

## Supporting Information

### Quadrupole central transition $^{17}\text{O}$ NMR spectroscopy of biological macromolecules in aqueous solution

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#### Theoretical background

If the nuclear quadrupole relaxation dominates, the time evolutions of the density matrix elements,  $\sigma_{ij}$ , that are associated with single-quantum coherences (related to the transverse magnetization) and populations (related to the longitudinal magnetization) are determined by the following differential equations:

$$\frac{d}{dt} \begin{pmatrix} \sigma_{12}(t) \\ \sigma_{23}(t) \\ \sigma_{34}(t) \\ \sigma_{45}(t) \\ \sigma_{56}(t) \end{pmatrix} = -R^{(2)} \begin{pmatrix} \sigma_{12}(t) \\ \sigma_{23}(t) \\ \sigma_{34}(t) \\ \sigma_{45}(t) \\ \sigma_{56}(t) \end{pmatrix} \quad (\text{Eq. S1})$$

and

$$\frac{d}{dt} \begin{pmatrix} \Delta\sigma_{11}(t) \\ \Delta\sigma_{22}(t) \\ \Delta\sigma_{33}(t) \\ \Delta\sigma_{44}(t) \\ \Delta\sigma_{55}(t) \\ \Delta\sigma_{66}(t) \end{pmatrix} = -R^{(1)} \begin{pmatrix} \Delta\sigma_{11}(t) \\ \Delta\sigma_{22}(t) \\ \Delta\sigma_{33}(t) \\ \Delta\sigma_{44}(t) \\ \Delta\sigma_{55}(t) \\ \Delta\sigma_{66}(t) \end{pmatrix} \quad (\text{Eq. S2})$$

where  $\Delta\sigma_{ii}(t) = \sigma_{ii}(t) - \sigma_{ii}^{\text{eq}}$ ,  $R^{(2)}$  and  $R^{(1)}$  are known as the transverse and longitudinal Redfield relaxation matrices, respectively. For spin-5/2 nuclei, these matrices take the following forms:

$$R^{(2)} = K \begin{pmatrix} 24J_0 + 48J_1 + 28J_2 & -8\sqrt{10}J_1 & -12\sqrt{5}J_2 & 0 & 0 \\ -8\sqrt{10}J_1 & 6J_0 + 36J_1 + 46J_2 & 0 & -36J_2 & 0 \\ -12\sqrt{5}J_2 & 0 & 16J_1 + 56J_2 & 0 & -12\sqrt{5}J_2 \\ 0 & -36J_2 & 0 & 6J_0 + 36J_1 + 46J_2 & -8\sqrt{10}J_1 \\ 0 & 0 & -12\sqrt{5}J_2 & -8\sqrt{10}J_1 & 24J_0 + 48J_1 + 28J_2 \end{pmatrix} \quad (\text{Eq. S3})$$

and

$$R^{(1)} = K \begin{pmatrix} 40J_1 + 20J_2 & -40J_1 & -20J_2 & 0 & 0 & 0 \\ -40J_1 & 56J_1 + 36J_2 & -16J_1 & -36J_2 & 0 & 0 \\ -20J_2 & -16J_1 & 16J_1 + 56J_2 & 0 & -36J_2 & 0 \\ 0 & -36J_2 & 0 & 16J_1 + 56J_2 & -16J_1 & -20J_2 \\ 0 & 0 & -36J_1 & -16J_1 & 56J_1 + 36J_2 & -40J_1 \\ 0 & 0 & 0 & -20J_2 & -40J_1 & 40J_1 + 20J_2 \end{pmatrix} \quad (\text{Eq. S4})$$

where

$$K = \frac{3\pi^2}{1000} P_Q^2 \quad (\text{Eq. S5})$$

and the normalized spectral density functions,  $J_n$  ( $n = 0, 1, 2$ ), are defined as

$$J_n = \frac{\tau_c}{1 + (n\omega_0\tau_c)^2} \quad (\text{Eq. S6})$$

Table 1S: Experimental  $^{17}\text{O}$  QCT NMR results for OTf-Al- $^{17}\text{O}_4$ oxalate and PK-Mg-ATP- $^{17}\text{O}_4$ oxalate in aqueous solution obtained at three magnetic fields and at 298 K.

System	$B_0/\text{T}$	O atom	QCT signal position (ppm)	QCT signal line width (Hz)
OTf-Al- $^{17}\text{O}_4$ oxalate	21.14	O1	259.5	1098
		O2	251.5	952
		O3	216.0	671
		O4	207.0	732
	14.09	O1	225.5	1058
		O2	222.0	1058
		O3	198.0	814
		O4	186.7	814
	11.74	O1	204.0	1422
		O2	199.0	1422
		O3	182.5	1000
		O4	173.0	1000
PK-Mg-ATP- $^{17}\text{O}_4$ oxalate	21.14	O1	265.0	976
		O2	236.2	854
		O3	223.8	854
		O4	211.0	769
	14.09	O1	226.5	651
		O2	207.0	448
		O3	199.2	448
		O4	187.5	500
	11.74	O1	201.0	948
		O2	187.0	609
		O3	180.5	576
		O4	171.0	609