Electronic supplementary material

for the manuscript

The nature of the nitrite disorder in Na_3ONO_2

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With $\sigma_{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$ and defining $\kappa_{st} = \dfrac{\sigma_{33} - \sigma_{22}}{\sigma_{33} - \sigma_{11}}$, we can define the CSA tensor components of the averaged CSA tensor as

$$\langle \sigma_{11} \rangle = \left(\left(\sigma_{11} - \left(\frac{|\kappa - \kappa_{st}| + (\kappa - \kappa_{st})}{2} \right) \left(\sigma_{11} - \frac{\sigma_{22} + \sigma_{11}}{2} \right) \frac{1}{(1 - \kappa_{st})} \right) - \sigma_{iso} \right) \rho + \sigma_{iso}$$

$$\langle \sigma_{22} \rangle = \left(\left(\frac{\sigma_{33} + \sigma_{22}}{2} - \kappa \left(\frac{\sigma_{33} + \sigma_{22}}{2} - \frac{\sigma_{22} + \sigma_{11}}{2} \right) \right) - \sigma_{iso} \right) \rho + \sigma_{iso}$$

$$\langle \sigma_{33} \rangle = \left(\left(\sigma_{33} - \left(\frac{|\kappa - \kappa_{st}| - (\kappa - \kappa_{st})}{2} \right) \left(\sigma_{33} - \frac{\sigma_{33} + \sigma_{22}}{2} \right) \frac{1}{\kappa_{st}} \right) - \sigma_{iso} \right) \rho + \sigma_{iso}.$$

The parameter κ ($0 \leq \kappa \leq 1$) denotes the symmetry of the averaged CSA tensor, ρ ($0 \leq \rho \leq 1$) is related to the overall width of the tensor. With these definitions we can describe all possible CSA tensors for the nitrite ions.

The static CSA tensor for example is obtained setting $\kappa = \kappa_{st}$ and $\rho = 1$, $\langle \vec{\boldsymbol{\sigma}} \rangle (\kappa = \kappa_{st}, \rho = 1)$, as can be easily seen from inspection of the above equation.

With $\langle \vec{\boldsymbol{\sigma}} \rangle = \sum_{i=1}^{6} P_i \vec{\boldsymbol{\sigma}}_i$ a possible order model consistent with the above definition for the averaged CSA-tensor is given by the occupancies

$$P_1 = \frac{1-\rho}{6} + \left(1 - \left(\frac{|\kappa - \kappa_{st}| - (\kappa - \kappa_{st})}{4\kappa_{st}}\right) - \left(\frac{|\kappa - \kappa_{st}| + (\kappa - \kappa_{st})}{4(1-\kappa_{st})}\right)\right)\rho$$

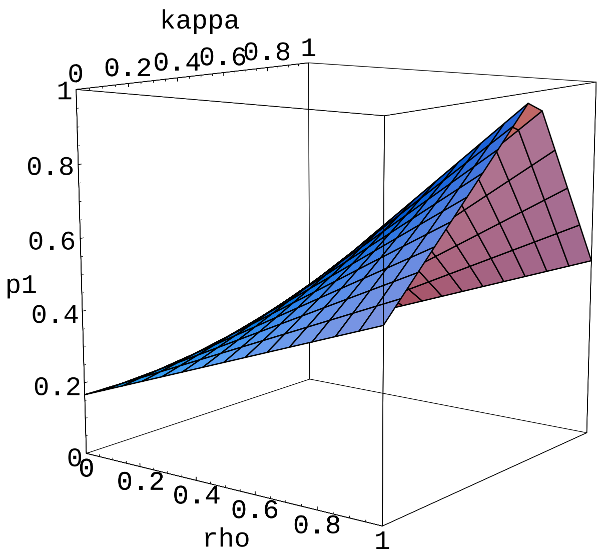
$$P_5 = \frac{1-\rho}{6} + \left(\frac{|\kappa - \kappa_{st}| - (\kappa - \kappa_{st})}{4\kappa_{st}}\right)\rho$$

$$P_2 = \frac{1-\rho}{6} + \left(\frac{|\kappa - \kappa_{st}| + (\kappa - \kappa_{st})}{4(1-\kappa_{st})}\right)\rho$$

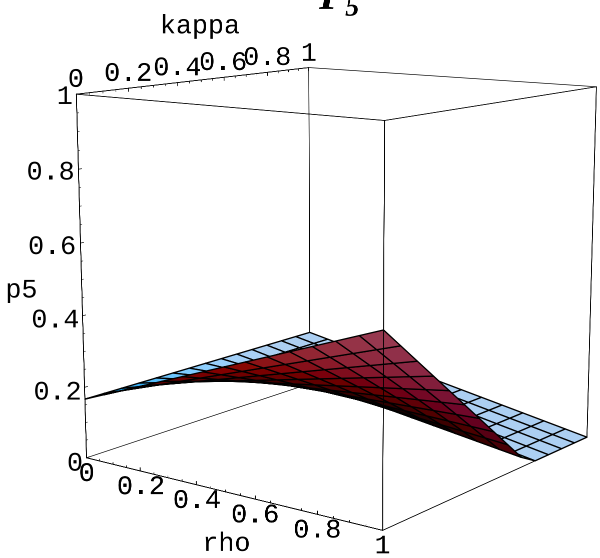
$$P_3 = P_4 = P_6 = \frac{1-\rho}{6}.$$

So we have three different classes of occupancies, $P_1 > P_2 > P_3, P_4, P_5, P_6$ or $P_1 > P_5 > P_3, P_4, P_5, P_2$, depending on the value of κ. The following plots illustrate the dependencies of the occupancies P_i on κ and ρ.

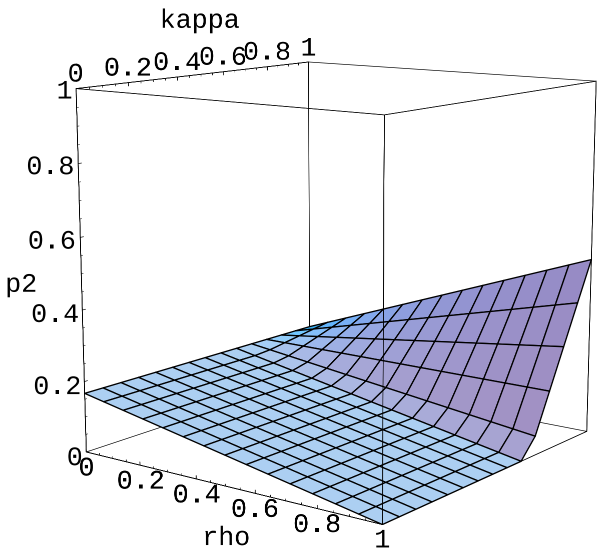
***P*$_1$**



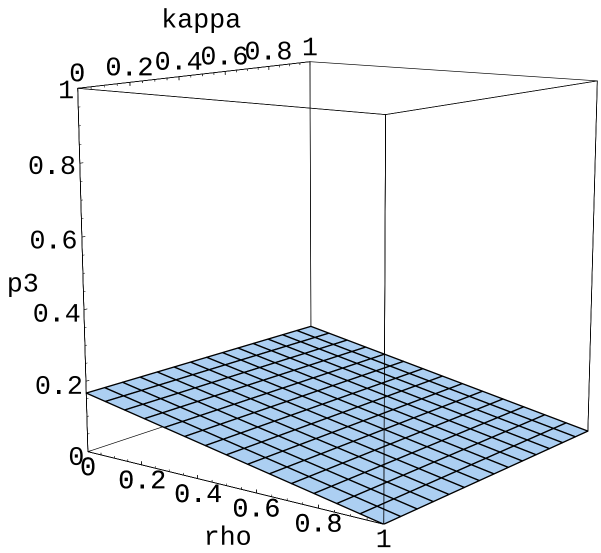
***P*$_5$**



P_2



P_3, P_4, P_6



The simulations of the static ^{15}N-NMR spectra (Fig. 8 of the manuscript) were obtained using the above equations for the occupancies P_i assuming a gaussian distribution for κ and ρ:

$$\kappa = \exp\left(\frac{-(\kappa-\kappa_0)^2 \ln(2)}{\Delta^2\kappa}\right) \quad \text{and} \quad \rho = \exp\left(\frac{-(\rho-\rho_0)^2 \ln(2)}{\Delta^2\rho}\right).$$

The values used in the simulations are given in the following table.

T/K	κ_0	$\Delta\kappa$	ρ_0	$\Delta\rho$
183	0.58	0.22	0.89	0.10
193	0.55	0.20	0.84	0.08
203	0.56	0.22	0.76	0.08
213	0.55	0.24	0.70	0.12
223	0.50	0.24	0.66	0.12
233	0.50	0.18	0.55	0.10
243	0.50	0.25	0.30	0.25
253	0.45	0.10	0.00	0.15