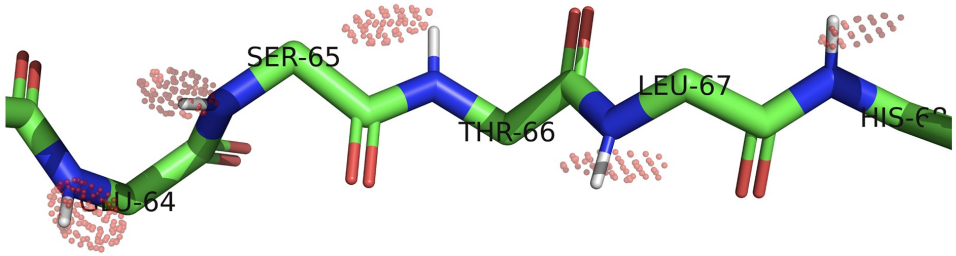
paramagnetism in NMR

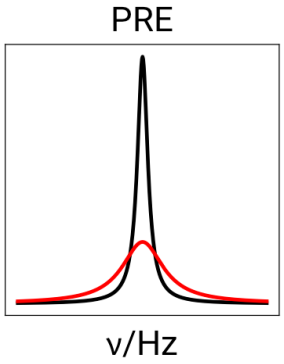


Paramagnetism: a compound that becomes magnetic in a magnetic field and, in an inhomogenous magnetic field, is pulled into the region of higher magnetic field. Paramagnetism arises from unpaired electrons.

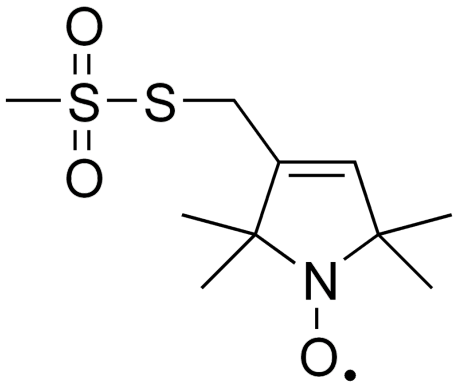
Diamagnetism: a compound that becomes magnetic in a magnetic field and, in an inhomogenous magnetic field, tries to move away from the region of higher magnetic field.

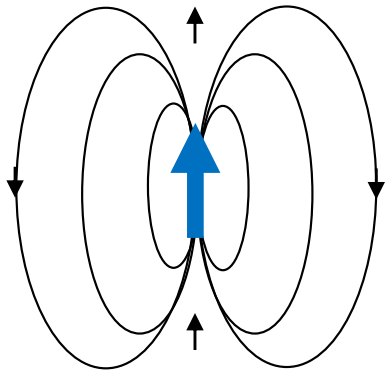
diamagnetism https://www.youtube.com/watch?v=KlJsVqc0ywM&t=34s

paramagnetic relaxation enhancement

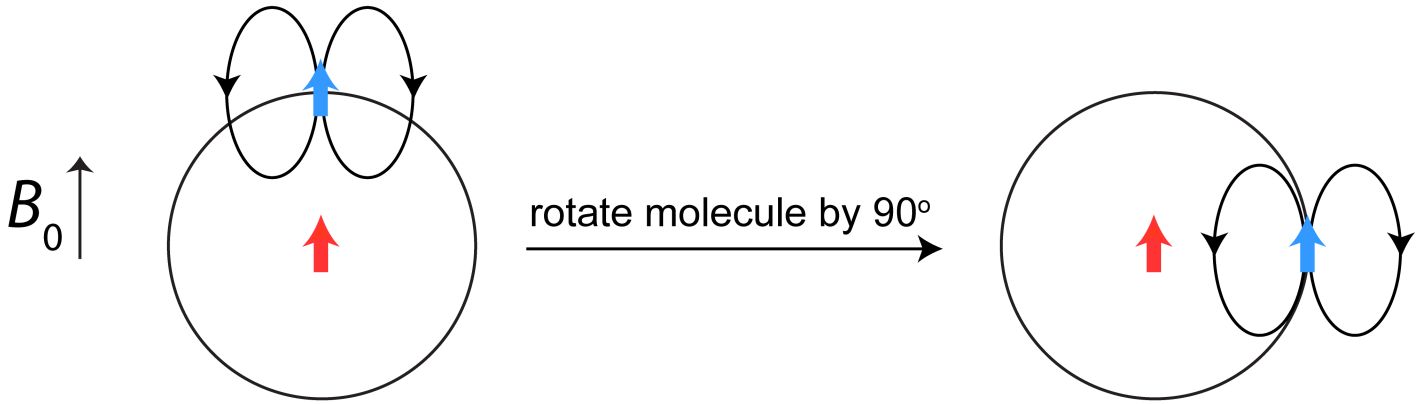


MTSL





dipole-dipole interaction



paramagnetic relaxation enhancement, PRE

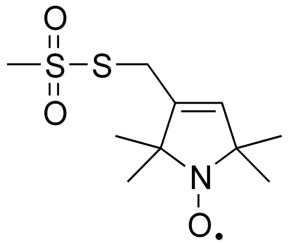
$$R_2^{\mathrm{SBM}} = \frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_\mathrm{I}^2 g_\mathrm{e}^2 \mu_\mathrm{B}^2 S(S+1)}{r_{\mathrm{IS}}^6}\left(4\tau_\mathrm{c} + \frac{3\tau_\mathrm{c}}{1+\omega_\mathrm{I}^2\tau_\mathrm{c}^2} + \frac{13\tau_\mathrm{c}}{1+\omega_\mathrm{S}^2\tau_\mathrm{c}^2}\right)$$

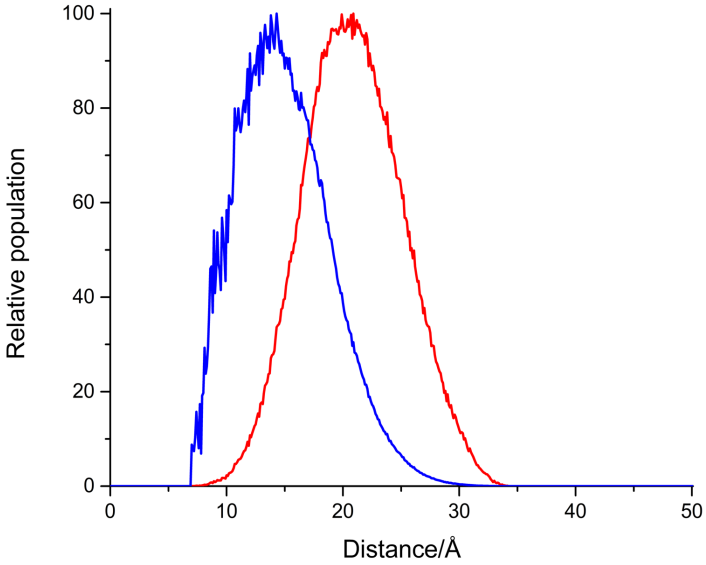
$$R_2^{\mathrm{SBM}} = C \times S(S+1)\tau_\mathrm{c}/r^6$$

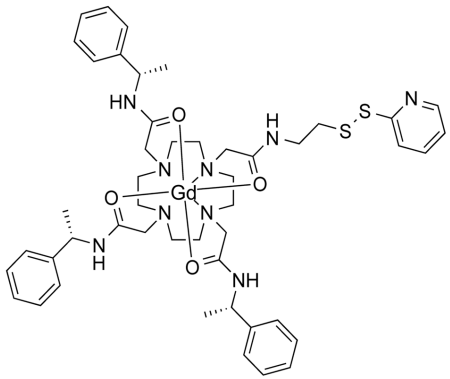
$$C = 6.5 \times 10^{16}\ \text{Å}^6\ \mathrm{s}^{-2}$$

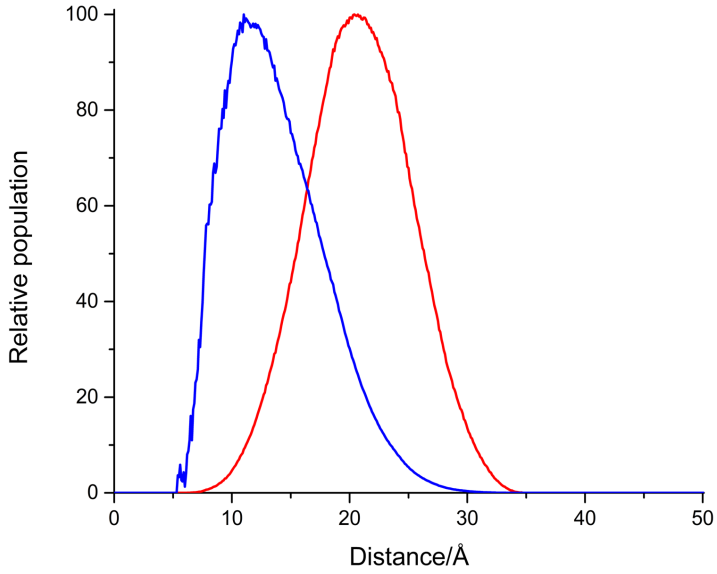
$$\tau_\mathrm{c}^{-1} = \tau_\mathrm{r}^{-1} + \tau_\mathrm{s}^{-1}$$

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



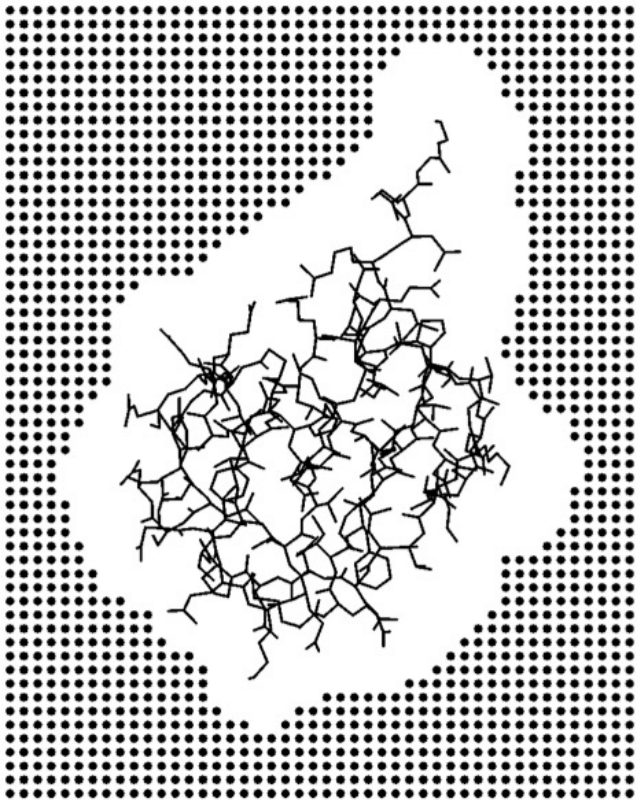


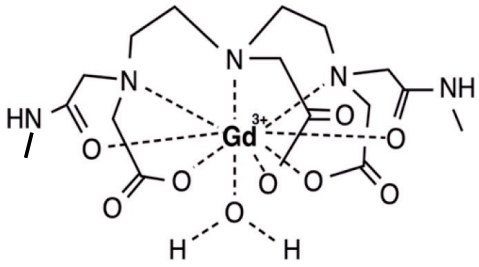


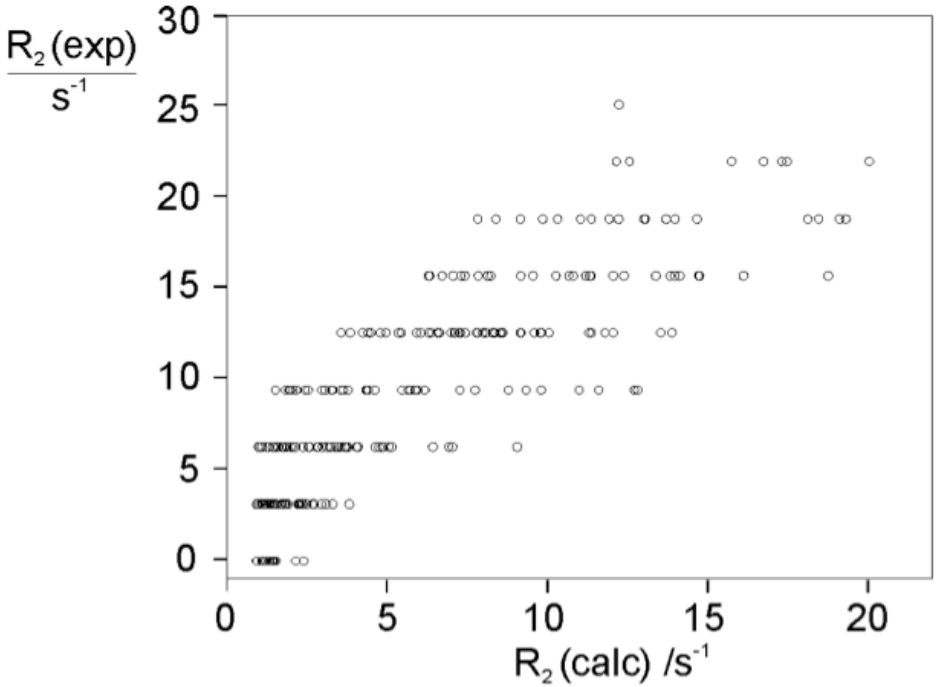


J. Am. Chem. Soc. 2021, 143, 1133-1143

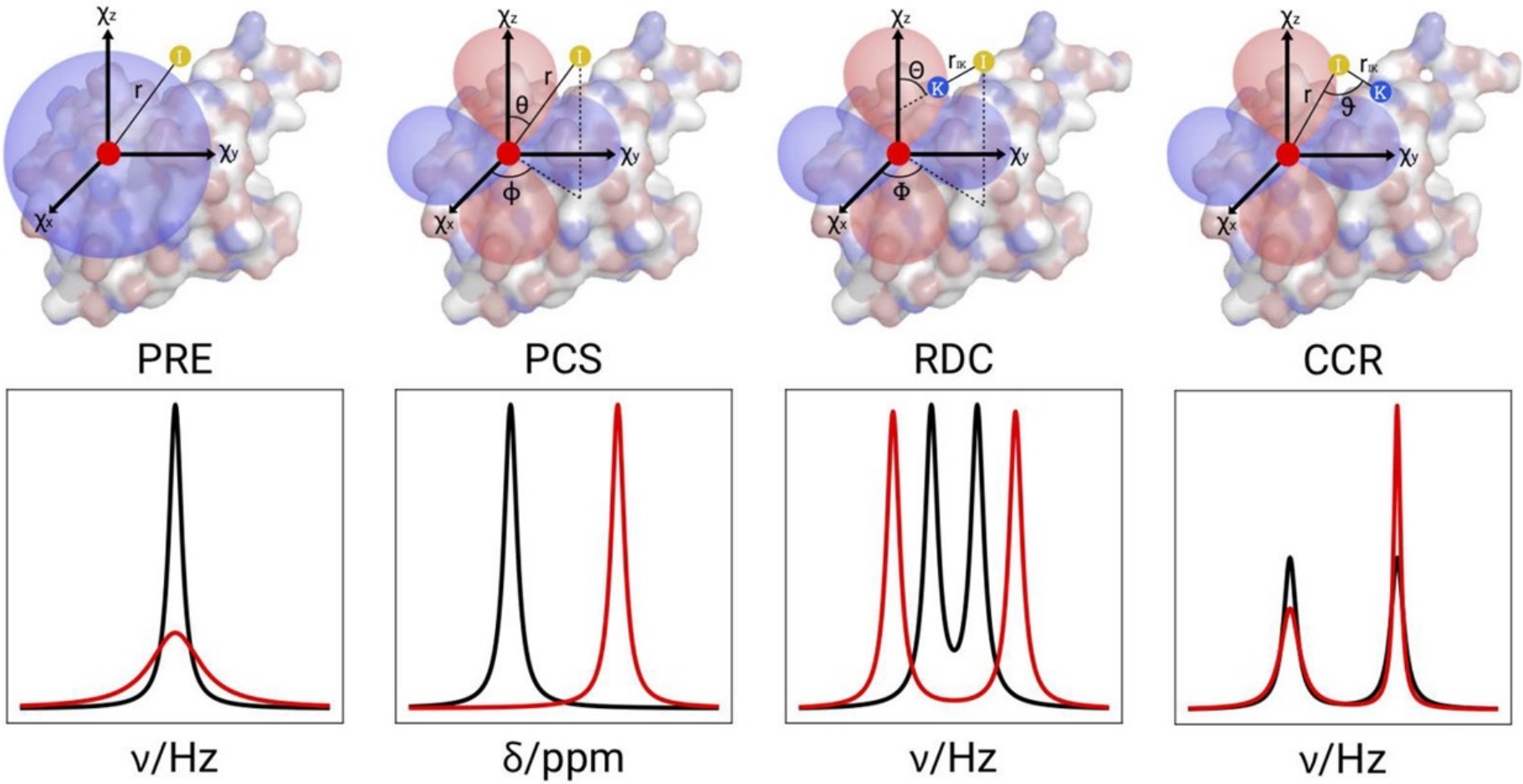
Intermolecular PRE







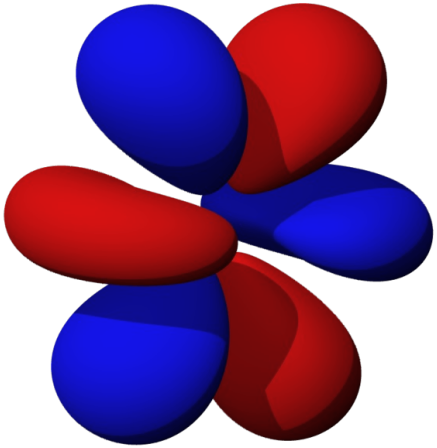
Pintacuda & Otting, J. Am. Chem. Soc. 2002, 372-373

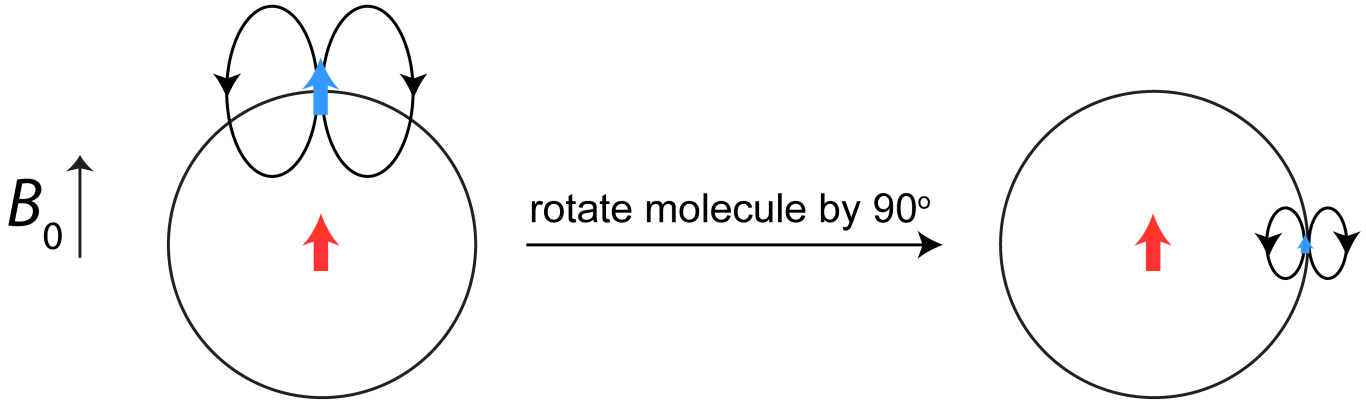


Chem. Rev. 2022, 122, 9571-9642

pseudocontact shifts

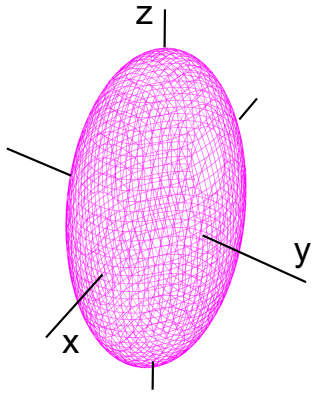
an orbital (f_{xz^2})





https://en.wikipedia.org/wiki/Atomic_orbital

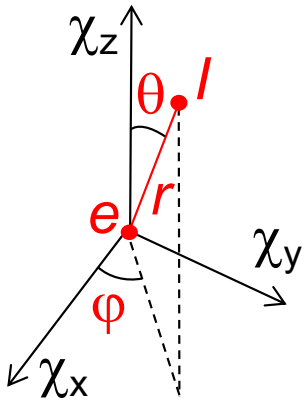
χ: magnetic susceptibility tensor

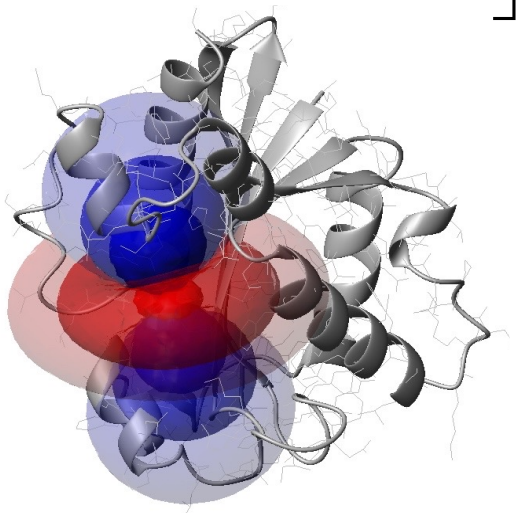


$\Delta\chi$: magnetic susceptibility anisotropy tensor

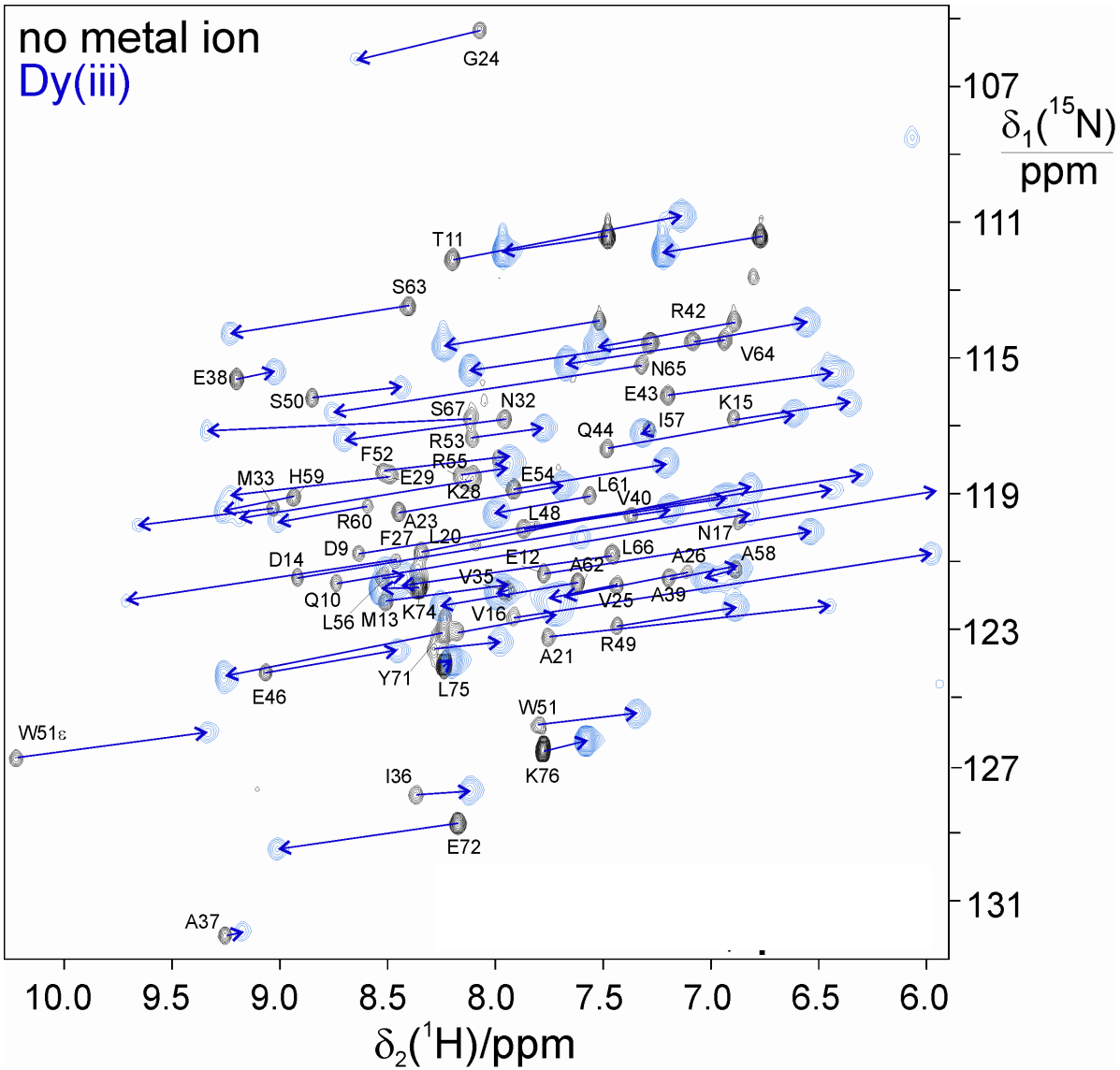
$$\underbrace{\chi_z - \frac{\chi_x + \chi_y}{2}}_{\Delta\chi_{ax}} \qquad \underbrace{\chi_x - \chi_y}_{\Delta\chi_{rh}}$$

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





pseudocontact shifts



lanthanoid ions

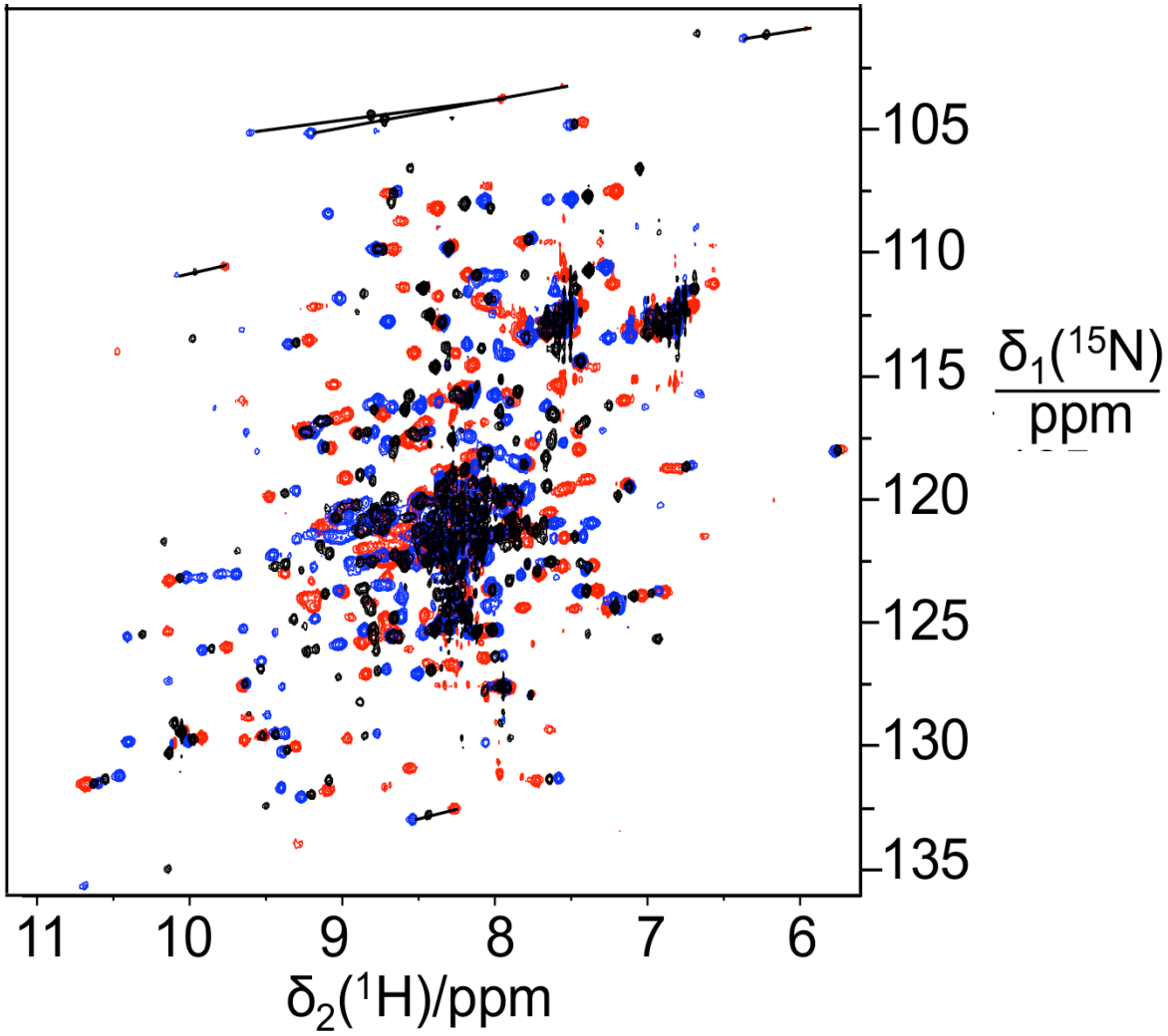
	Cerium	Praseodymium	Neodymium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium
	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Tb
χ_{iso}	5.6	11.2	11.4	0.6	~6	55.1	82.7	99.2	98.4	80.3	50.0	18.0
PRE												
	20Å											
PCS												
$\Delta\chi_{ax}$	2.1	3.4	1.7	0.2	2.4	0.0	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

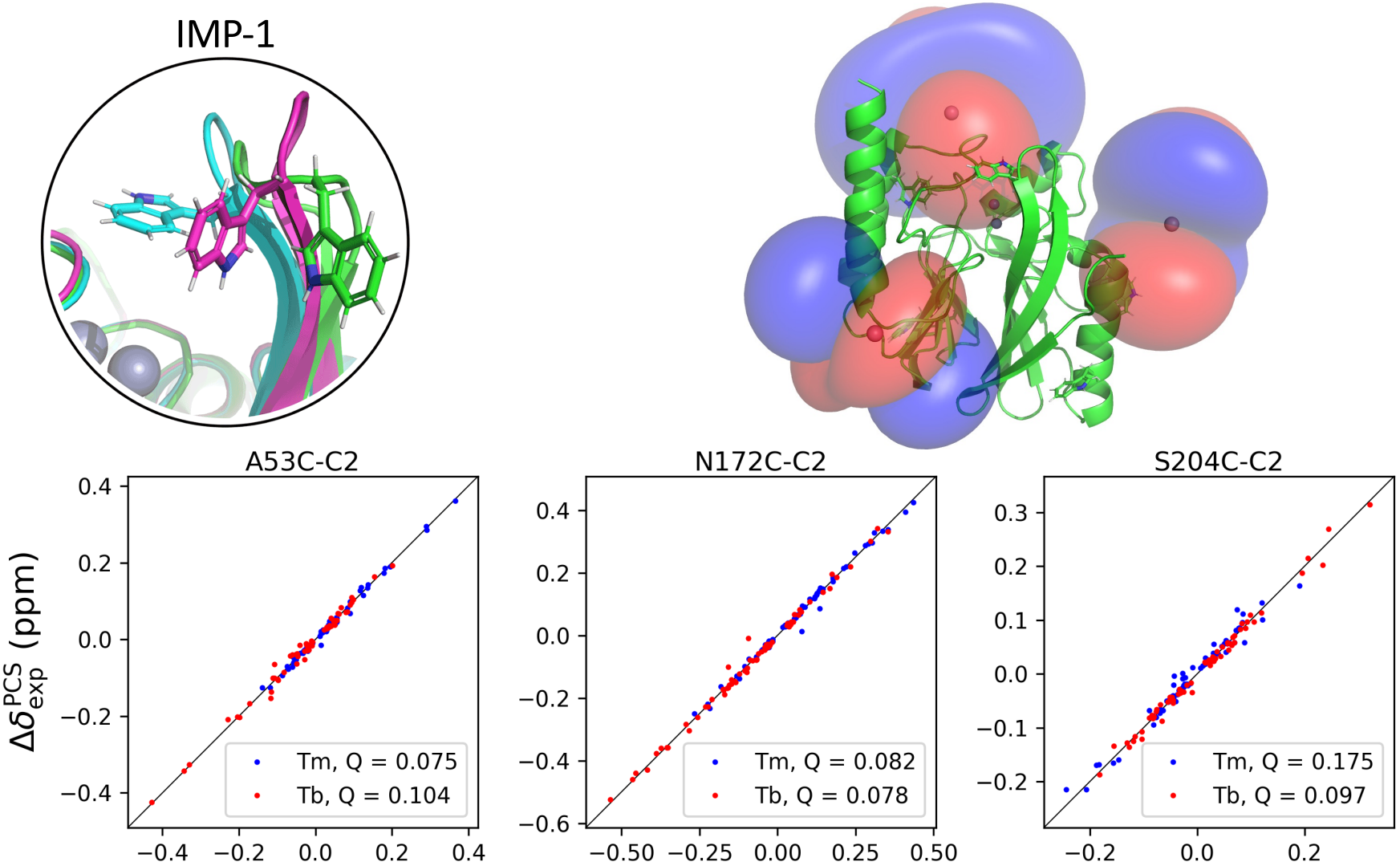
Chem. Rev. 2022, 122, 9571-9642

Y^{3+}

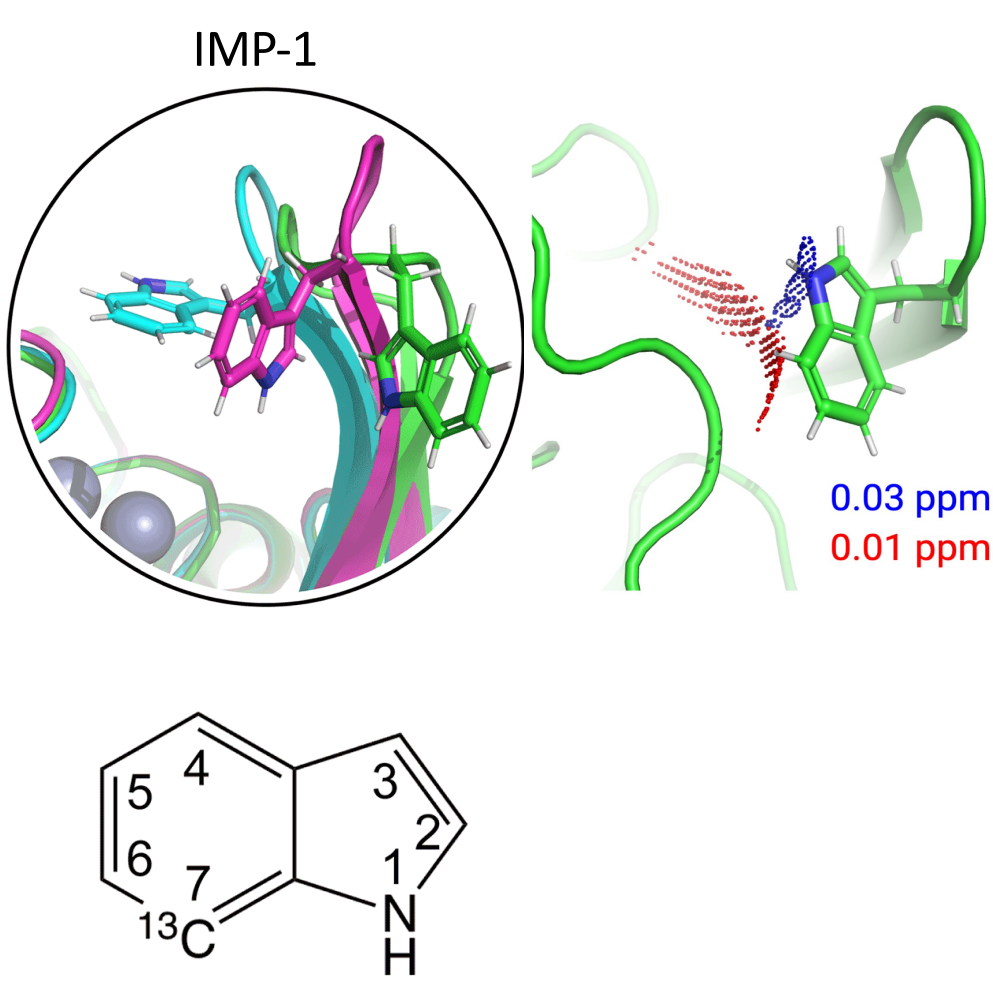
Tm^{3+}

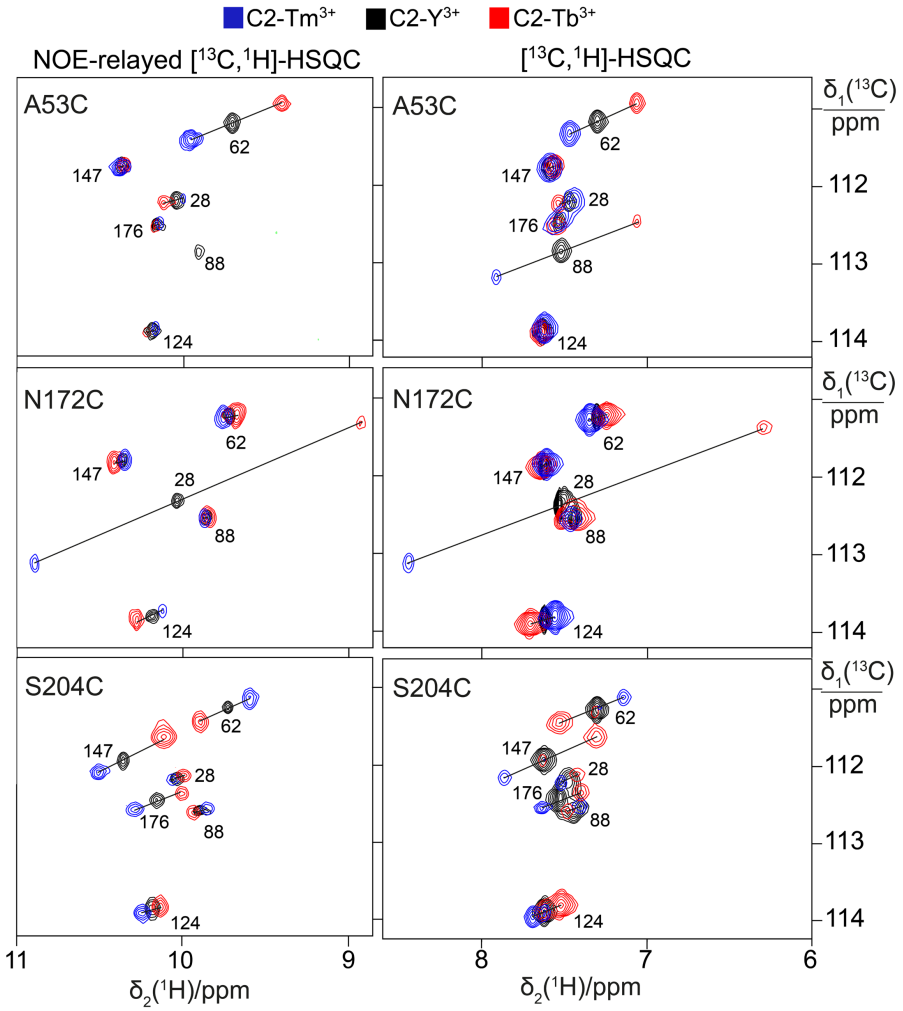
Tb^{3+}



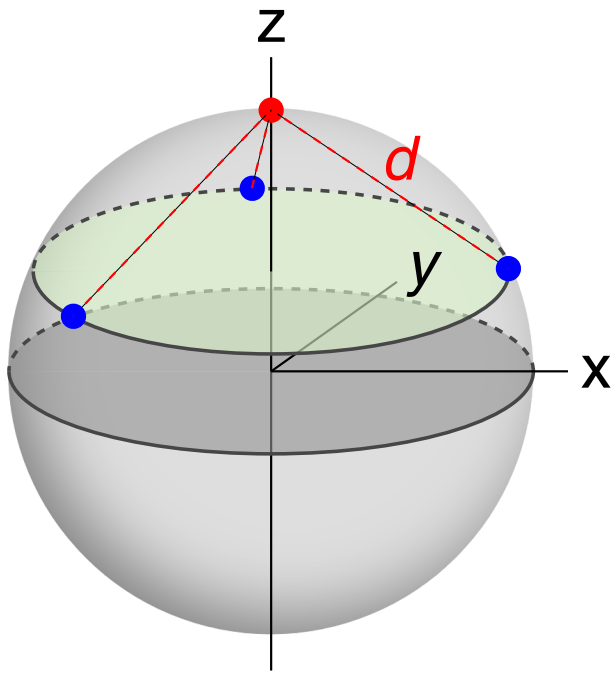


Magn. Reson. 2022, 3, 1-13



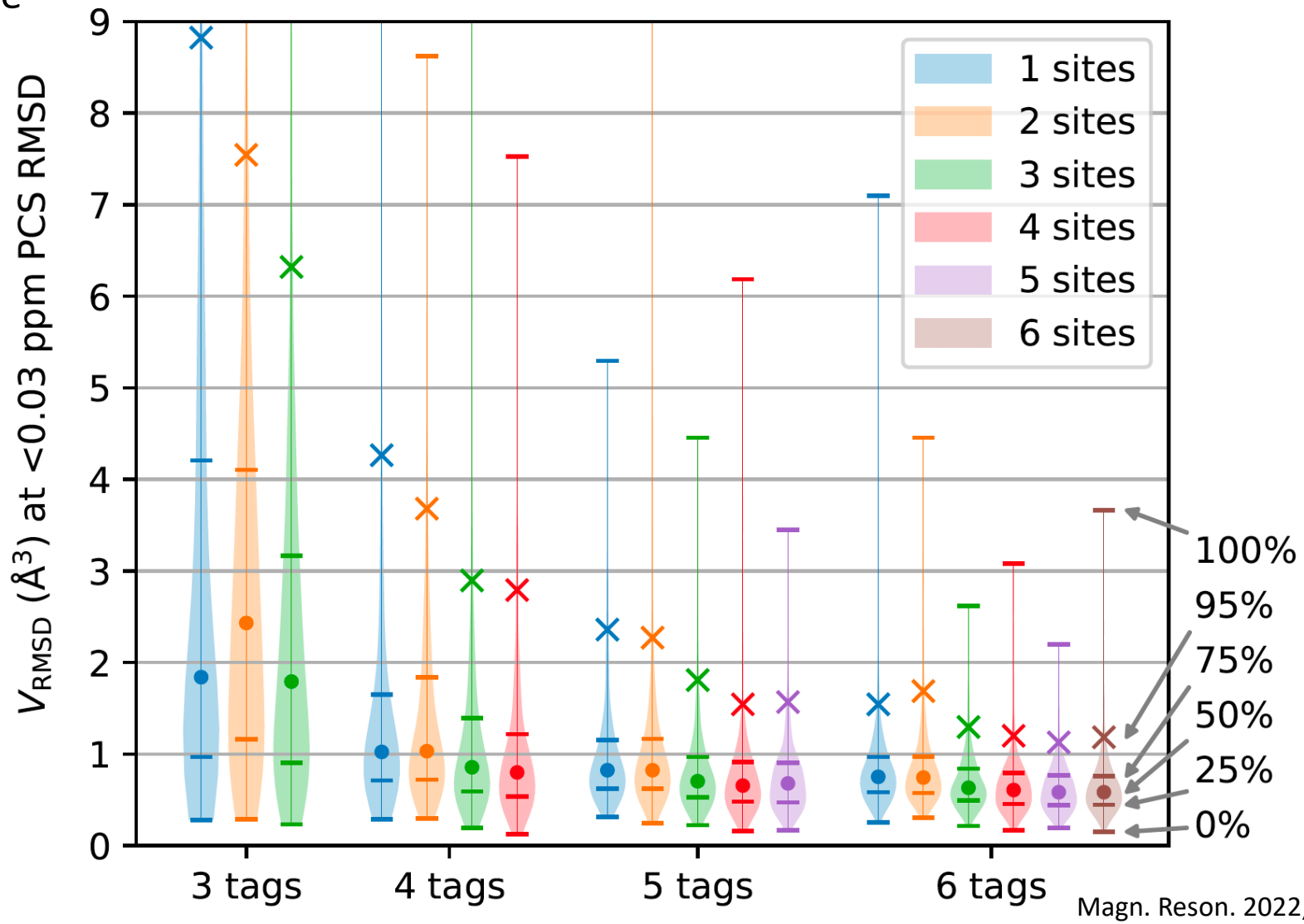


Magn. Reson. 2022, 3, 1-13

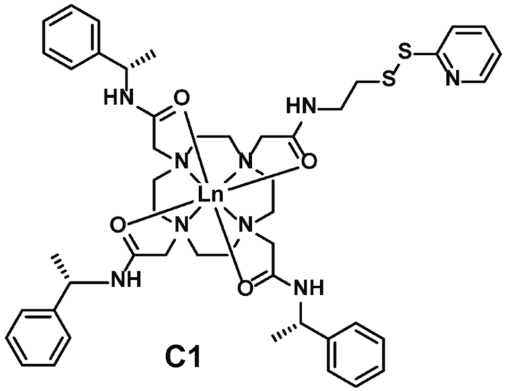


Magn. Reson. 2022, 3, 65-76

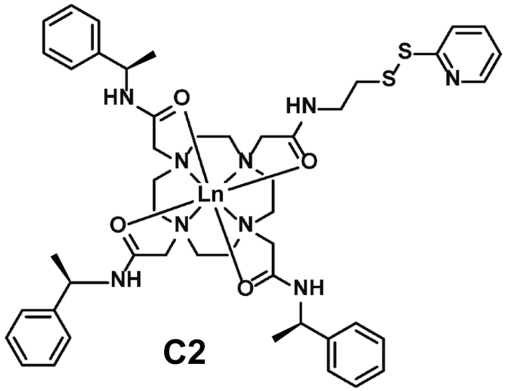
localisation space



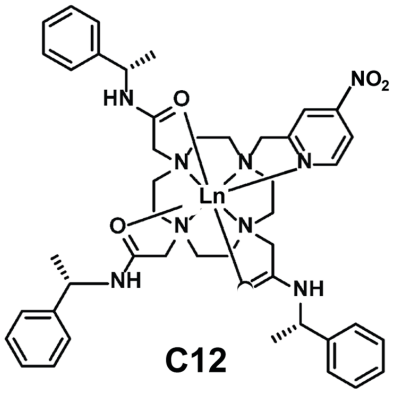
Magn. Reson. 2022, 3, 65-76



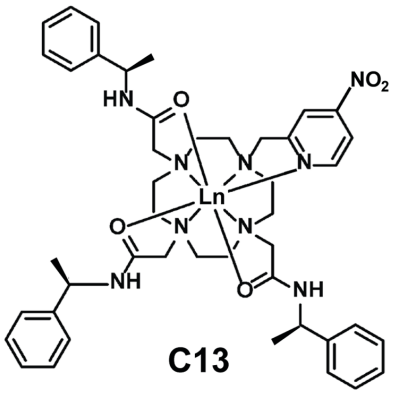
C1



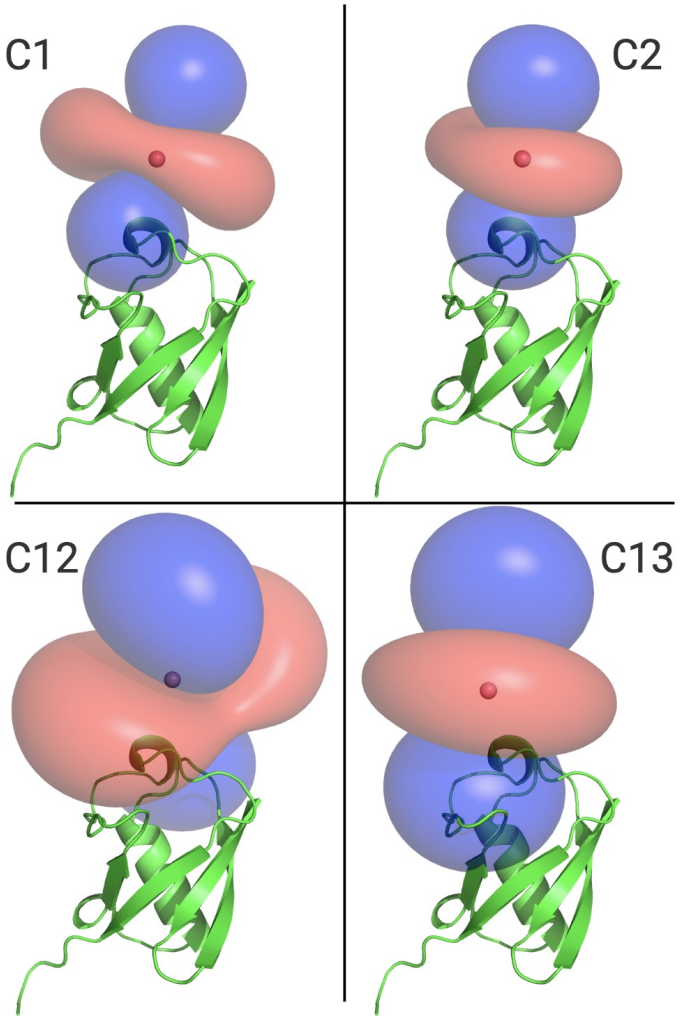
C2



C12

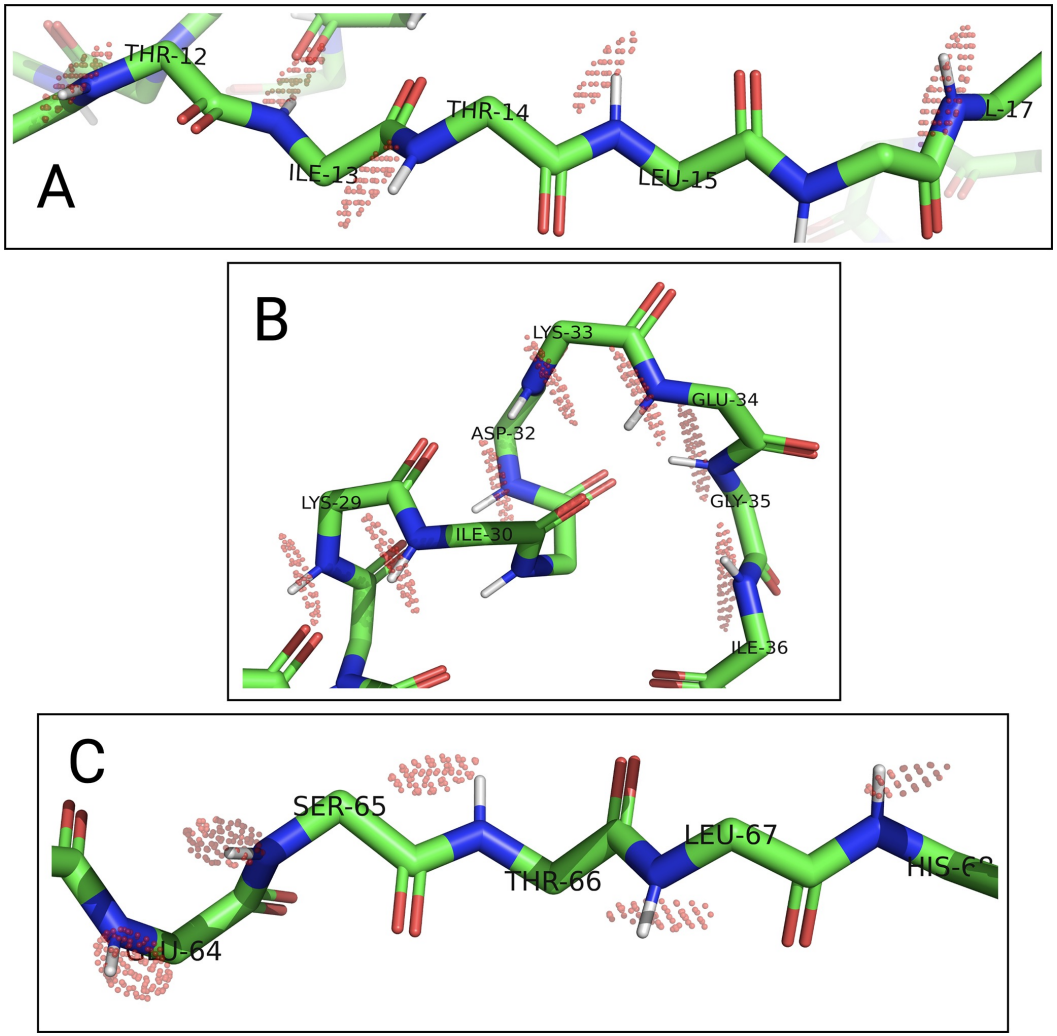


C13



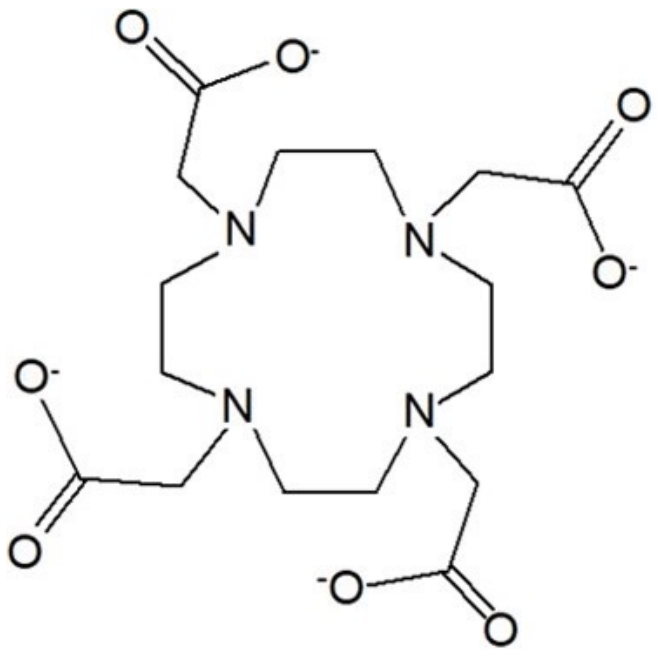
Magn. Reson. 2022, 3, 65-76

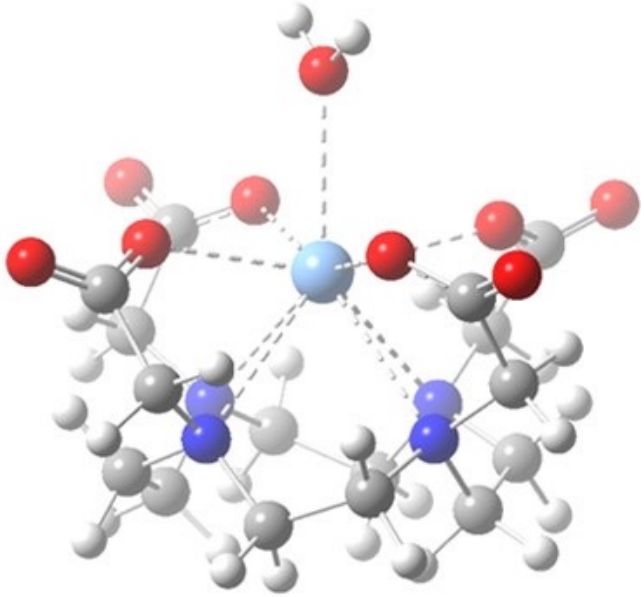
localisation space: ubiquitin S57C



Magn. Reson. 2022, 3, 65-76

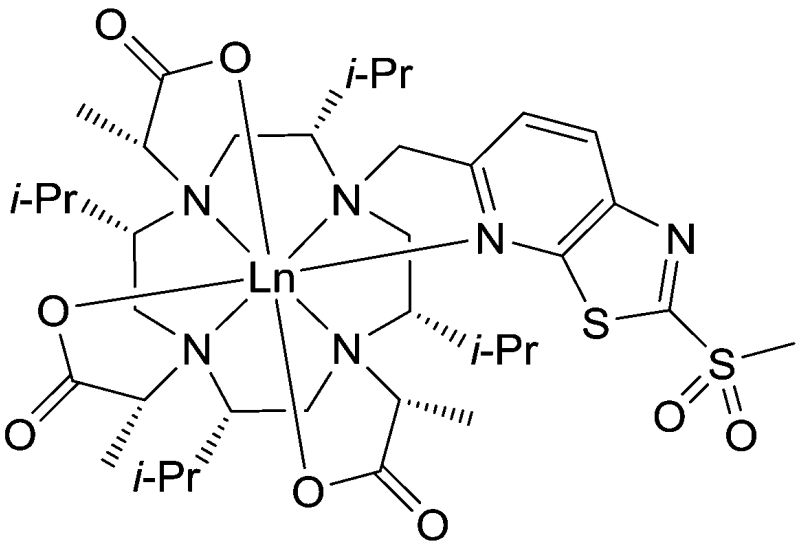
DOTA





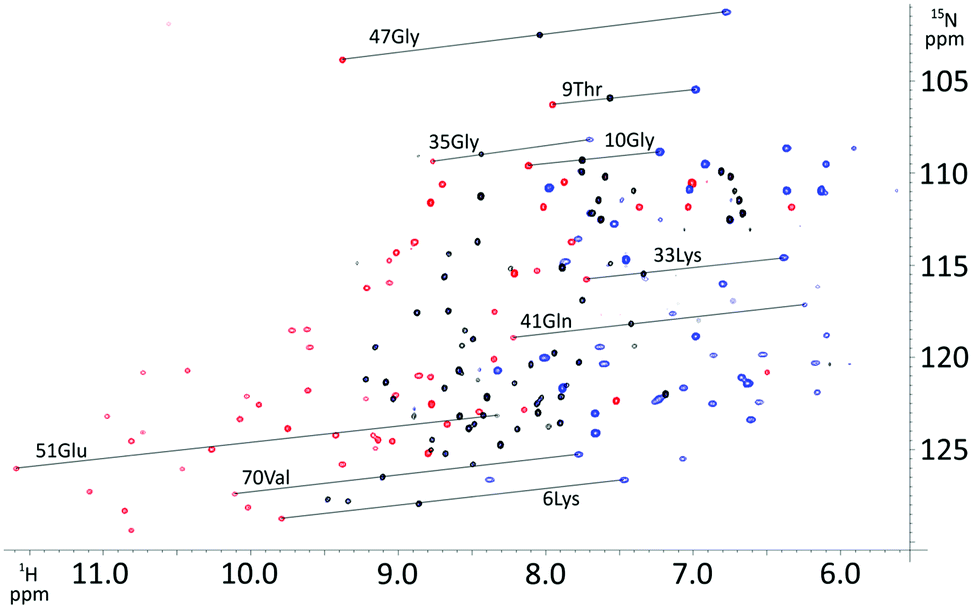
ACS Omega 2021, 6, 13321-13330

P4T-DOTA



ubiquitin S57C

Tm^{3+} Lu^{3+} Dy^{3+}



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

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

Q = 0.045

Joss & Häussinger, Chem. Commun. 2019, 55, 10543-10546

quality factor

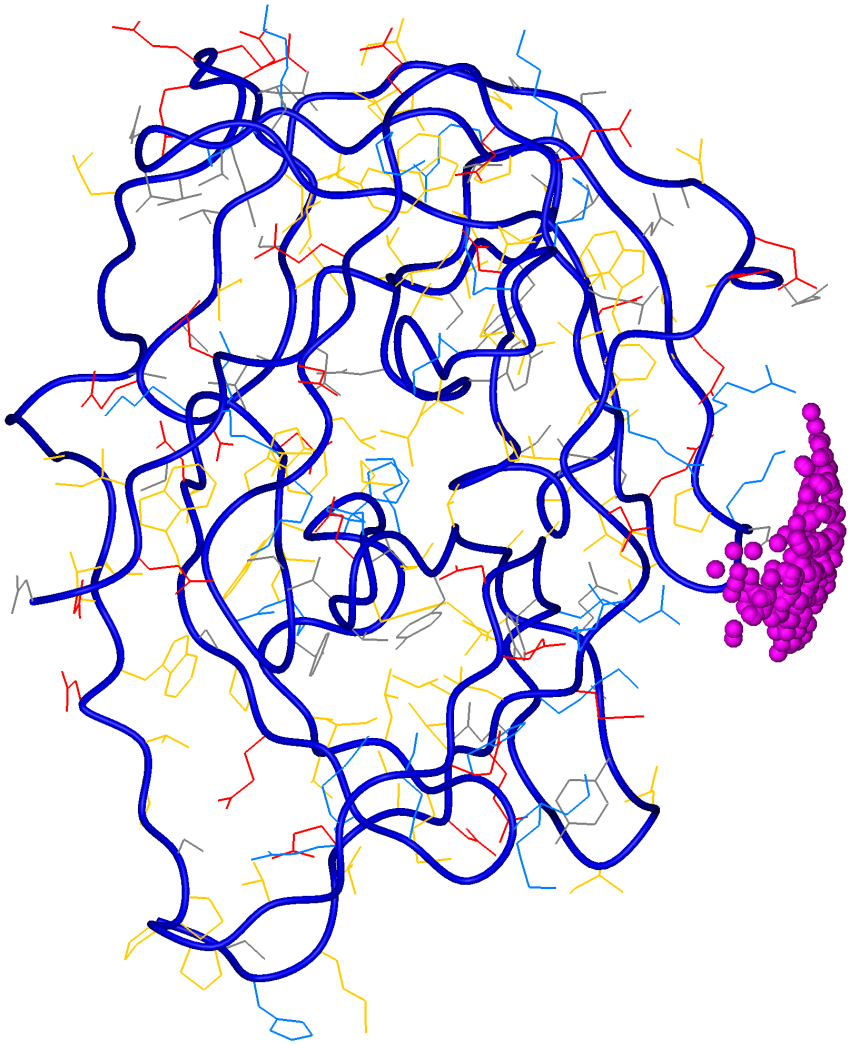
Paramagpy

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

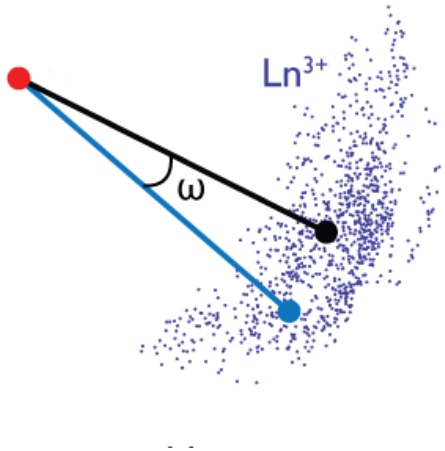
$$Q = \sqrt{\sum_i \frac{(C_i - E_i)^2}{(E_i)^2}}$$

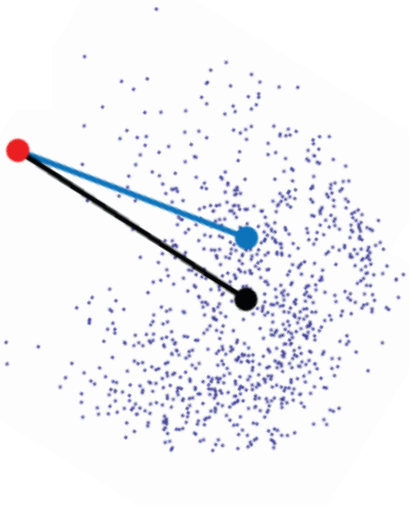
Orton et al., Magn. Reson. 2020, 1, 1-12

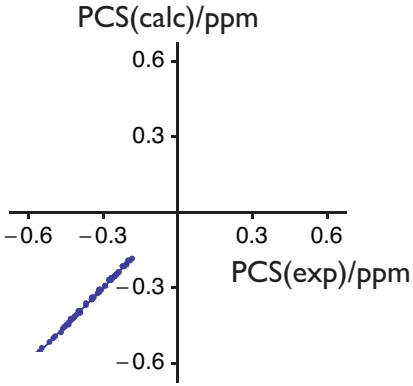
most tags are mobile

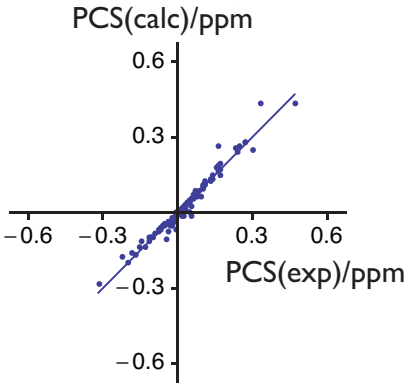


effective $\Delta\chi$ tensor



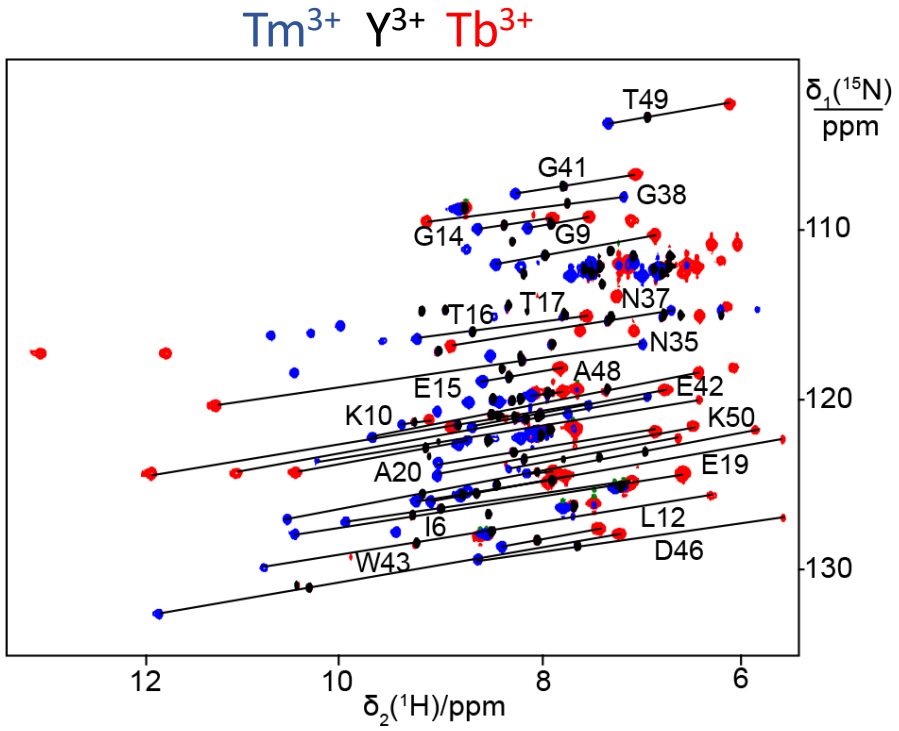


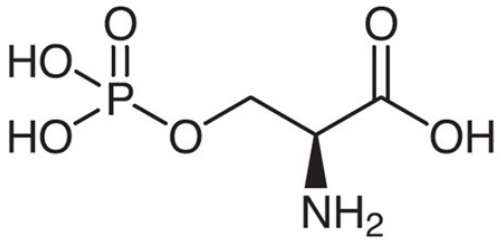


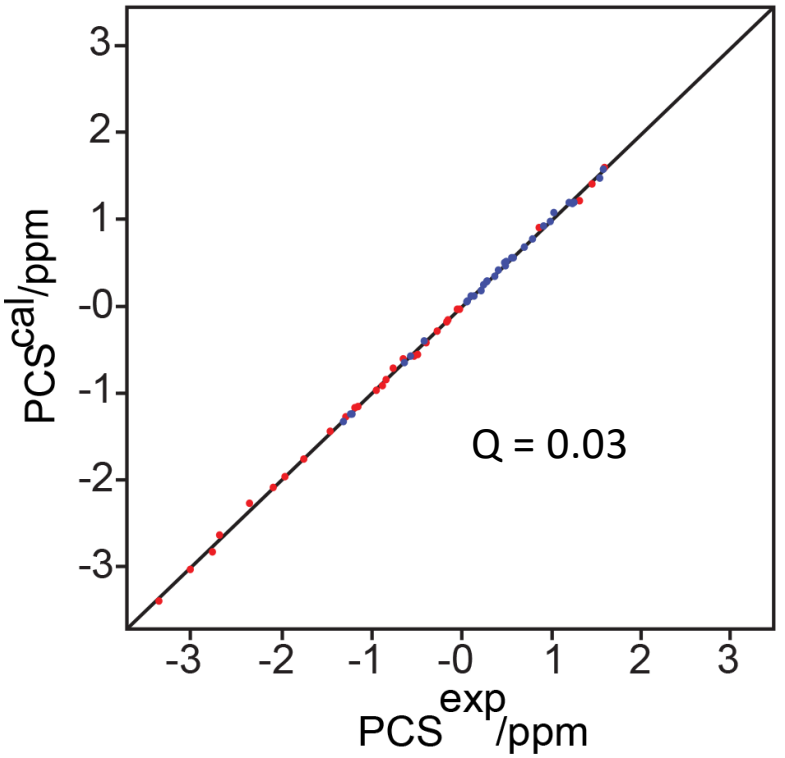


D. Shishmarev, PhD ANU 2014

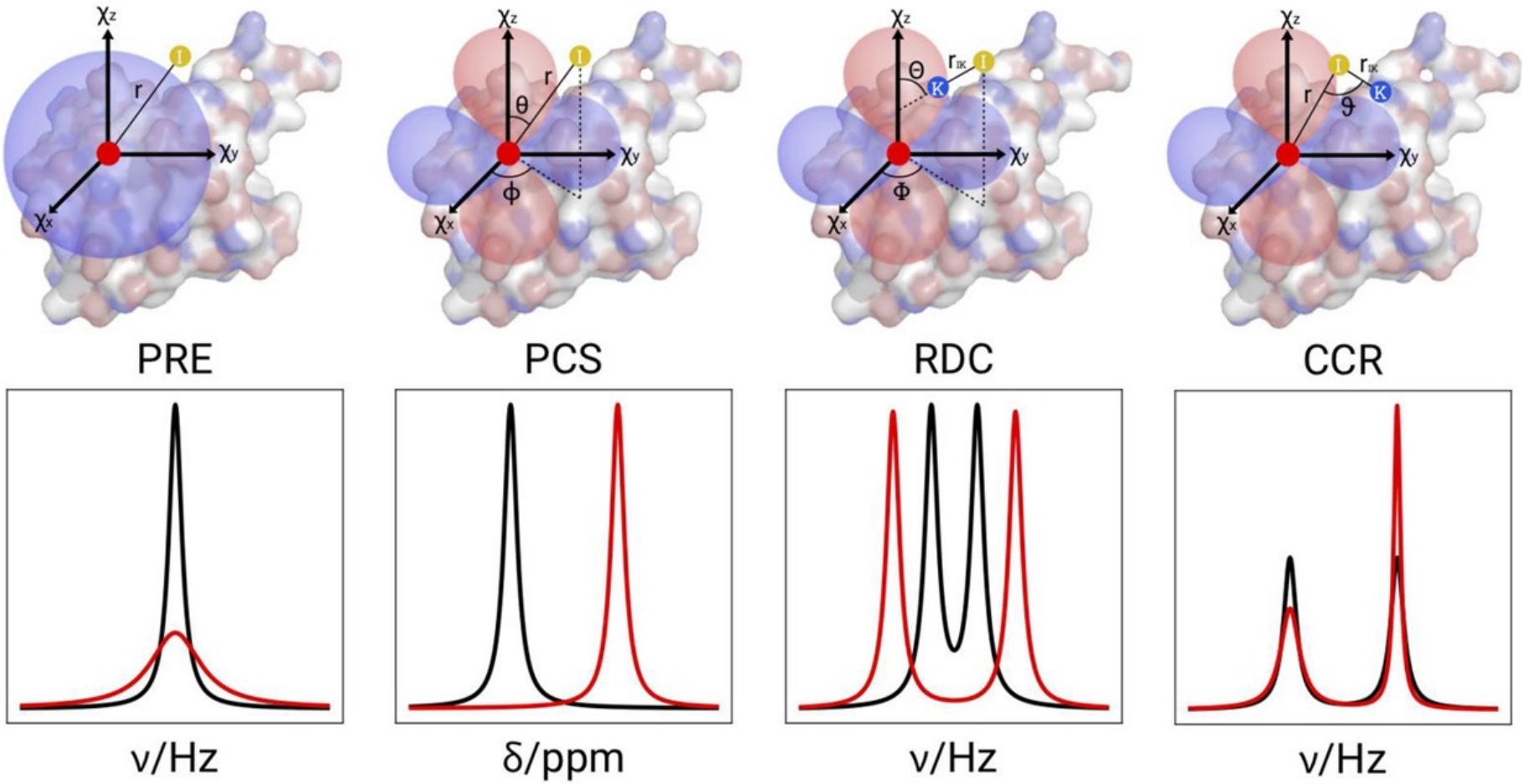
GB1 A24Sep/K28Sep







Magn. Reson. 2021, 2, 1-13



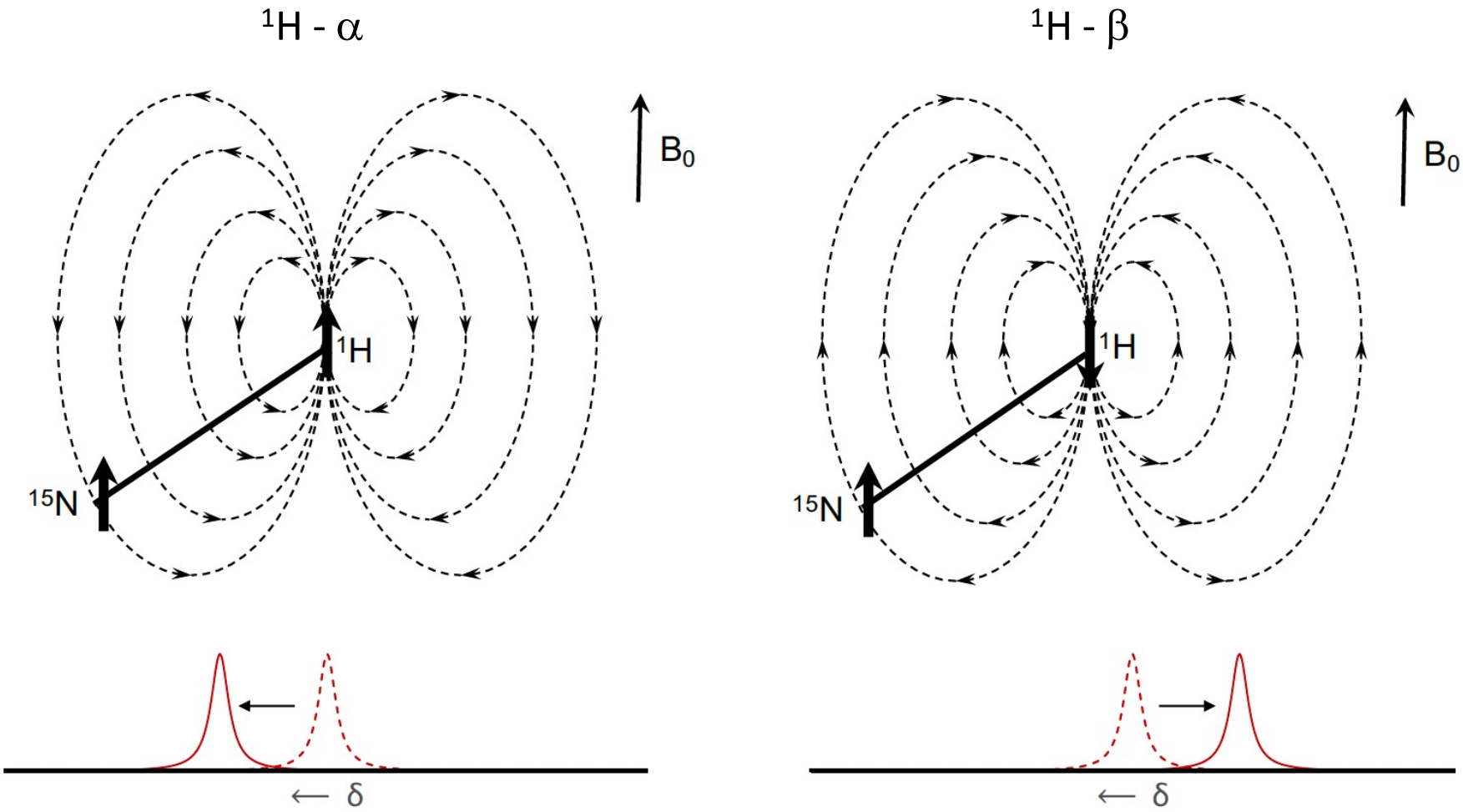
Chem. Rev. 2022, 122, 9571-9642

residual dipolar couplings (RDC)

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

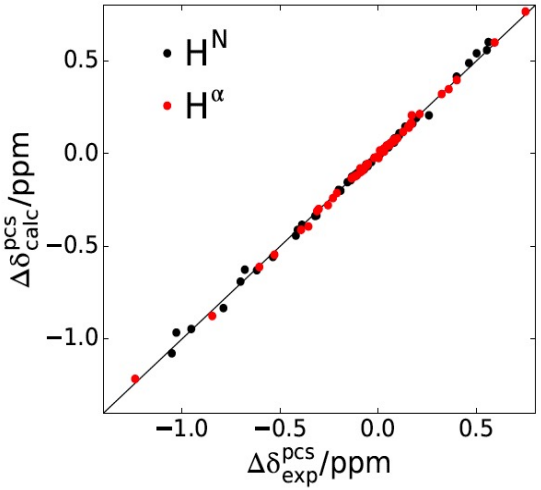
Chem. Rev. 2022, 122, 9571-9642

residual dipolar couplings (RDC)

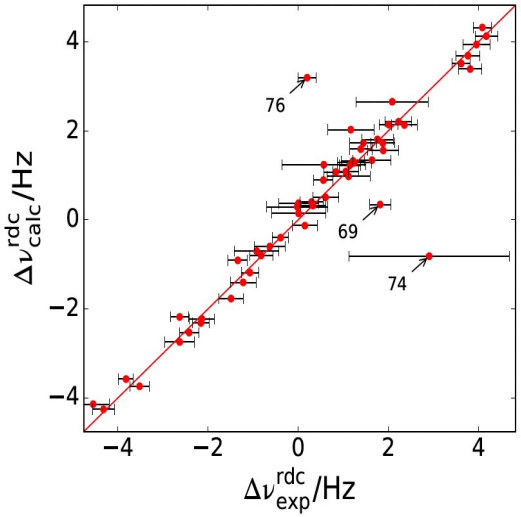


B. G. J. Pearce, Honours thesis ANU 2016

residual dipolar couplings (RDC)



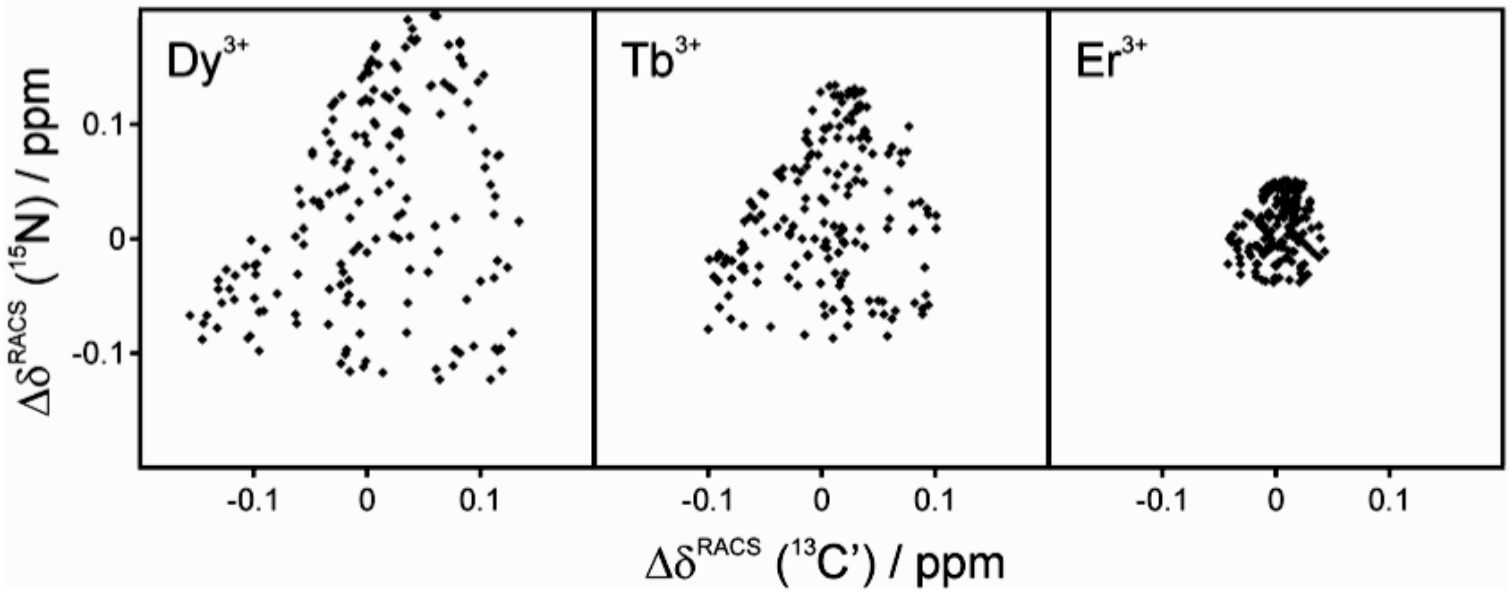
$\Delta\chi_{ax}$ = -9*10^{-32} m^3 Q = 0.06



$\Delta\chi_{ax}$ = -6*10^{-32} m^3 Q = 0.11

B. G. J. Pearce, Honours thesis ANU 2016

residual anisotropic chemical shifts (RACS)

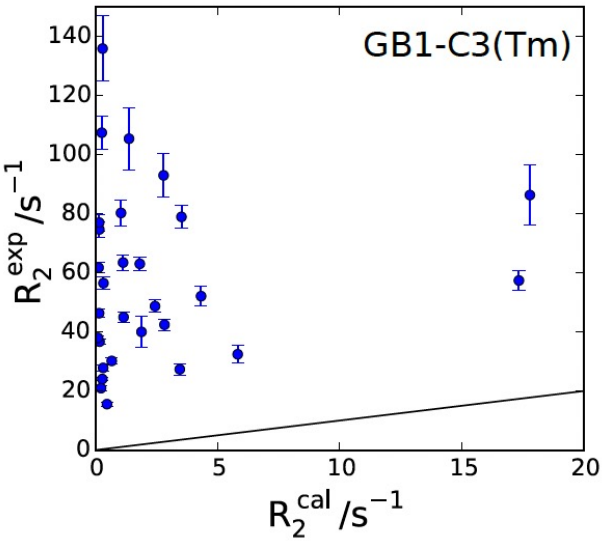


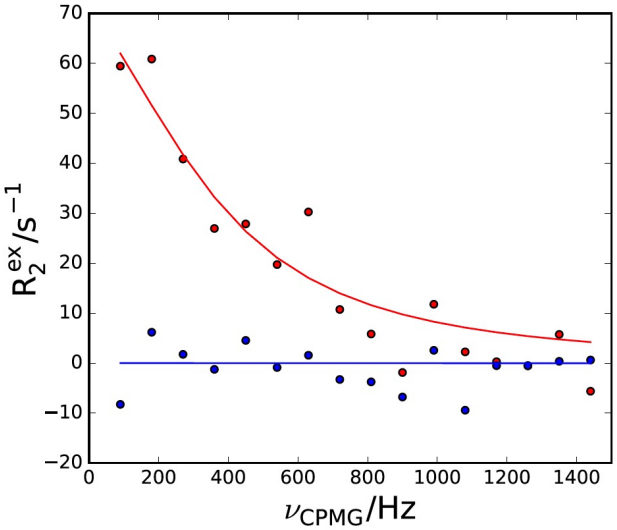
$\Delta\chi_{ax} = 40*10^{-32}$ m^3 $\Delta\chi_{ax} = 27*10^{-32}$ m^3 $\Delta\chi_{ax} = -10*10^{-32}$ m^3

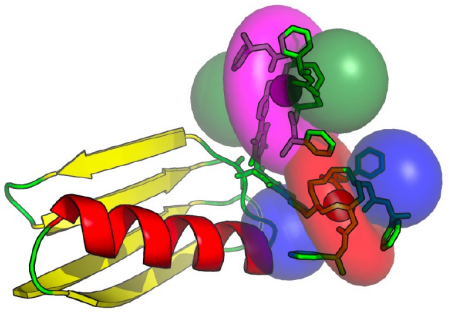
$$\Delta\delta^{\mathrm{RACS}} = \frac{B_0^{\,2}}{15\mu_0 kT}\sum_{ij}\delta_{ii}^{\mathrm{CSA}}\cos^2\theta_{ij}\Delta\chi_{jj}$$

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

measuring PREs with metals that generate PCSs





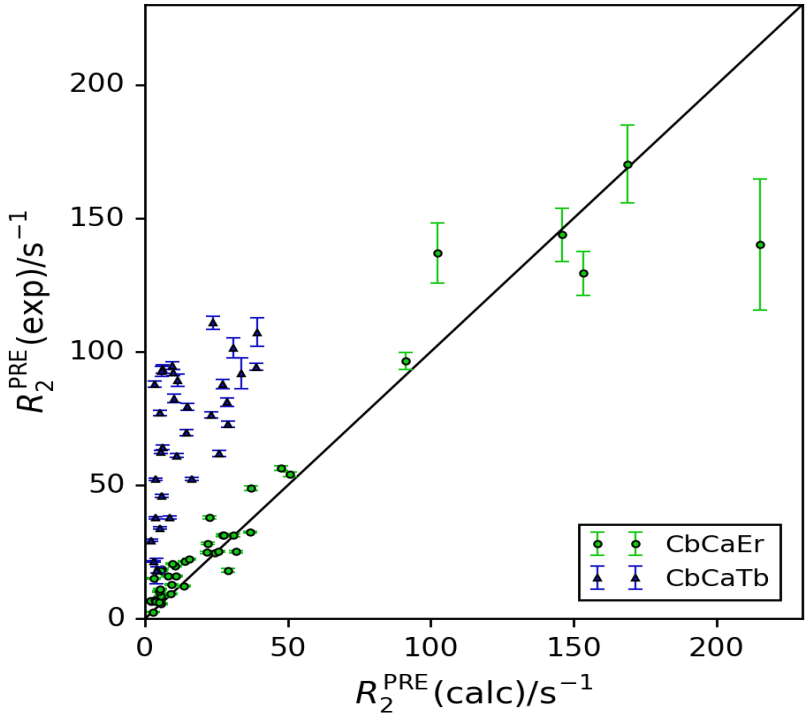


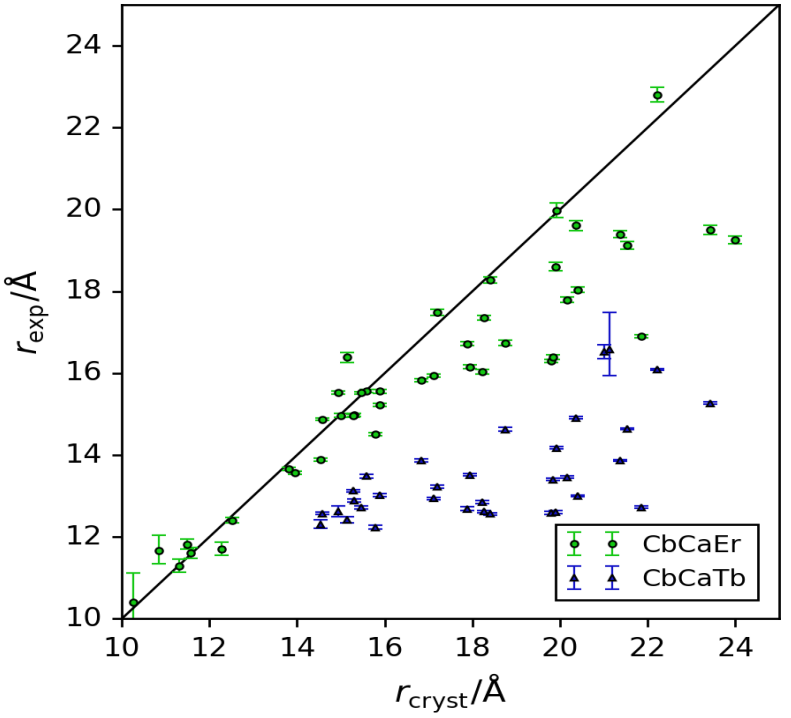
$$R_2^{\text{Curie}} = \frac{1}{45}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\omega_I^2 g_e^4 \mu_B^4 S^2(S+1)^2}{(k_B T)^2 r_{IS}^6}\left(4\tau_r + \frac{3\tau_r}{1+\omega_I^2\tau_r^2}\right)$$

$$\omega_I^2(\Delta\sigma_I^{DSA})^2$$

H. W. Orton, Honours thesis ANU 2016

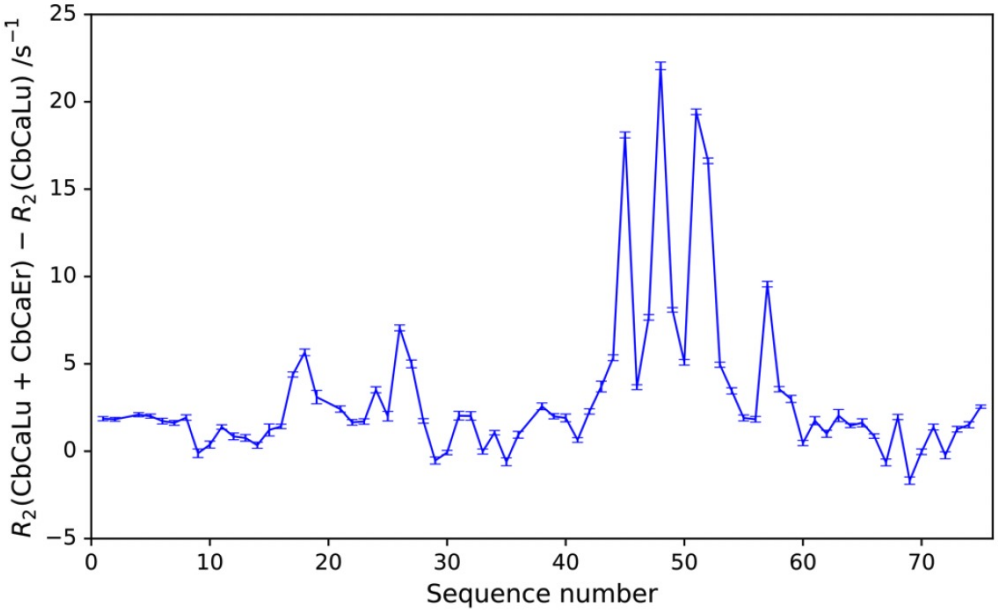
distances from ^{1}H PREs

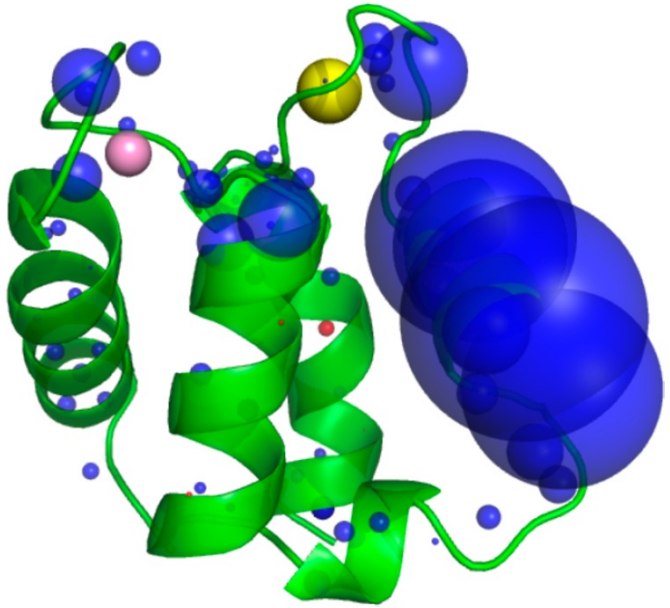




J. Am. Chem. Soc. 2018, 140, 7688−7697

distances from ^{1}H PREs

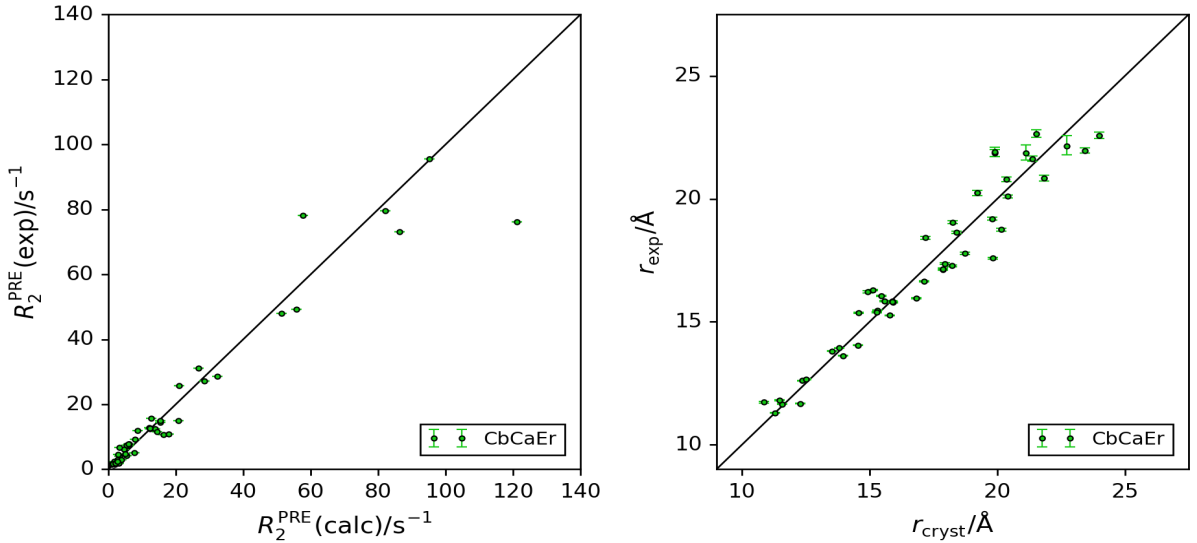




2.5 mM CbCaLu + 2.5 mM CbCaEr

J. Am. Chem. Soc. 2018, 140, 7688−7697

distances from ^{1}H PREs

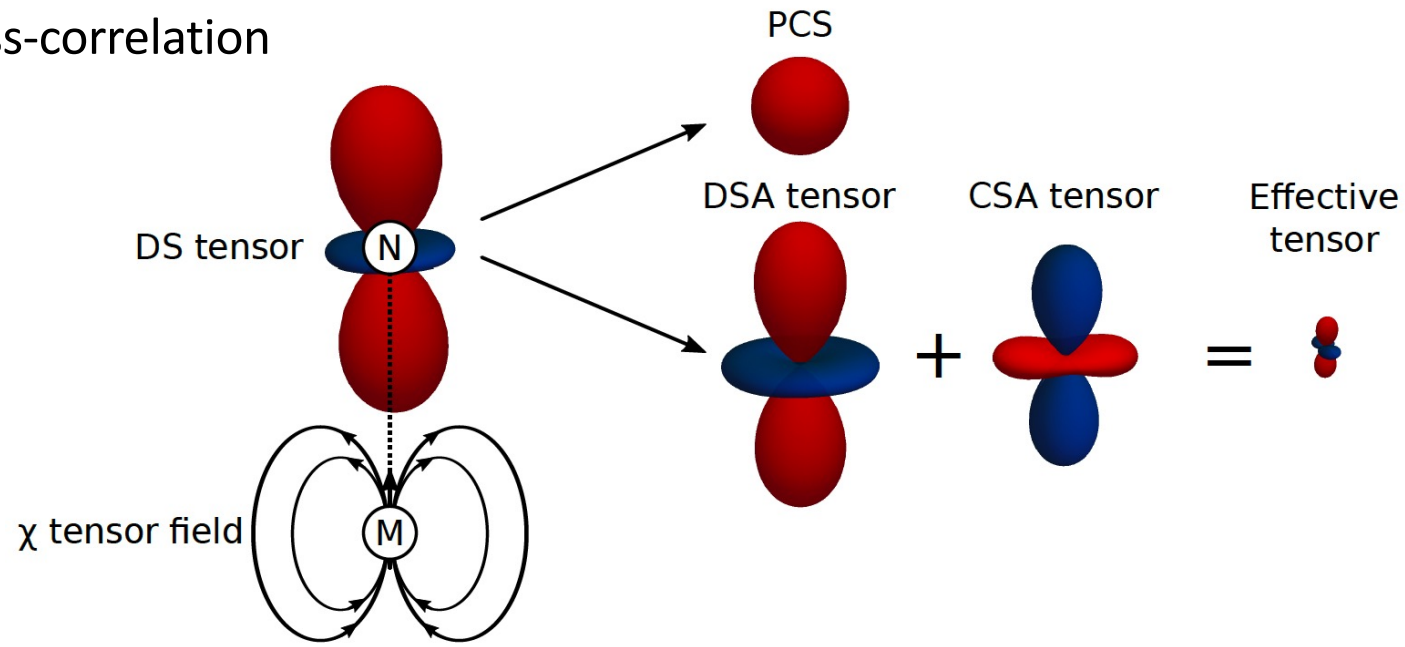


- Use Er^{3+}
- Short relaxation delays <10 ms
- Low field (600 MHz)
- Internal diamagnetic reference
- Measure R_2(^{1}H) in HNCO

J. Am. Chem. Soc. 2018, 140, 7688−7697

relaxation can be slower in a paramagnetic sample

DSA-CSA cross-correlation



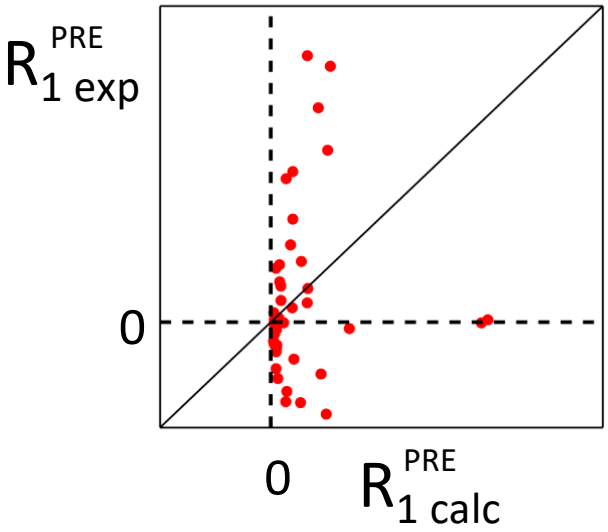
$$R_1^{\mathrm{DSA}} = \frac{1}{4\pi}\xi_{\mathrm{DSA}}^2\left(\frac{\tau_c}{1+(\omega_I\tau_c)^2}\right) \qquad R_2^{\mathrm{DSA}} = \frac{1}{24\pi}\xi_{\mathrm{DSA}}^2\left(4\tau_c + \frac{3\cdot\tau_c}{1+(\omega_I\tau_c)^2}\right)$$

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

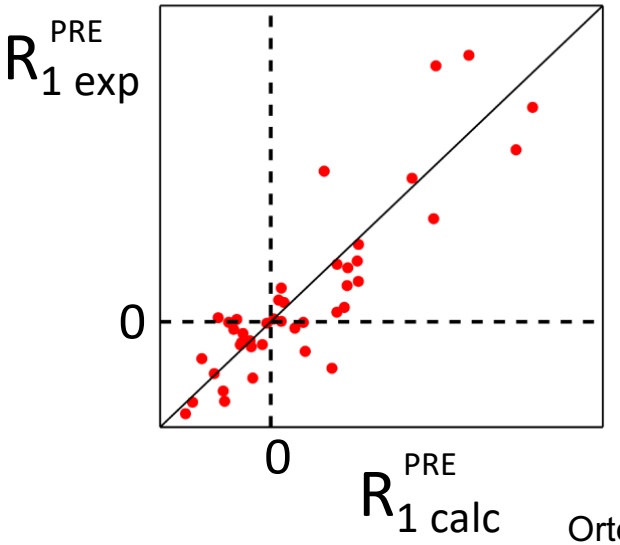
H. W. Orton, Honours thesis ANU 2016

DSA-CSA cross-correlation

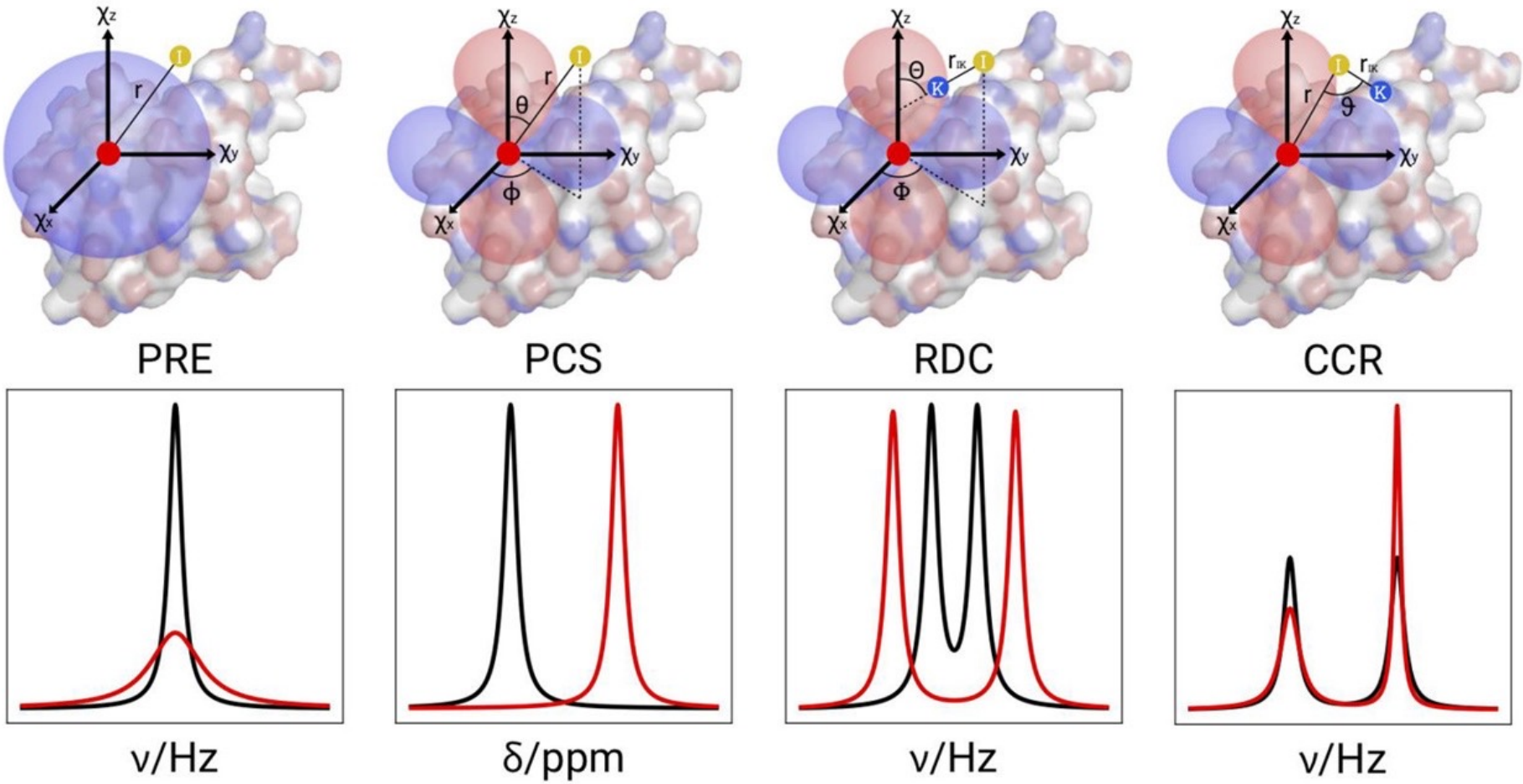
DSA



DSA + CSA

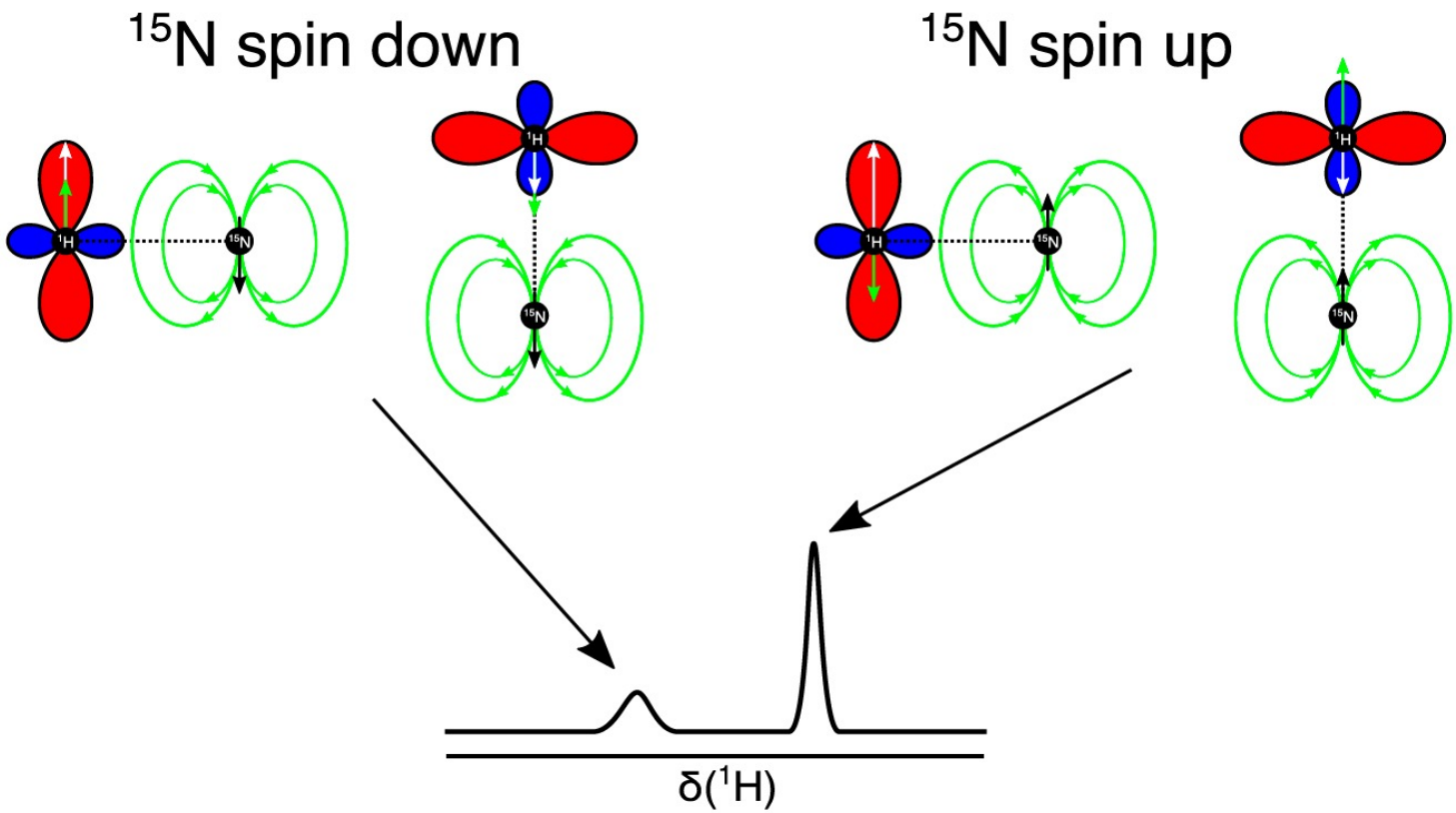


Orton et al., *J. Phys. Chem. Lett*. 2016, 7, 4815-4818



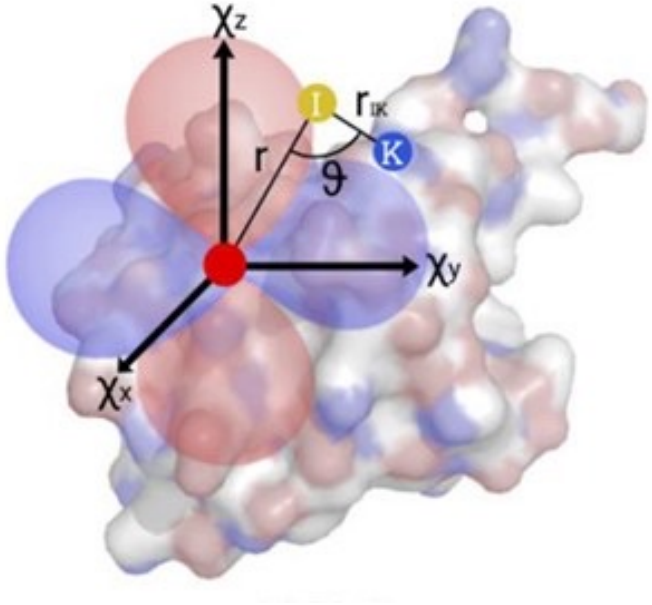
Chem. Rev. 2022, 122, 9571-9642

CCR



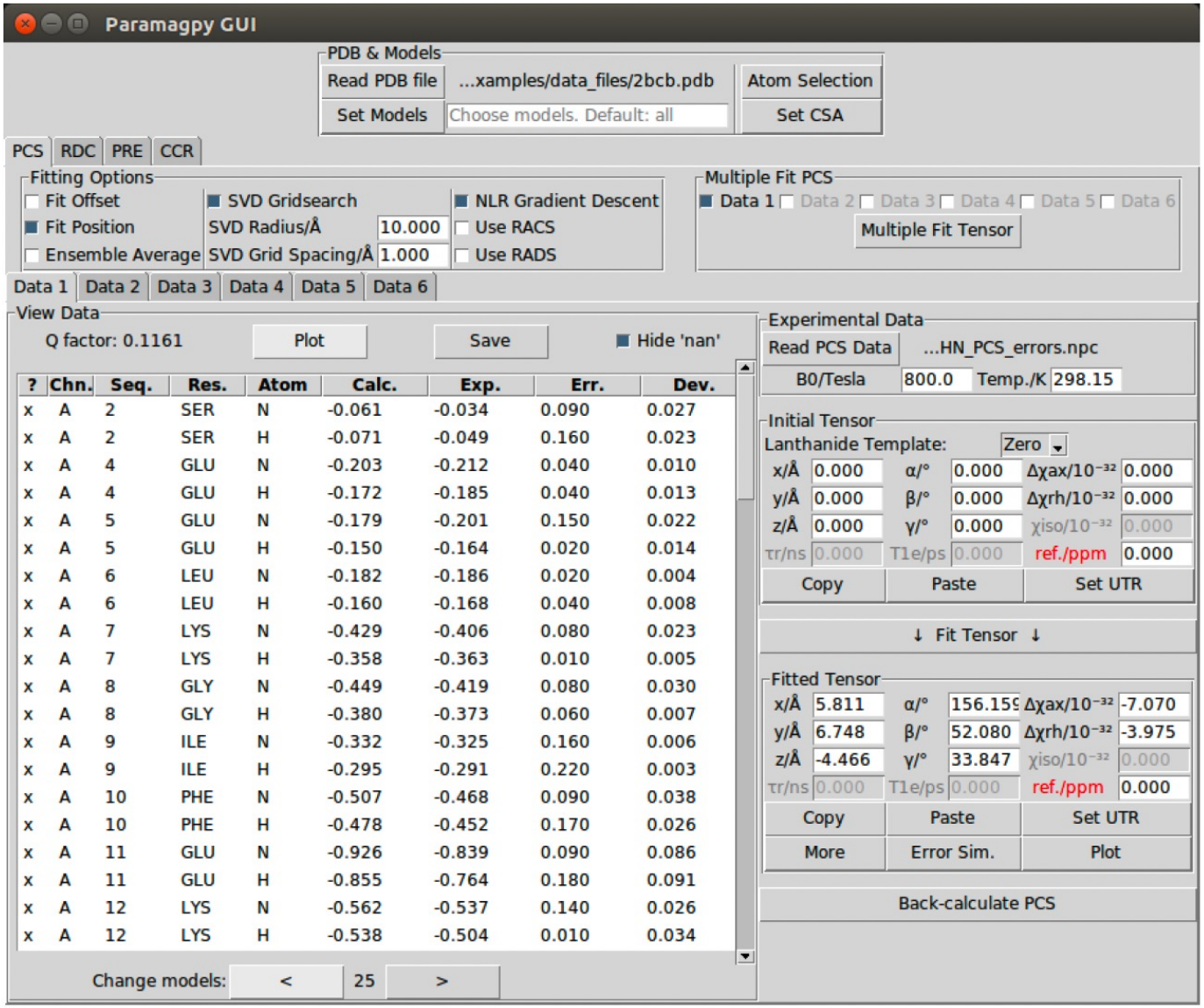
H. W. Orton, PhD ANU 2020

CCR



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

Paramagpy



Magn. Reson. 2020, 1, 1-12

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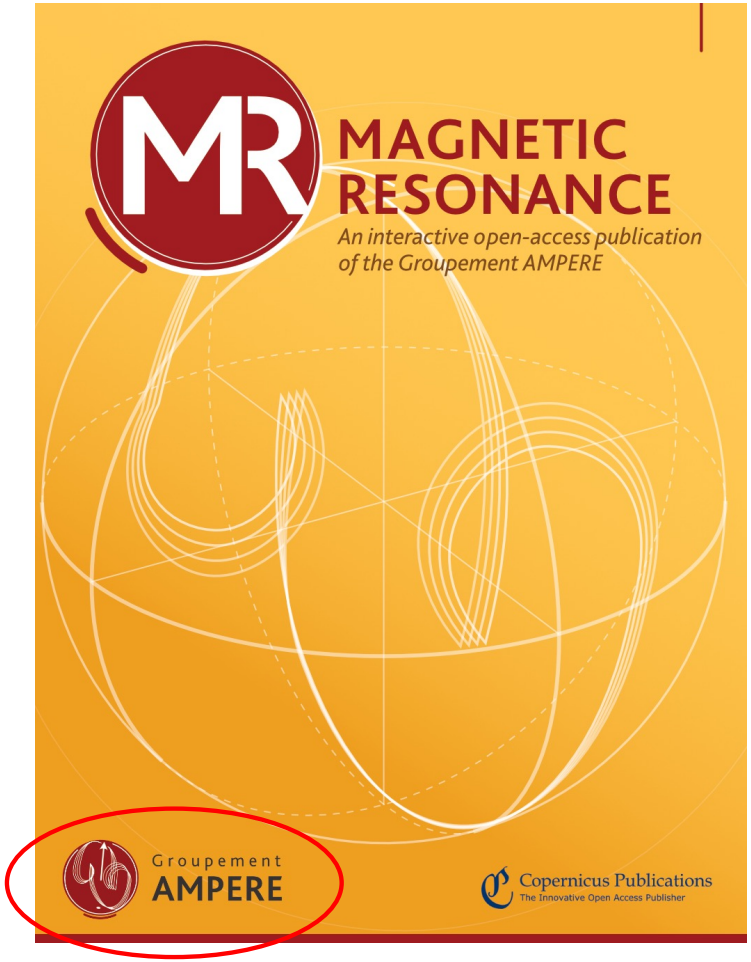

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