Supplementary information: Prediction of low-field nuclear singlet lifetimes by molecular dynamics and quantum-chemical property surface

Pär Håkansson

School of Chemistry, University of Southampton, SO17 1BJ Southampton, UK, current address: NMR research unit, University of Oulu, P.O. Box 3000, FI–90014 Oulu, Finland

Email: nils.hakansson@oulu.fi

Section **1** provides simulated translational diffusion together with corresponding experimental data. In section **2** The simulation estimate of T1 CSA is given for $^{15}N_2O$ in DMSO. The section **3** expands on the selected internal regions for molecule III.

1.   MD Translation diffusion estimates

The translational diffusion constant is estimated by computing the mean square solvent radial displacement. From the relation:

$$D = \lim_{\tau \to \infty} \frac{\overline{|r(t_0) - r(t_0 + \tau)|^2}}{6\tau} \quad ,$$

where r is the position of center of mass the of the solvent, D is the translational diffusion constant and τ is the displacement time. The diffusion constant is extracted as the slope in the long τ limit. The solvent diffusion constants are listed in table S1, showing good agreement with experiment with largest deviation of ~30% for DMSO solvent.

Table S1: Neat solvent translational diffusion constant from MD (298K) and experiment.

Solvent (sim)	D_{Cal} (μm^2/ms)	D_{exp} (μm^2/ms)	Ref
CH_3OH	2.57	2.42	1
DMSO-h_6	0.95	0.74 (0.83[a])	3, 2
DMSO-d_6	0.87	0.65	3

   a) Measured at 299.2K

1.1   References

(1) Hurle, R. L.; Woolf, L. A. *Aust. J. Chem.* **1980**, 33, 1947–1952.
(2) Packer, K. J.; Tomlinson, D. J. *Trans. Faraday Soc.* **1970**, 586, 1302–1314.
(3) Holz, M; Mao, X.; Seiferling, D.;Sacco, A. *J. Chem. Phys.* **1996**, 669-679.

2. T_1 CSA estimate for $^{15}N_2O$

The chemical shift anisotropy (CSA) relaxation for $^{15}N_2O$ in DMSO is computed from the MD simulation and QC CSA tensors. The anisotropy: ($\Delta\sigma$=357.446ppm, central N) and ($\Delta\sigma$=490.501ppm, terminal N) are computed with DFT (B3PW91/aug-cc-pVDT) and (static) vacuum structure. The $1/T_1$ contribution[4] is computed from:

$$\frac{1}{T_1(CSA)} = \frac{2}{15}(\gamma B_0)^2 (\Delta\sigma)^2 \frac{\tau_c}{1+(\gamma B_0 \tau_c)},$$

where τ_c is the second rank reorientational correlation time (τ_c=5.3 ps, estimated from the MD simulation with DMSO-d_6 and 0.5 M $^{15}N_2O$) at the static field B_0=7.04T. This provides $1/T_1$[CSA]: 6.2 10^{-3} s^{-1} and 3.3 10^{-3} s^{-1} for Central and terminal ^{15}N respectively.

2.1   References

(4) Kowalewski, J.; Mäler, L. Nuclear Spin Relaxation in Liquids: Theory, Experiments, and Applications; Taylor & Francis Group: New York, U.S.A., 2006.

3. Internal region for molecule III

The ratio of integrated time correlation functions (TCFs) for the difference in internal angular velocity and the overall angular velocity for various internal regions are listed in figure S1. In figure S2 the set of studied internal regions are listed. Several combinations give almost the same magnitude. All of the large fluctuating regions listed in figure S1 are various combinations that include the NNO angle bending. Several of the largest fluctuating regions are tested in T_S calculation and give similar result. The region #4 and #2 are associated with central terminal spin ^{15}N respectively and discussed in the main text.
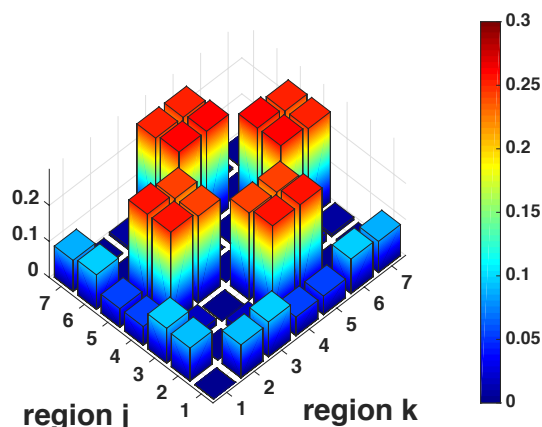

Figure S1: Integrated TCFs [<Δ^3>τ_Δ]/[<ω^3>τ_ω] (notation see main text).

N_j N_j^{k} N_k N_k N_k N_j N_k

N_j N_j

O O O N_j

O

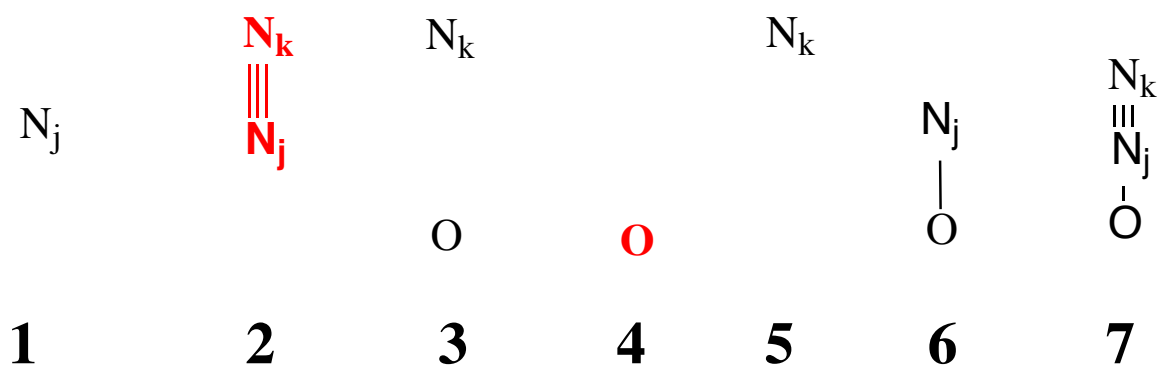1   2   3   4   5   6   7

Figure S2: The explored internal regions for molecule III. The combination of region 4 and 2 are selected for central spin (j) and terminal spin (k) respectively. Chosen regions are 4, and 2 for central (j) and terminal (k) nitrogen respectively.