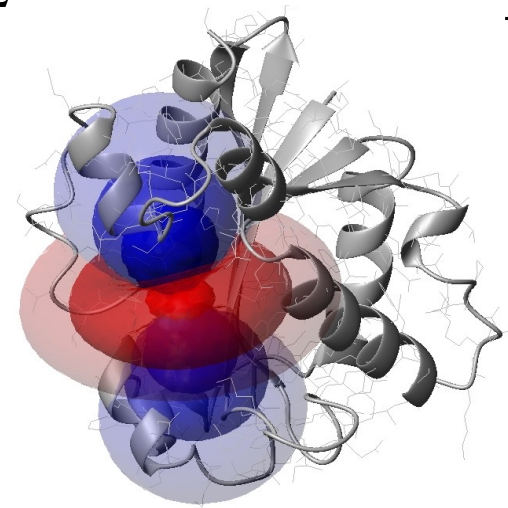
χ : magnetic susceptibility tensor



$\Delta\chi$: magnetic susceptibility anisotropy tensor

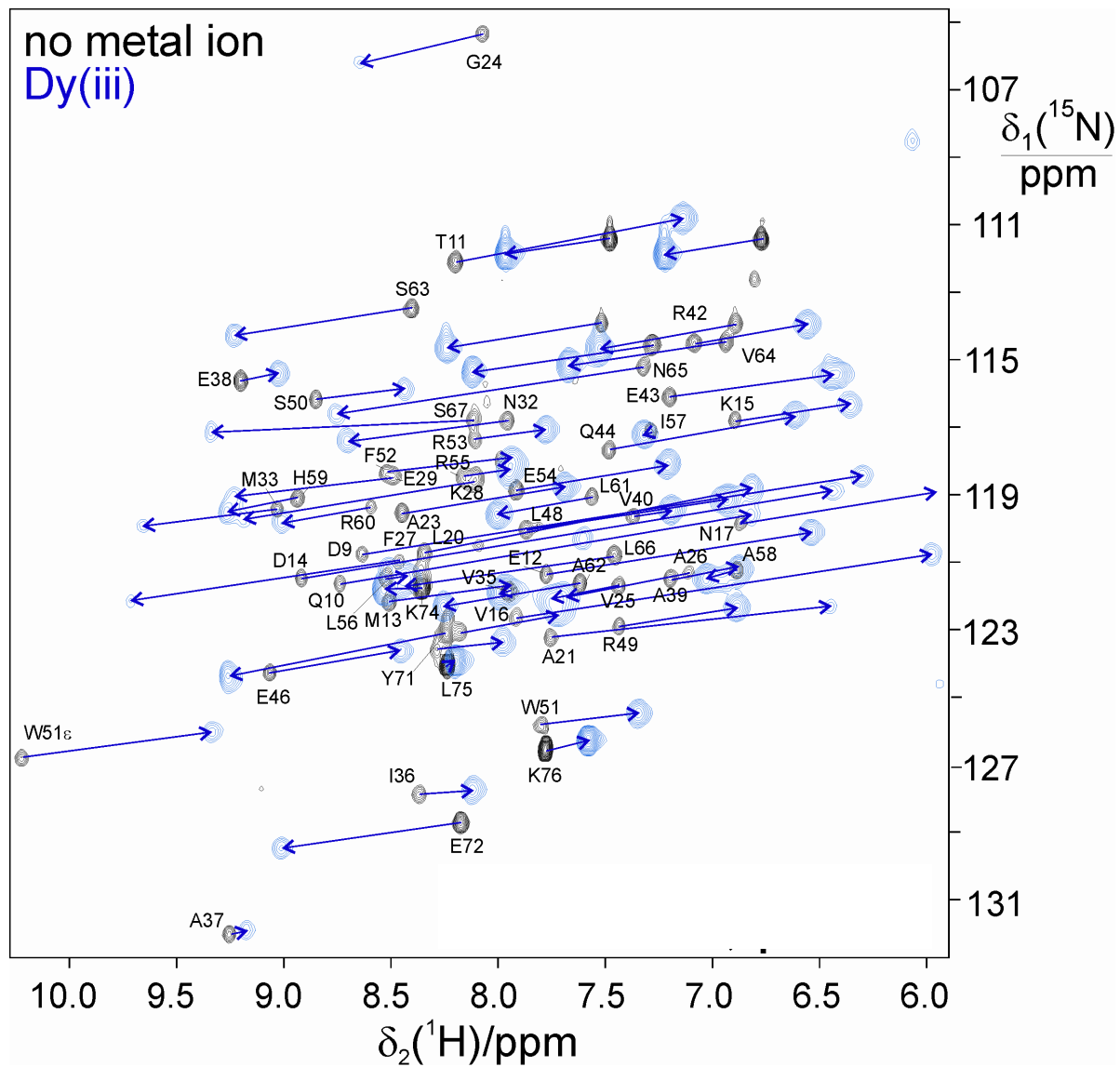
$$\underbrace{\Delta\chi_{ax}}_{\chi_z - \frac{\chi_x + \chi_y}{2}} \quad \underbrace{\Delta\chi_{rh}}_{\chi_x - \chi_y}$$

$$\delta^{pc} = \frac{1}{12\pi r^3} \left[\Delta\chi_{ax} (3 \cos^2 \theta - 1) + \frac{3}{2} \Delta\chi_{rh} \sin^2 \theta \cos 2\varphi \right]$$








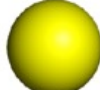









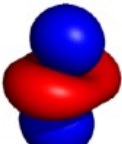
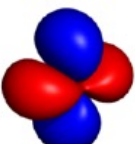
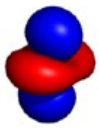

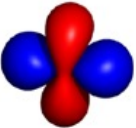



pseudocontact shifts

no metal ion
Dy(III)



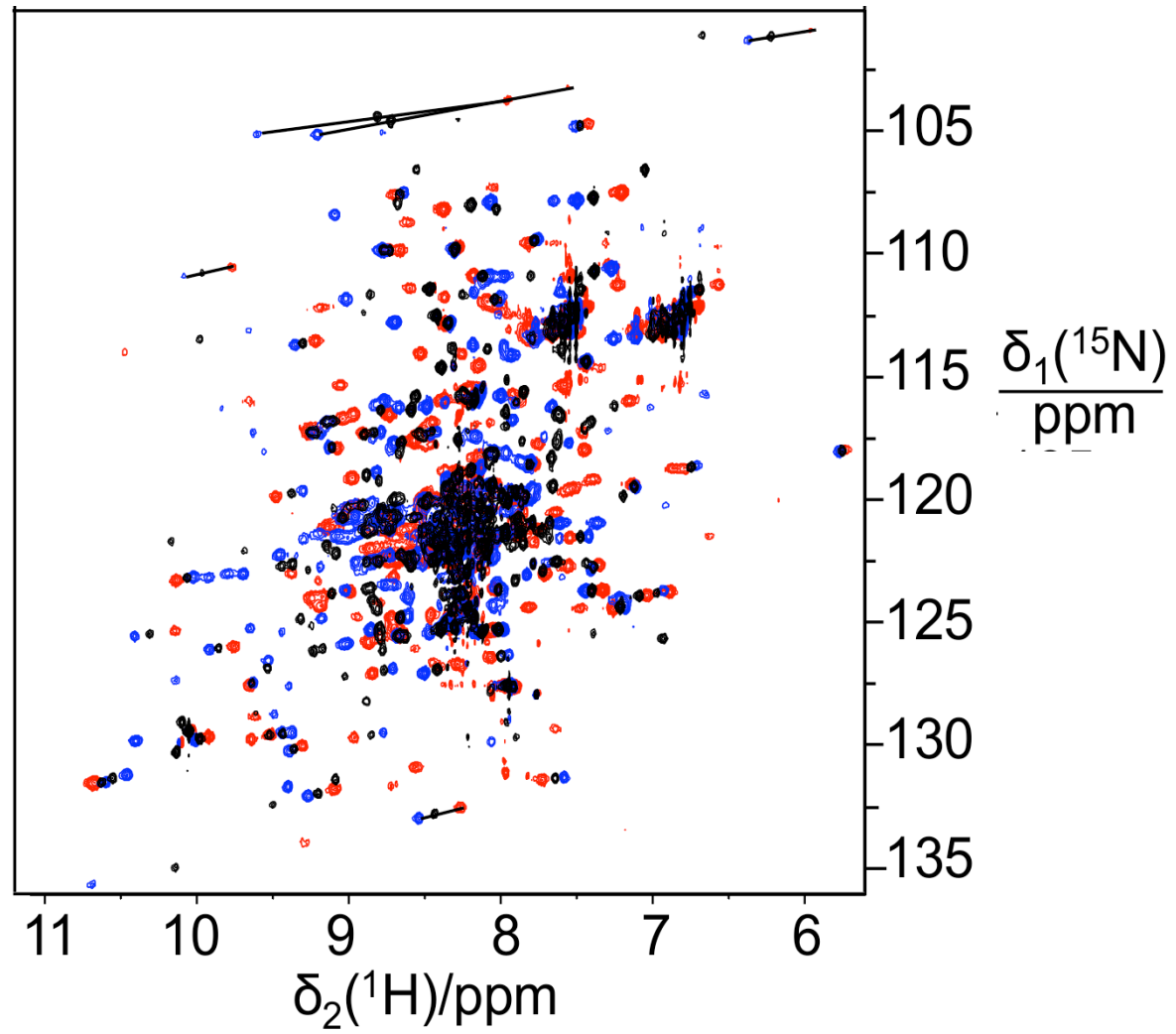
lanthanoid ions

	Cerium	Praseodymium	Neodymium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium
	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Tb
χ_{iso}	5.6	11.2	11.4	0.6	~ 6	55.1	82.7	99.2	98.4	80.3	50.0	18.0
PRE												
PCS												
$\Delta\chi_{ax}$	2.1	3.4	1.7	0.2	2.4	0.0	42.1	34.7	18.5	12.2	26.0	8.5
$\Delta\chi_{rh}$	0.7	2.1	0.5	0.1	1.5	0.0	11.2	20.3	5.8	7.3	11.9	5.3
T_{1e}/ps	0.13	0.05	0.21	0.07	0.02	10^5	0.25	0.24	0.21	0.19	0.27	0.16

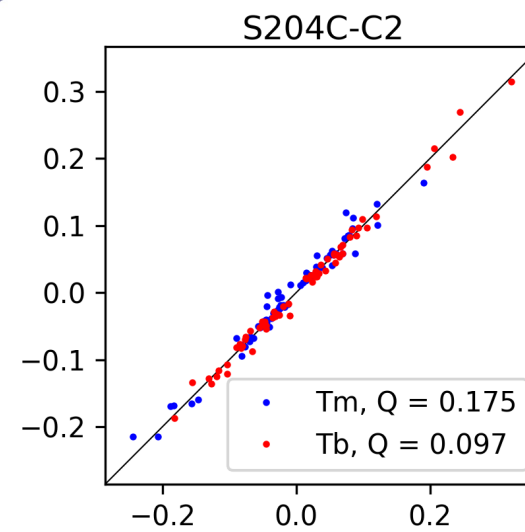
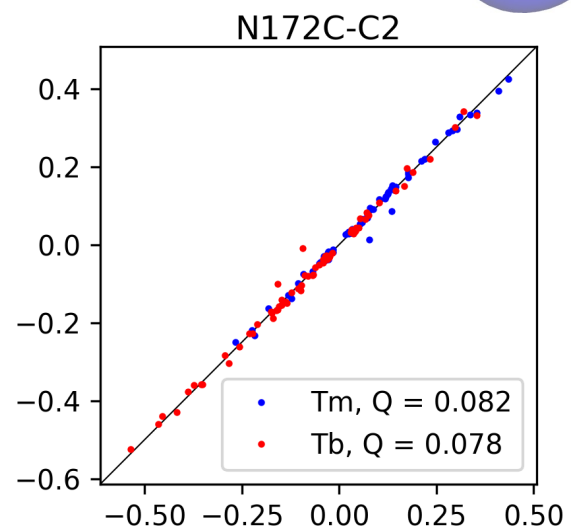
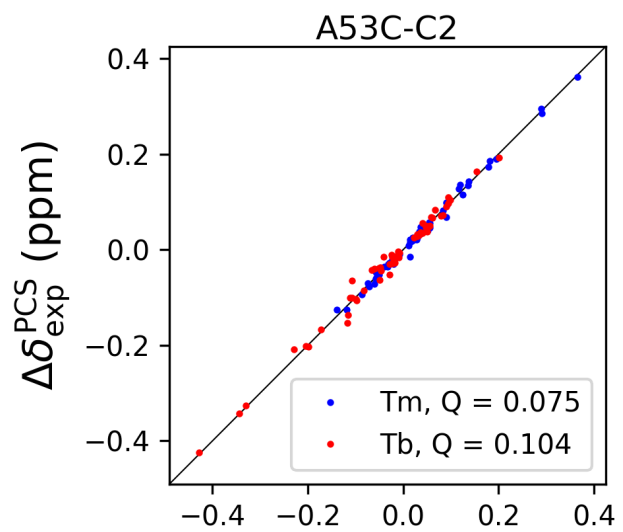
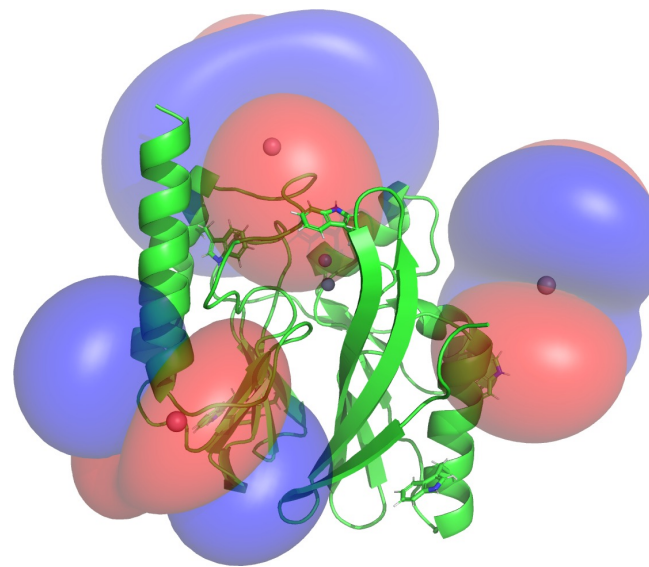
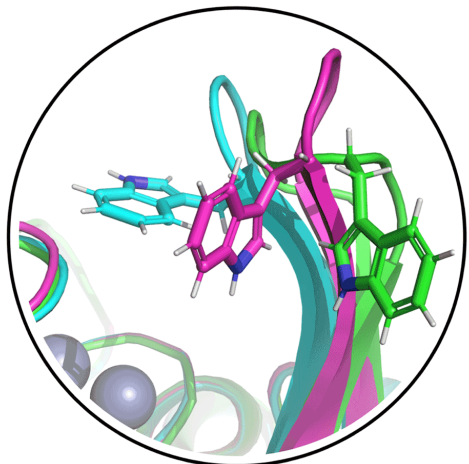
Y^{3+}

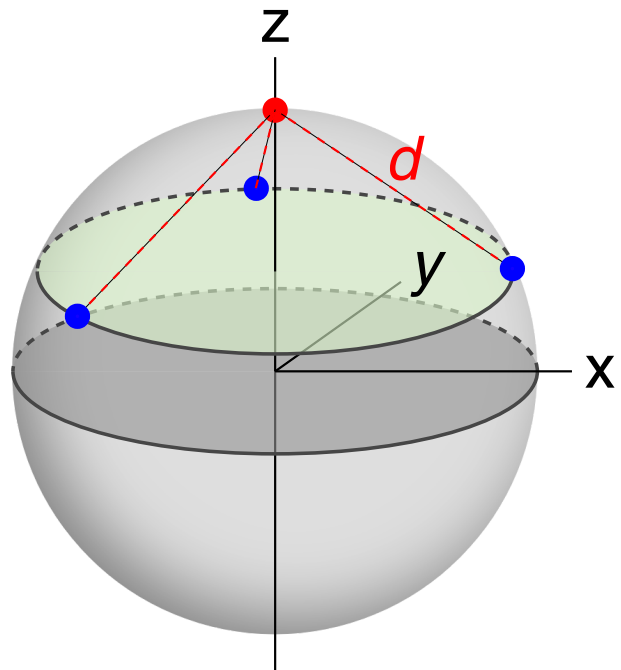
Tm^{3+}

Tb^{3+}

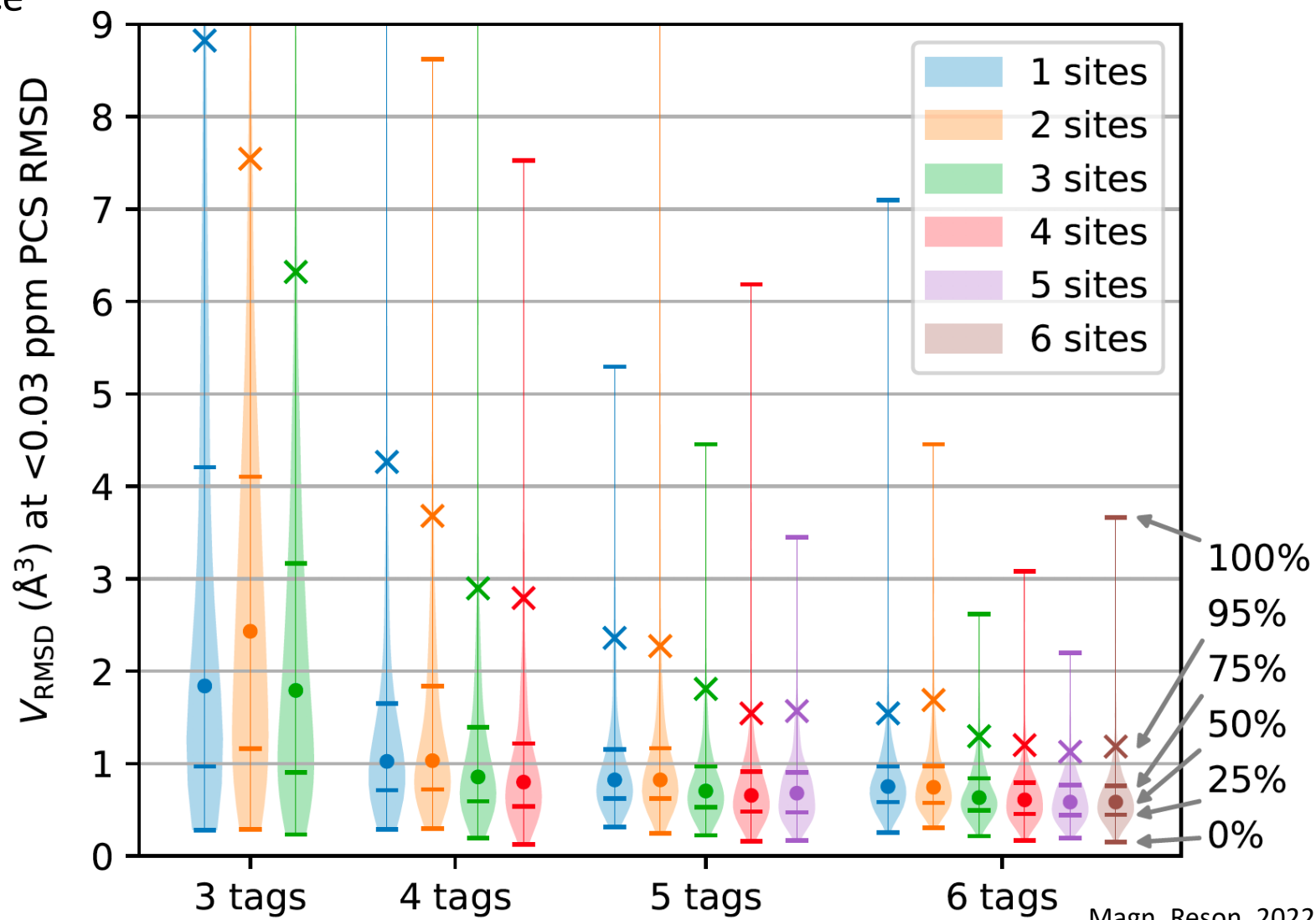


IMP-1

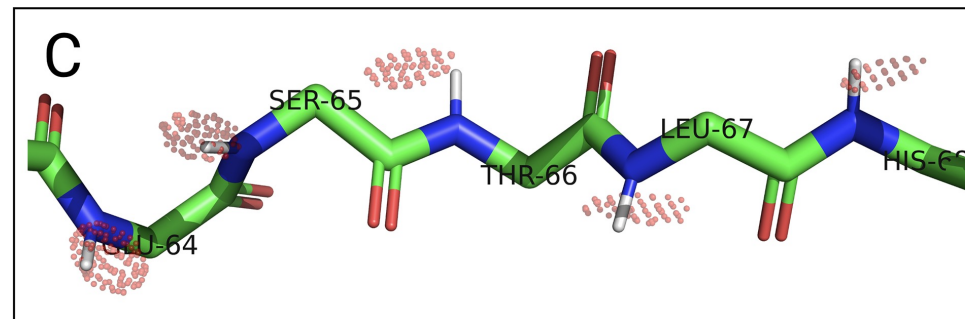
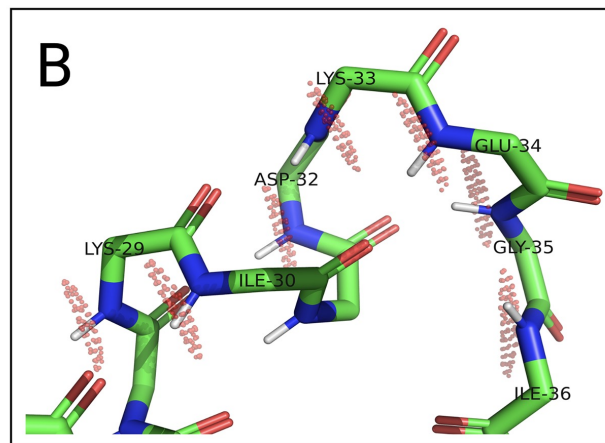
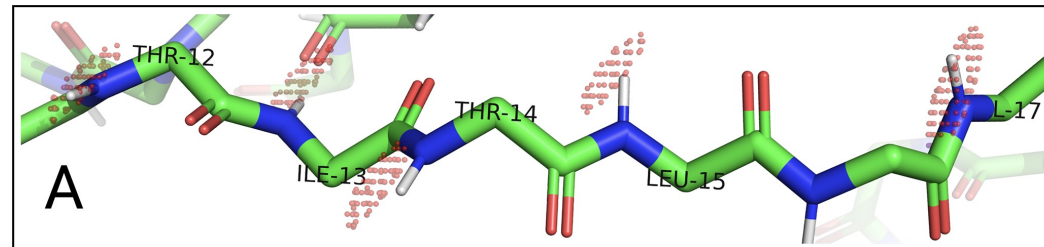




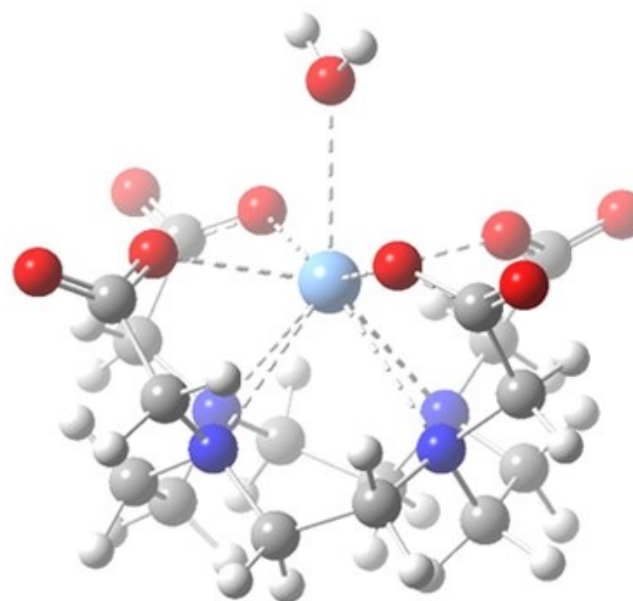
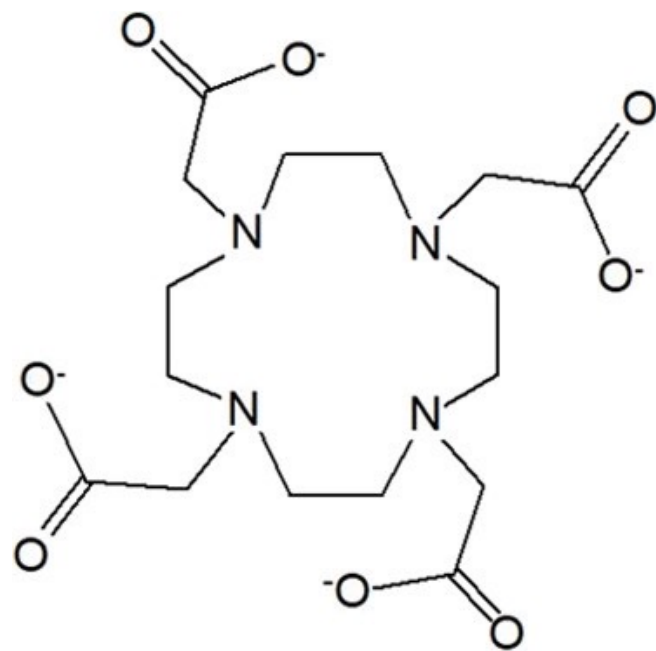
localisation space



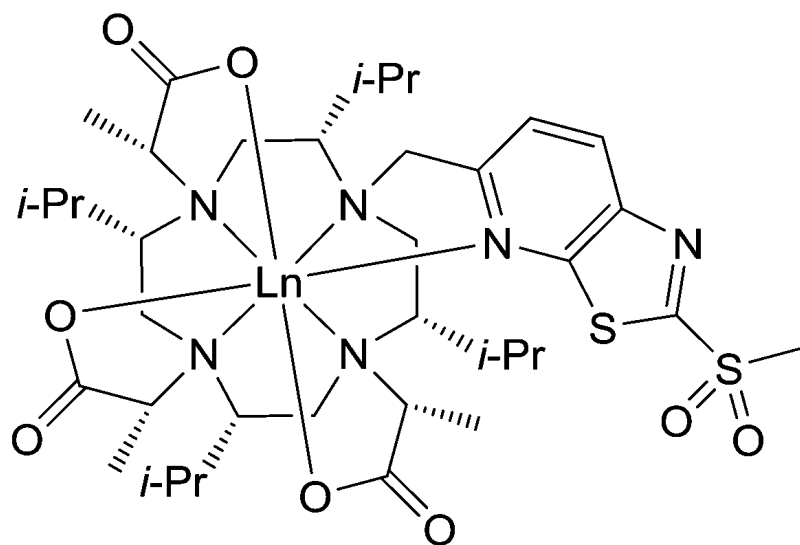
localisation space: ubiquitin S57C



DOTA

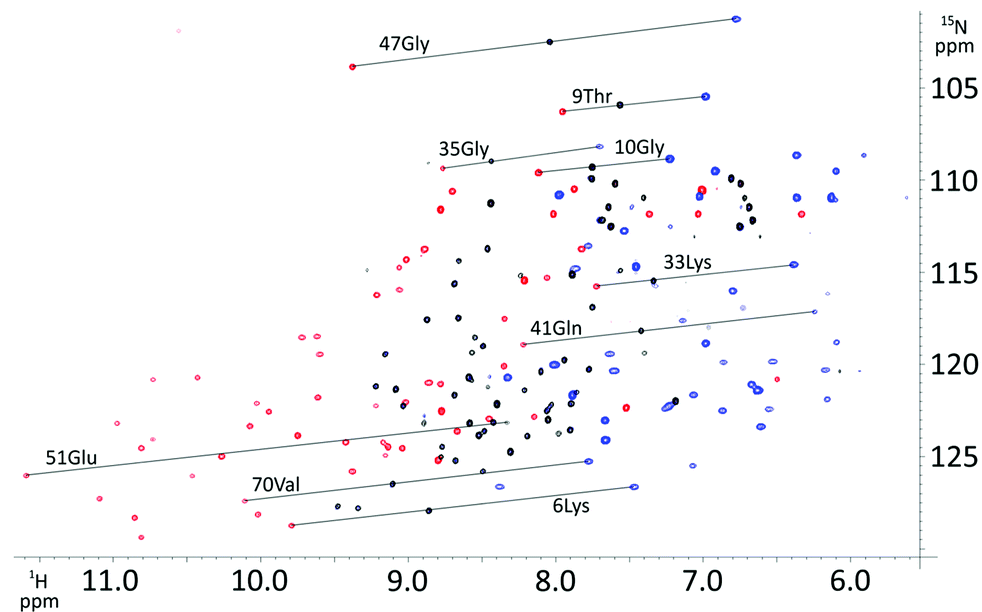


P4T-DOTA



ubiquitin S57C

Tm³⁺ Lu³⁺ Dy³⁺



$$\Delta\chi_{ax} = 54 \cdot 10^{-32} \text{ m}^3$$

$$Q = 0.045$$

$$\Delta\chi_{rh} = 27 \cdot 10^{-32} \text{ m}^3$$

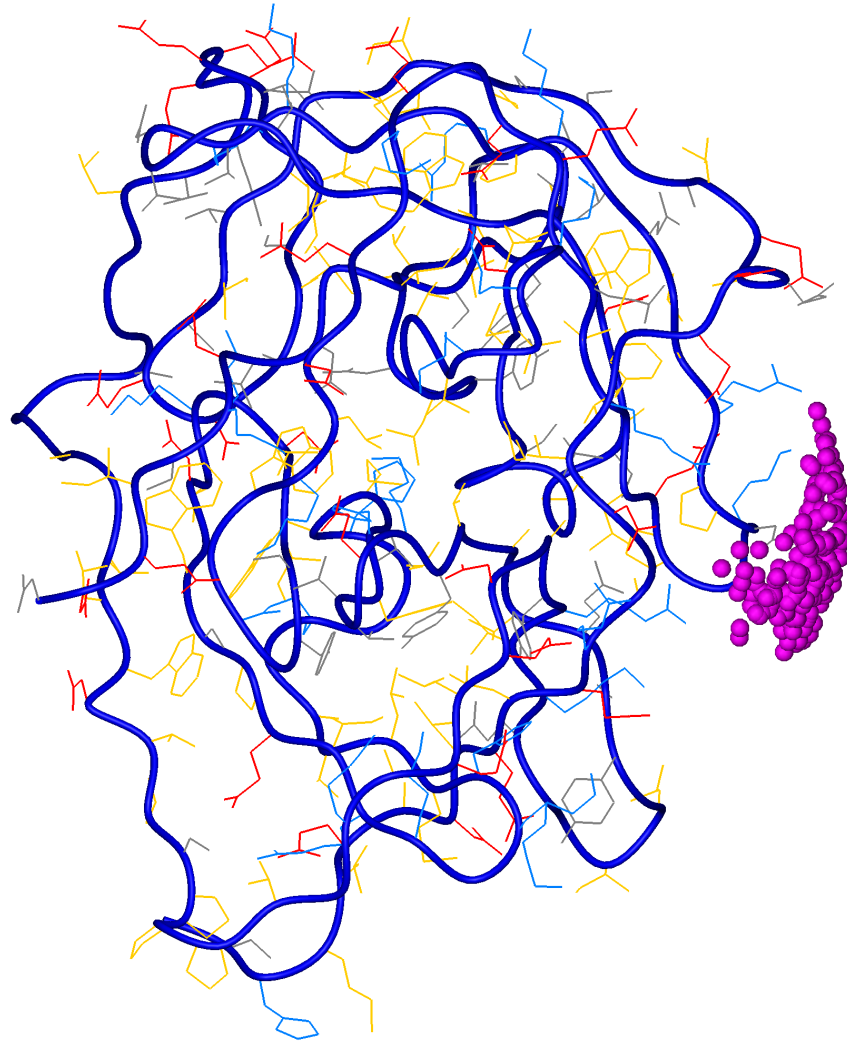
quality factor

Paramagpy

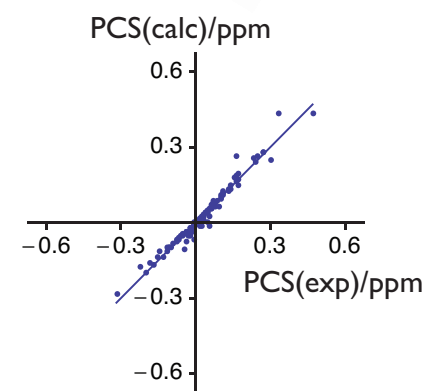
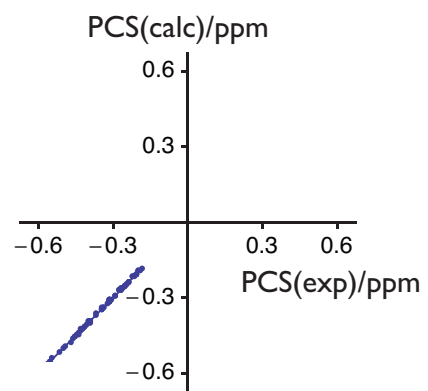
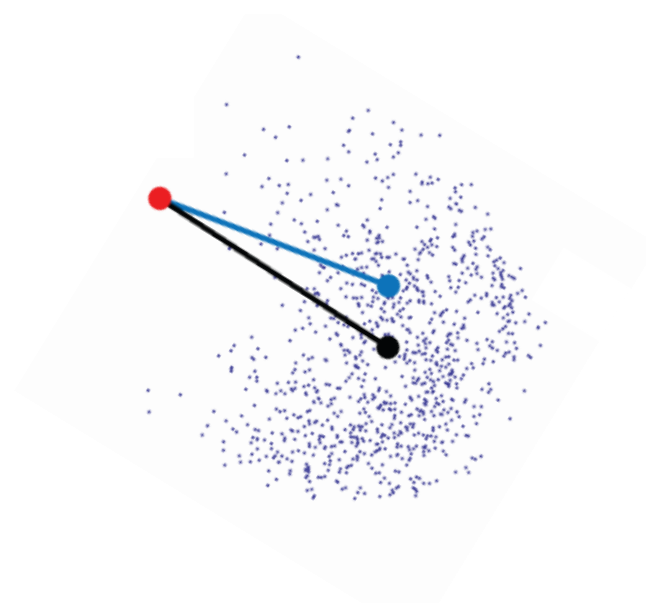
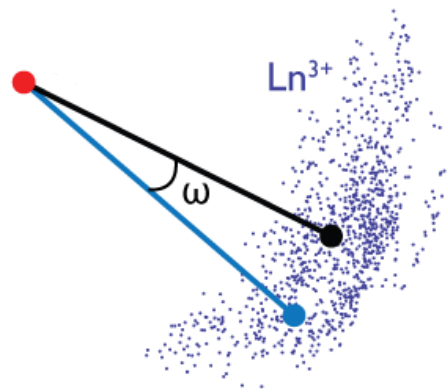
$$\text{cost} = \sum_i \frac{(\text{PCS}_i^{\text{cal}} - \text{PCS}_i^{\text{exp}})^2}{S_{\text{PCS},i}^2}$$

$$Q = \sqrt{\sum_i \frac{(C_i - E_i)^2}{(E_i)^2}}$$

most tags are mobile

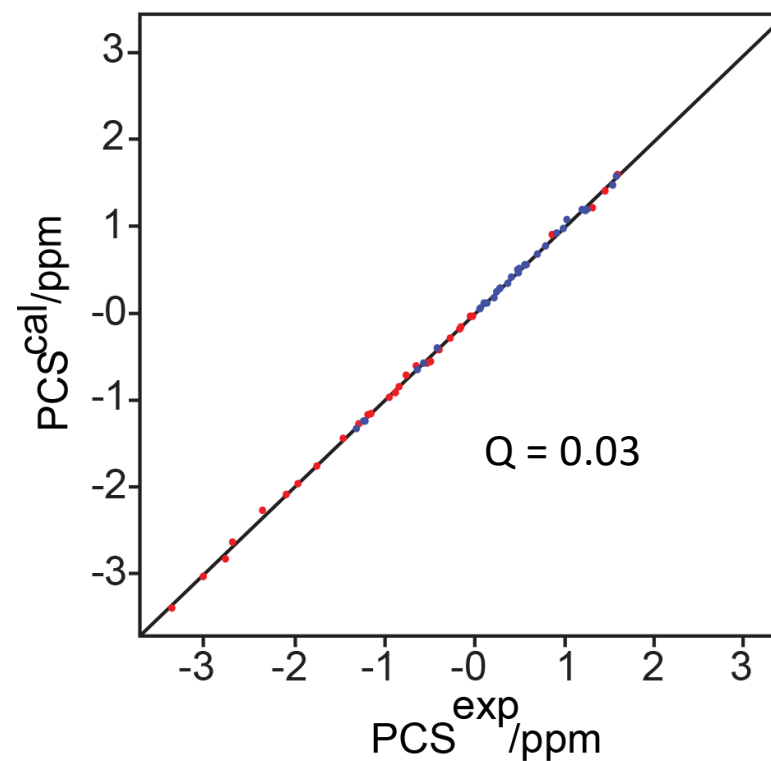
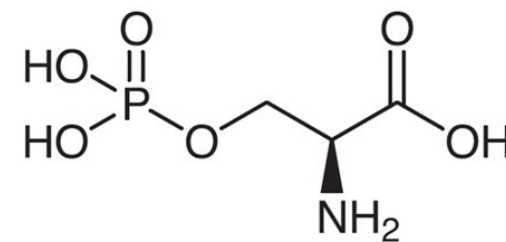
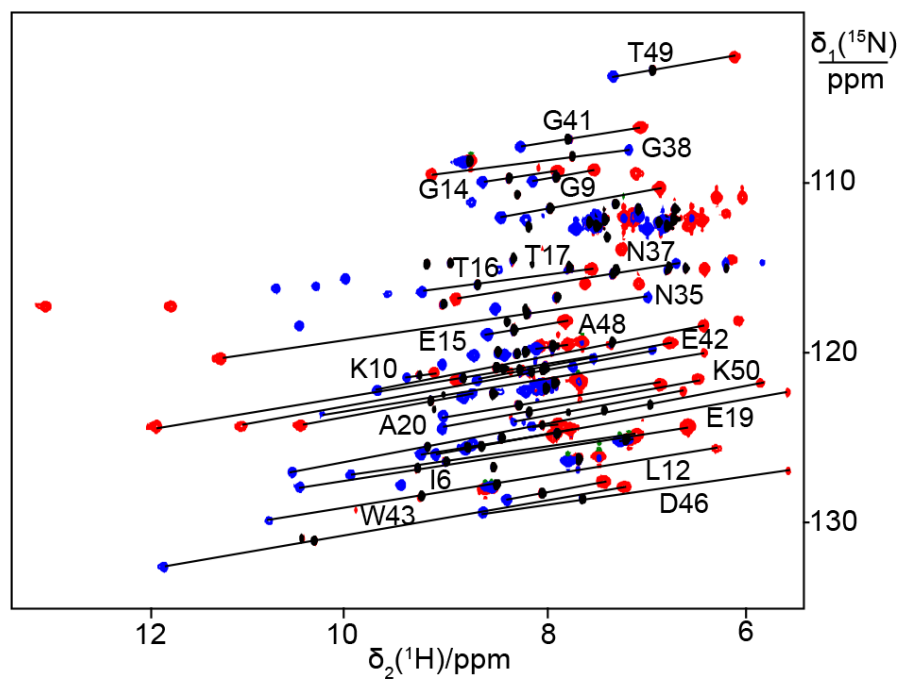


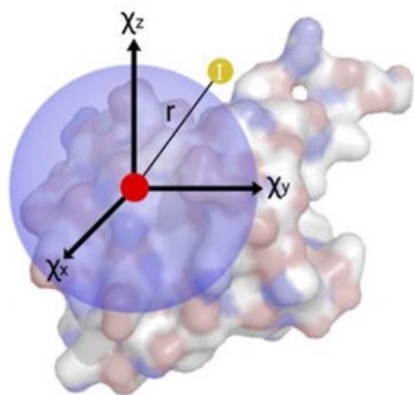
effective $\Delta\chi$ tensor



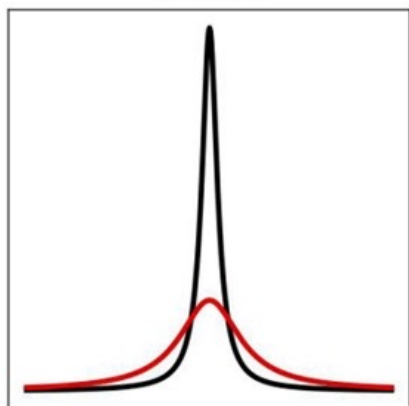
GB1 A24Sep/K28Sep

Tm³⁺ Y³⁺ Tb³⁺

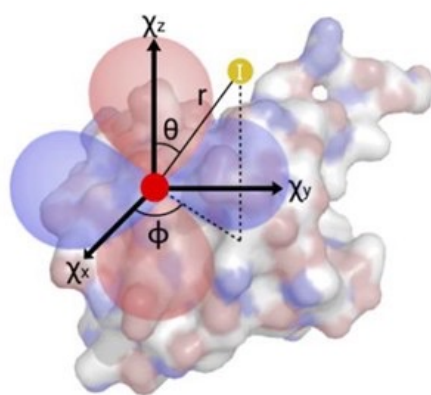




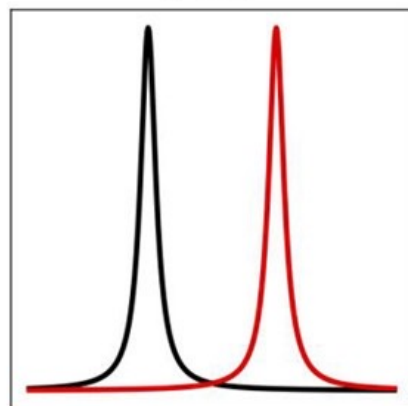
PRE



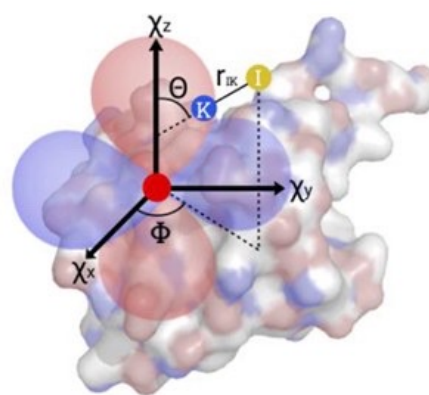
v/Hz



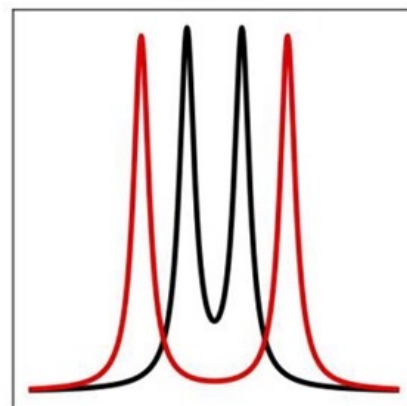
PCS



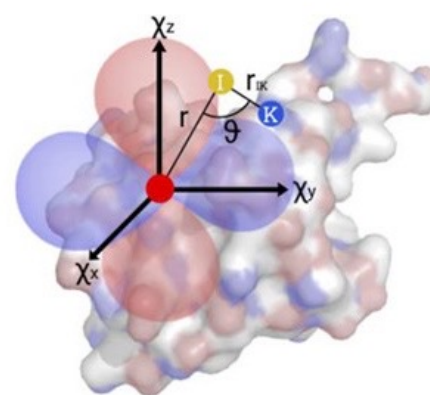
δ /ppm



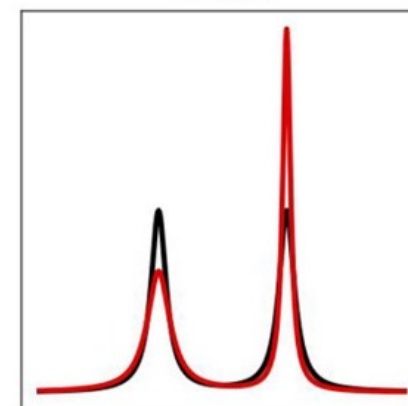
RDC



v/Hz



CCR



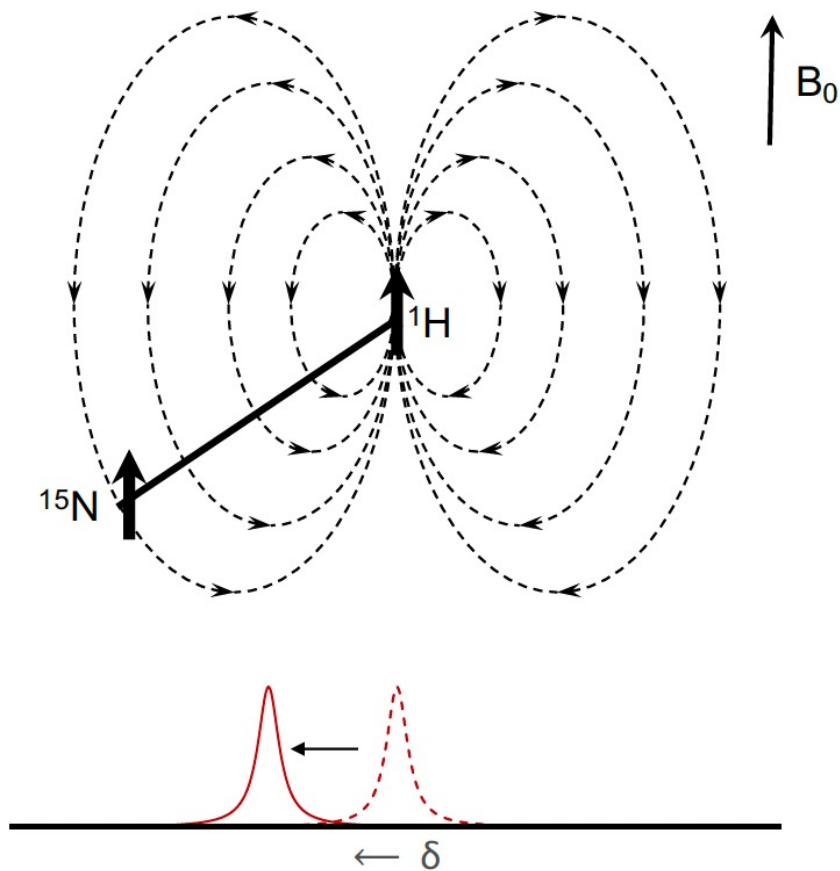
v/Hz

residual dipolar couplings (RDC)

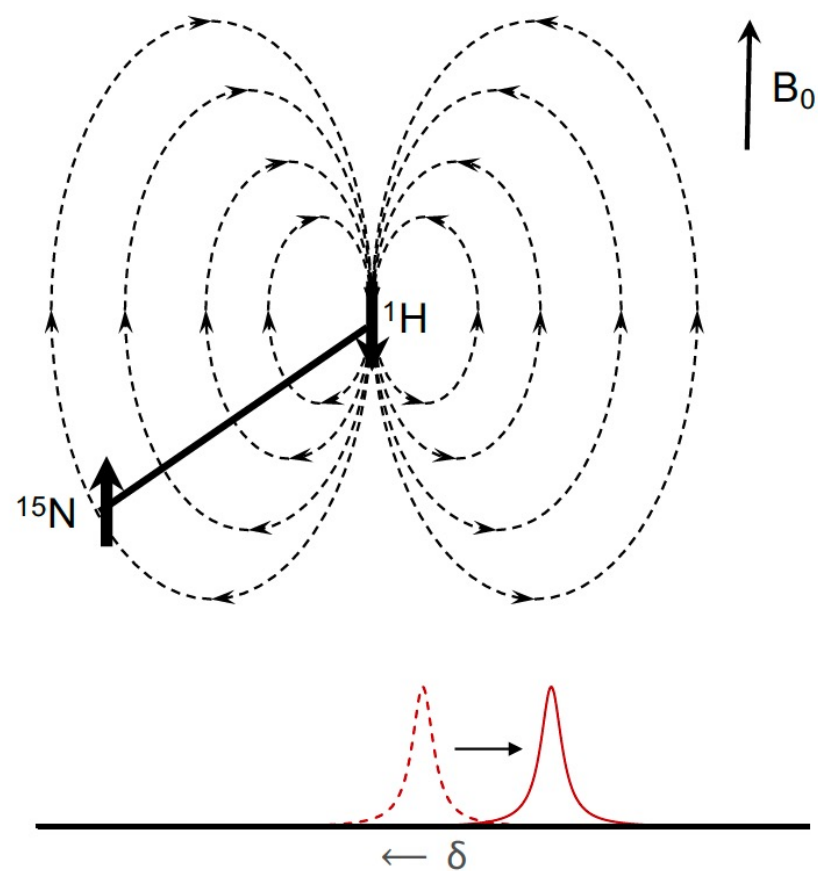
$$\mathbf{A} = \frac{B_0^2}{15\mu_0 k_B T} \Delta\chi$$

residual dipolar couplings (RDC)

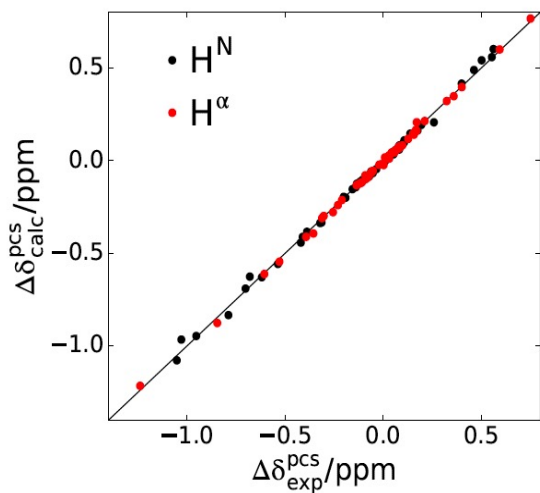
$^1\text{H} - \alpha$



$^1\text{H} - \beta$

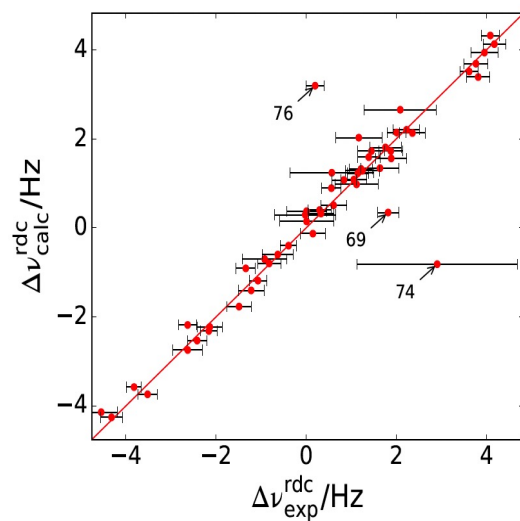


residual dipolar couplings (RDC)



$$\Delta\chi_{\text{ax}} = -9 \cdot 10^{-32} \text{ m}^3$$

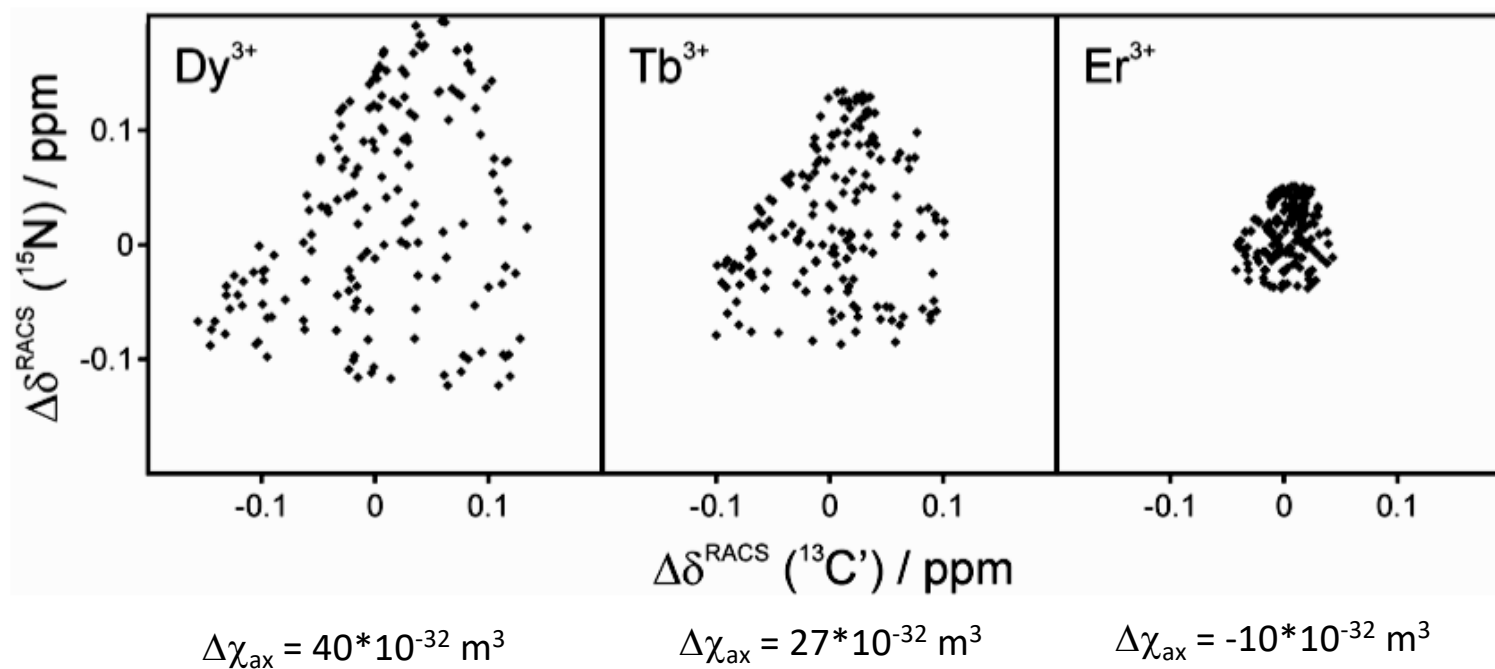
$$Q = 0.06$$



$$\Delta\chi_{\text{ax}} = -6 \cdot 10^{-32} \text{ m}^3$$

$$Q = 0.11$$

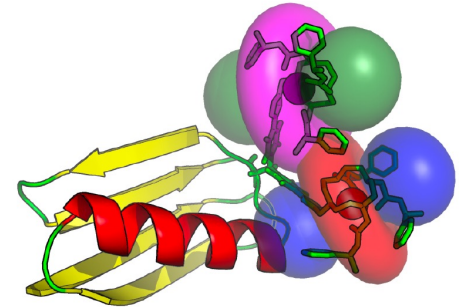
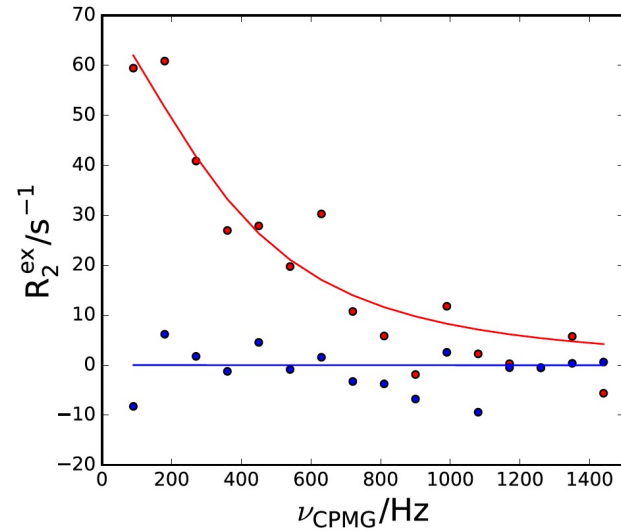
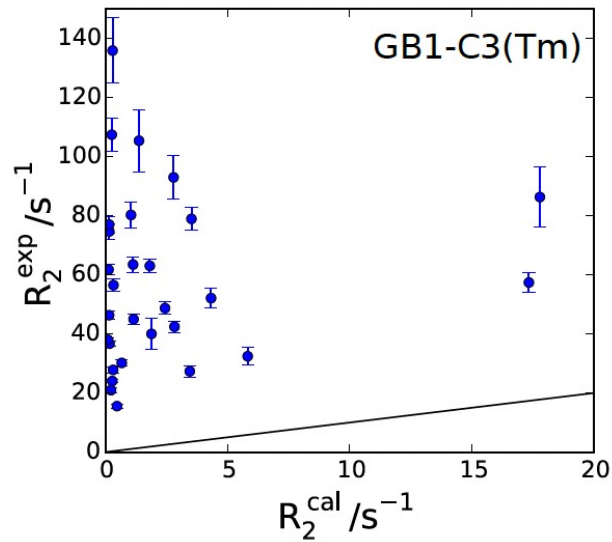
residual anisotropic chemical shifts (RACS)



$$\Delta\delta^{\text{RACS}} = \frac{B_0^2}{15\mu_0 kT} \sum_{ij} \delta_{ii}^{\text{CSA}} \cos^2 \theta_{ij} \Delta\chi_{jj}$$

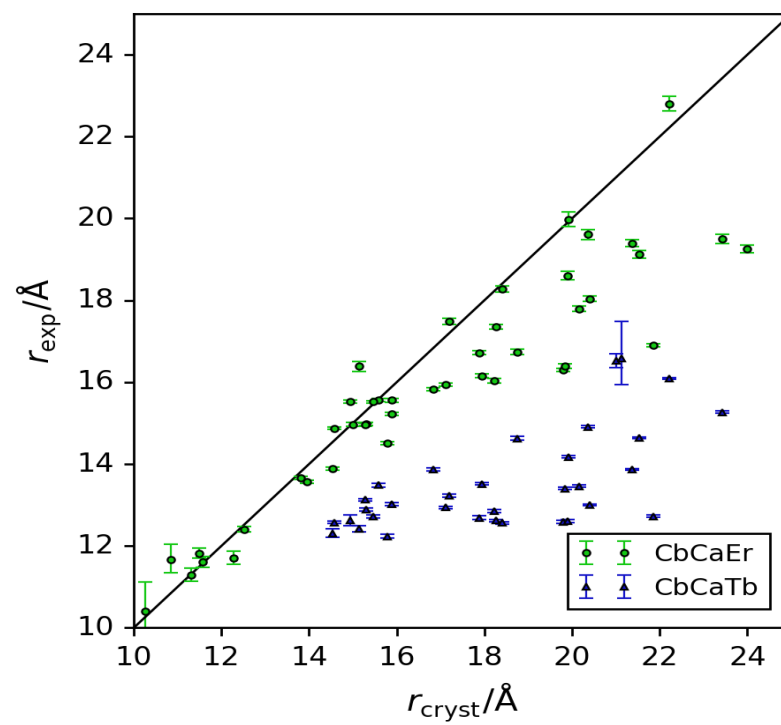
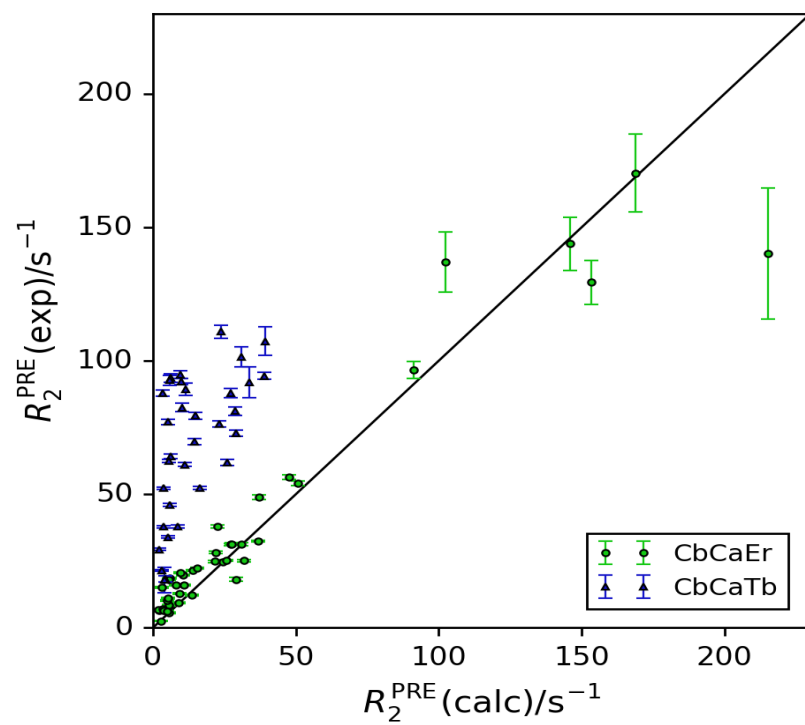
John et al., J. Am. Chem. Soc. 2005, 127, 17190-17191

measuring PREs with metals that generate PCSs

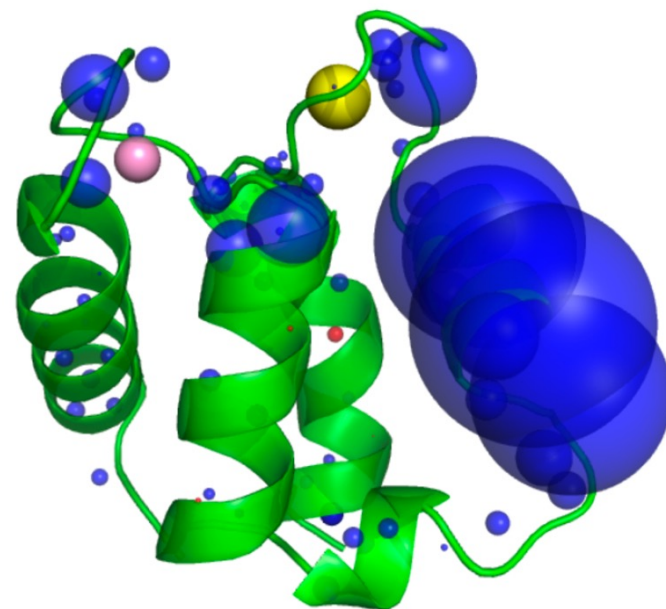
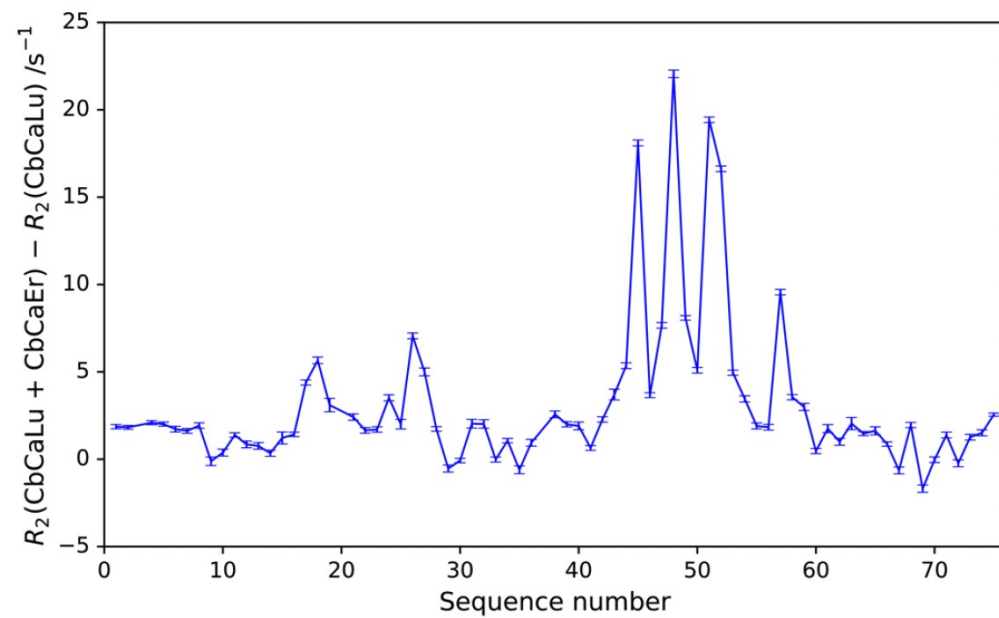


$$R_2^{\text{Curie}} = \underbrace{\frac{1}{45} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\omega_I^2 g_e^4 \mu_B^4 S^2 (S+1)^2}{(k_B T)^2 r_{\text{IS}}^6}}_{\omega_I^2 (\Delta\sigma_I^{\text{DSA}})^2} \left(4\tau_r + \frac{3\tau_r}{1 + \omega_I^2 \tau_r^2} \right)$$

distances from ^1H PREs

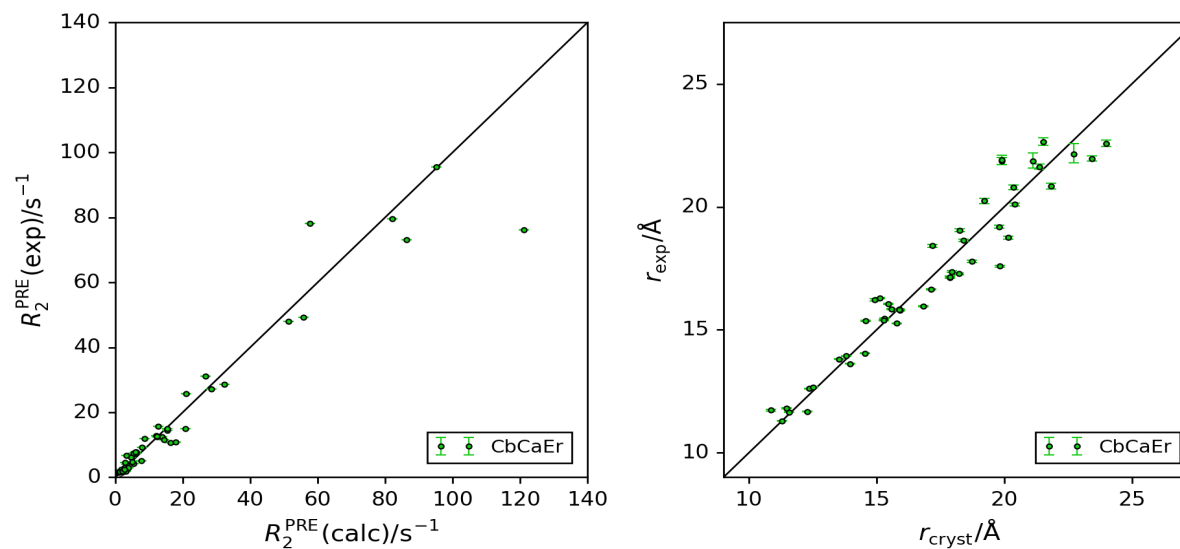


distances from ^1H PREs



2.5 mM CbCaLu + 2.5 mM CbCaEr

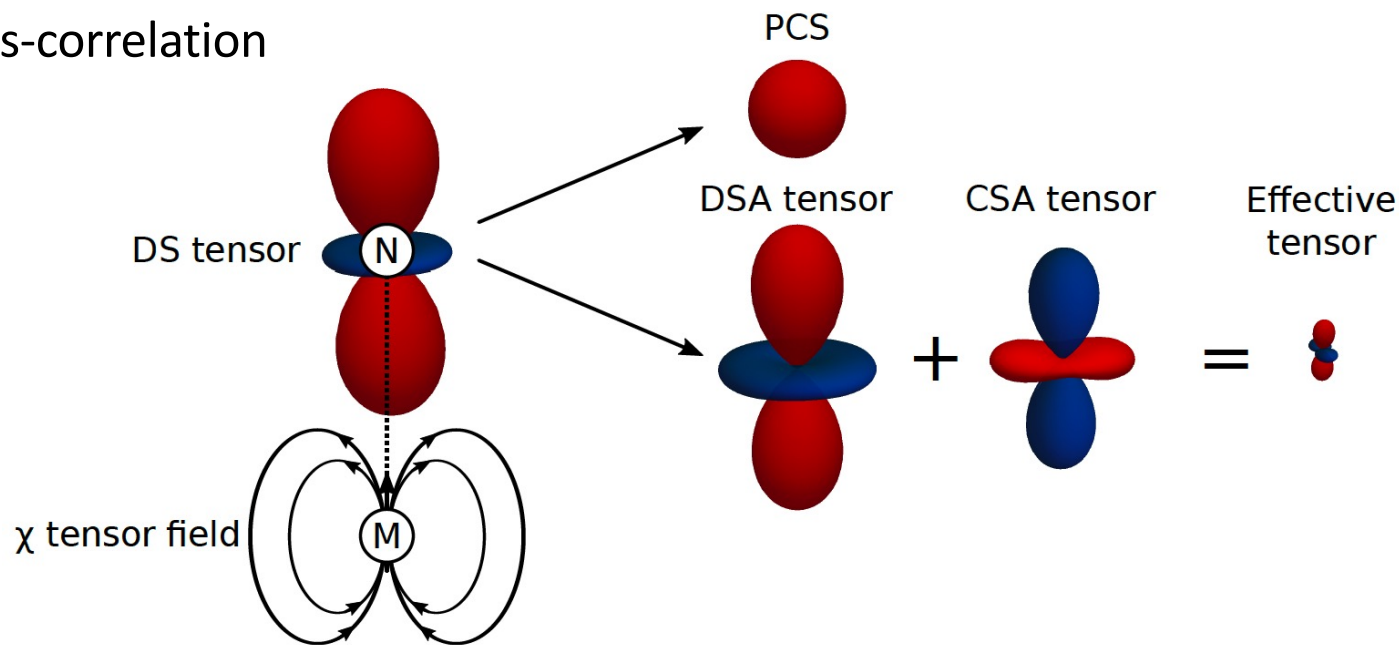
distances from ^1H PREs



- Use Er^{3+}
- Short relaxation delays <10 ms
- Low field (600 MHz)
- Internal diamagnetic reference
- Measure $R_2(^1\text{H})$ in HNCO

relaxation can be slower in a paramagnetic sample

DSA-CSA cross-correlation



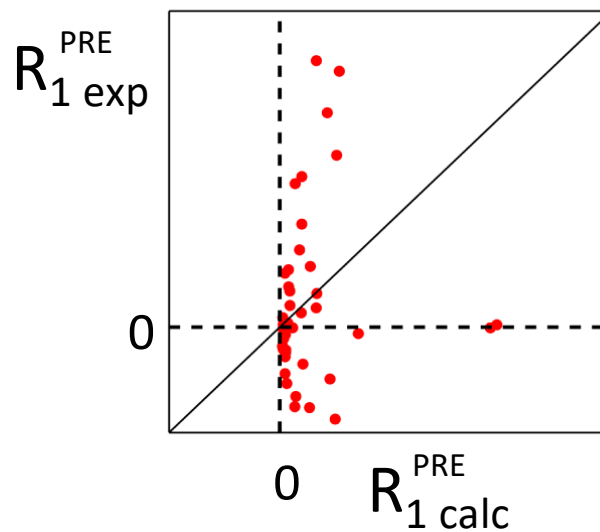
$$R_1^{\text{DSA}} = \frac{1}{4\pi} \xi_{\text{DSA}}^2 \left(\frac{\tau_c}{1 + (\omega_I \tau_c)^2} \right)$$

$$R_2^{\text{DSA}} = \frac{1}{24\pi} \xi_{\text{DSA}}^2 \left(4\tau_c + \frac{3 \cdot \tau_c}{1 + (\omega_I \tau_c)^2} \right)$$

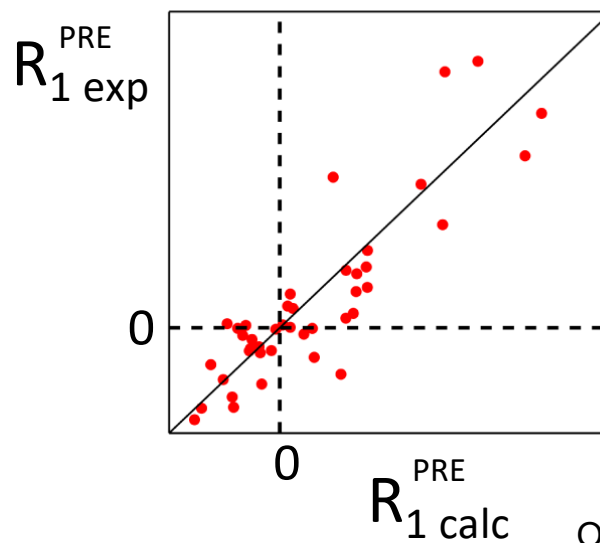
$$\xi_{\text{DSA}} = \sqrt{\frac{8\pi}{15} \gamma_I B_0 \Delta\sigma_I^{\text{DSA}}}$$

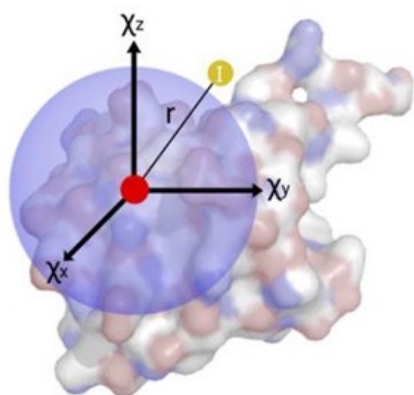
DSA-CSA cross-correlation

DSA

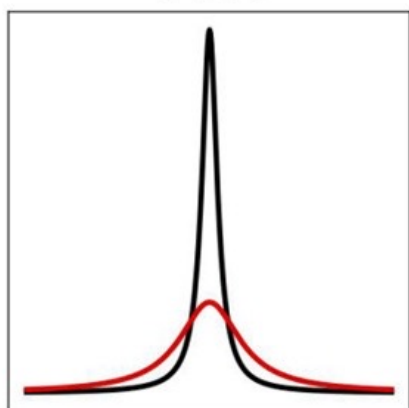


DSA + CSA

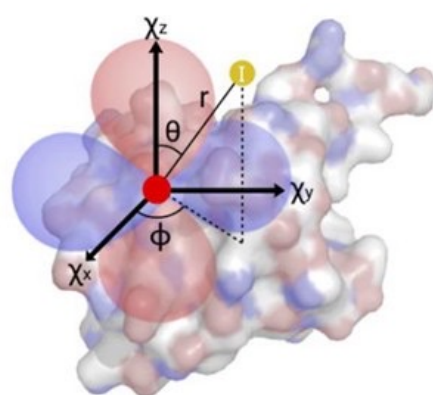




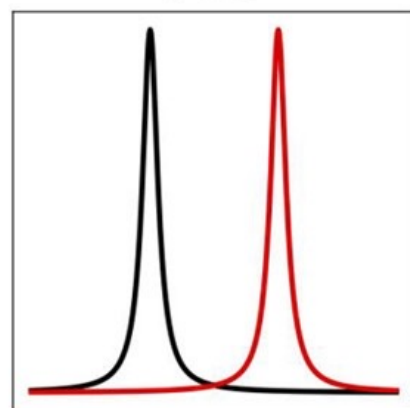
PRE



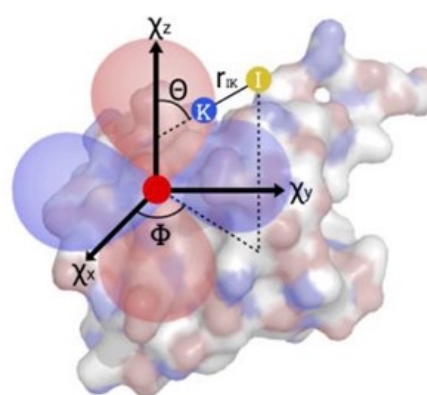
v/Hz



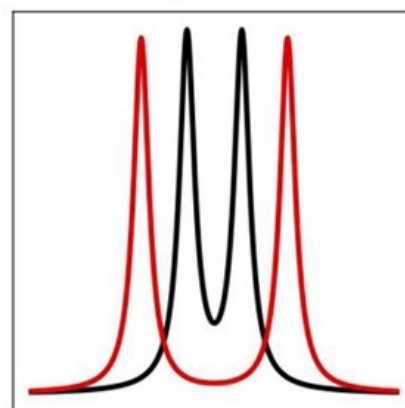
PCS



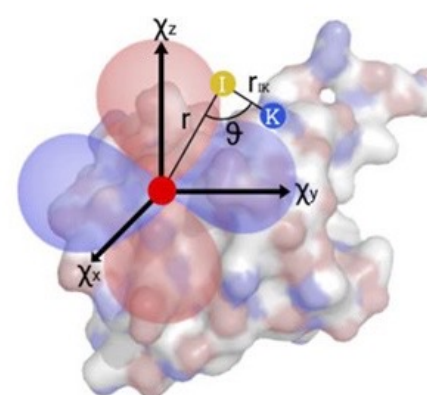
δ /ppm



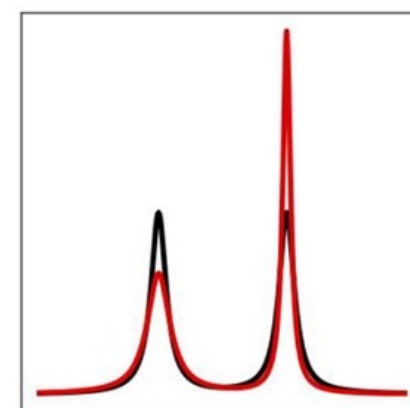
RDC



v/Hz

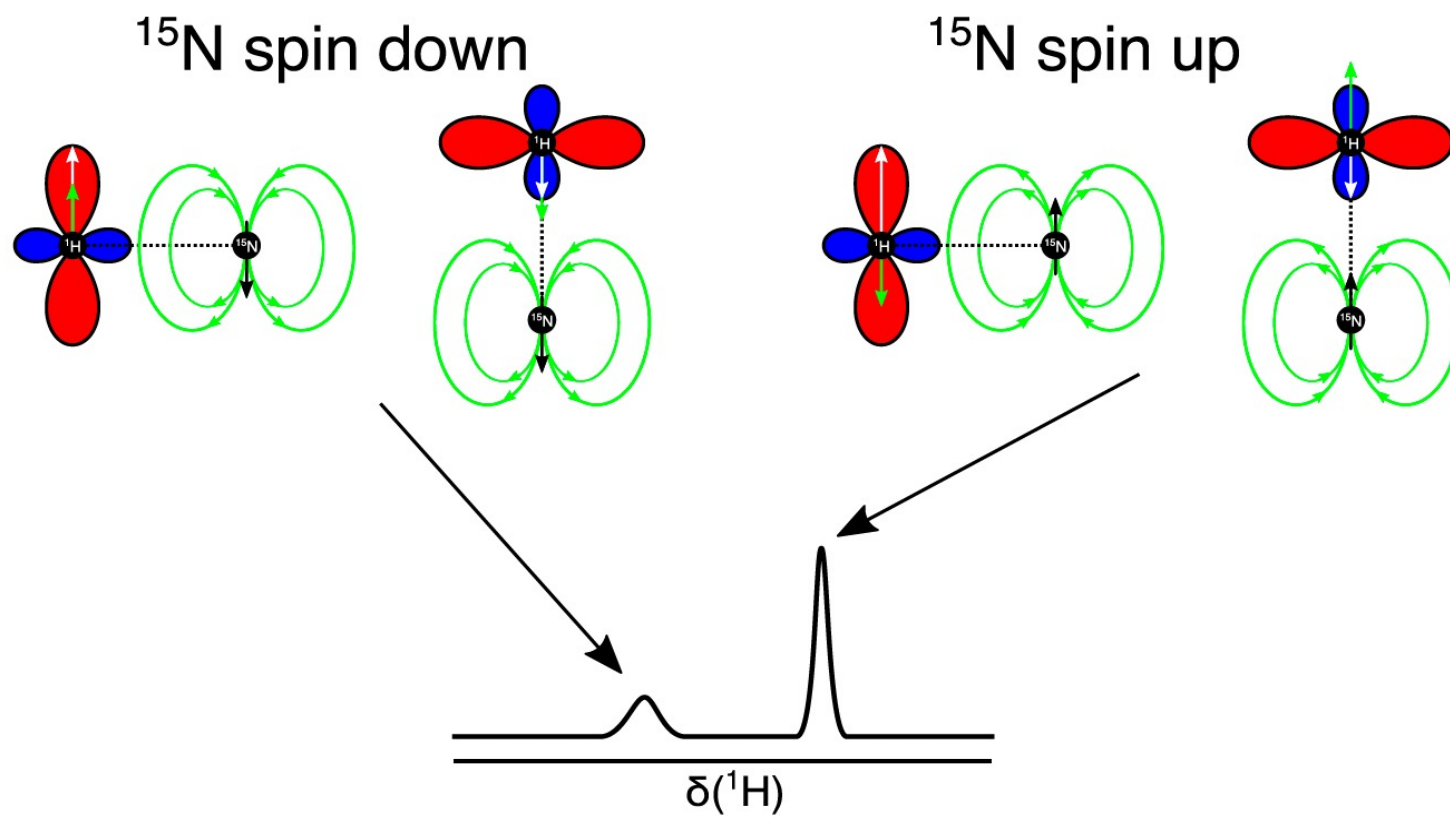


CCR

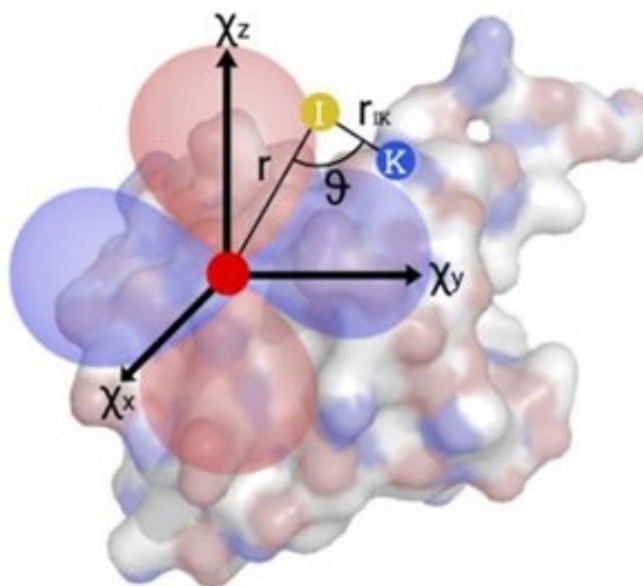


v/Hz

CCR



CCR



$$\eta^{\text{CCR}} = \kappa \frac{3 \cos^2 \vartheta - 1}{r^3} \left(4\tau_r + \frac{3\tau_r}{1 + \omega_{\text{H}}^2 \tau_r^2} \right)$$

Paramagpy

Paramagpy GUI

PDB & Models
 Read PDB file ...xamples/data_files/2bcx.pdb
 Set Models Choose models. Default: all
 Atom Selection
 Set CSA

PCS RDC PRE CCR

Fitting Options
 Fit Offset SVD Gridsearch NLR Gradient Descent
 Fit Position SVD Radius/Å 10.000 Use RACS
 Ensemble Average SVD Grid Spacing/Å 1.000 Use RADS

Multiple Fit PCS
 Data 1 Data 2 Data 3 Data 4 Data 5 Data 6
 Multiple Fit Tensor

Data 1 Data 2 Data 3 Data 4 Data 5 Data 6

View Data
 Q factor: 0.1161 Plot Save Hide 'nan'

?	Chn.	Seq.	Res.	Atom	Calc.	Exp.	Err.	Dev.
x	A	2	SER	N	-0.061	-0.034	0.090	0.027
x	A	2	SER	H	-0.071	-0.049	0.160	0.023
x	A	4	GLU	N	-0.203	-0.212	0.040	0.010
x	A	4	GLU	H	-0.172	-0.185	0.040	0.013
x	A	5	GLU	N	-0.179	-0.201	0.150	0.022
x	A	5	GLU	H	-0.150	-0.164	0.020	0.014
x	A	6	LEU	N	-0.182	-0.186	0.020	0.004
x	A	6	LEU	H	-0.160	-0.168	0.040	0.008
x	A	7	LYS	N	-0.429	-0.406	0.080	0.023
x	A	7	LYS	H	-0.358	-0.363	0.010	0.005
x	A	8	GLY	N	-0.449	-0.419	0.080	0.030
x	A	8	GLY	H	-0.380	-0.373	0.060	0.007
x	A	9	ILE	N	-0.332	-0.325	0.160	0.006
x	A	9	ILE	H	-0.295	-0.291	0.220	0.003
x	A	10	PHE	N	-0.507	-0.468	0.090	0.038
x	A	10	PHE	H	-0.478	-0.452	0.170	0.026
x	A	11	GLU	N	-0.926	-0.839	0.090	0.086
x	A	11	GLU	H	-0.855	-0.764	0.180	0.091
x	A	12	LYS	N	-0.562	-0.537	0.140	0.026
x	A	12	LYS	H	-0.538	-0.504	0.010	0.034

Change models: < 25 >

Experimental Data
 Read PCS Data ...HN_PCS_errors.npc
 B0/Tesla 800.0 Temp./K 298.15

Initial Tensor
 Lanthanide Template: Zero
 x/Å 0.000 α/° 0.000 Δχ_{ax}/10⁻³² 0.000
 y/Å 0.000 β/° 0.000 Δχ_{rh}/10⁻³² 0.000
 z/Å 0.000 γ/° 0.000 χ_{iso}/10⁻³² 0.000
 τ_r/ns 0.000 T_{1e}/ps 0.000 ref./ppm 0.000
 Copy Paste Set UTR

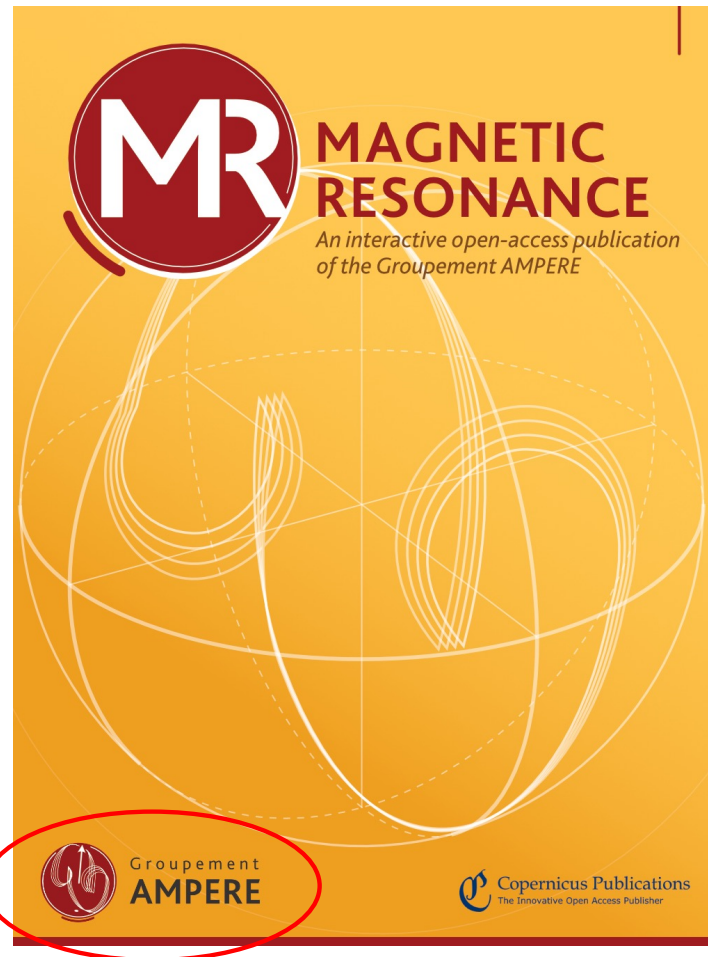
↓ Fit Tensor ↓

Fitted Tensor
 x/Å 5.811 α/° 156.155 Δχ_{ax}/10⁻³² -7.070
 y/Å 6.748 β/° 52.080 Δχ_{rh}/10⁻³² -3.975
 z/Å -4.466 γ/° 33.847 χ_{iso}/10⁻³² 0.000
 τ_r/ns 0.000 T_{1e}/ps 0.000 ref./ppm 0.000
 Copy Paste Set UTR
 More Error Sim. Plot

Back-calculate PCS

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Quality typesetting

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