

## **Proton NMR Relaxation from Molecular Dynamics: Intramolecular and Intermolecular Contributions in Water and Acetonitrile**

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Table S1:  $^1\text{H}$  relaxation results from individual 25 ps water simulations (PBE,NVE,350K)

	$\frac{1}{T_1}$ (Hz)	$\tau_c$ (ps)	$\langle F(0)^2 \rangle (10^9 \text{au}^{-6})$	$\frac{1}{T_1}$ intra(Hz)	$\frac{1}{T_1}$ inter(Hz)
1	0.183	3.883	9.036	0.109	0.074
2	0.234	5.243	9.624	0.131	0.103
3	0.239	5.211	8.823	0.146	0.093
4	0.124	2.696	9.147	0.071	0.053
5	0.232	4.913	9.290	0.147	0.091
6	0.203	4.570	8.815	0.123	0.080
7	0.111	2.400	9.112	0.064	0.047
8	0.221	4.791	8.995	0.131	0.091
9	0.338	7.172	8.942	0.208	0.130
10	0.405	8.835	9.314	0.269	0.173

Table S2:  $^1\text{H}$  relaxation results from individual 25 ps water simulations (PBE,NVT,350K)

	$\frac{1}{T_1}$ (Hz)	$\tau_c$ (ps)	$\langle F(0)^2 \rangle (10^9 \text{au}^{-6})$	$\frac{1}{T_1}$ intra(Hz)	$\frac{1}{T_1}$ inter(Hz)
1	0.159	3.405	8.839	0.101	0.059
2	0.149	3.246	9.089	0.091	0.057
3	0.108	2.374	9.141	0.060	0.047
4	0.138	2.986	9.127	0.086	0.052
5	0.130	2.750	8.995	0.074	0.055
6	0.123	2.723	9.160	0.070	0.053
7	0.124	2.646	8.744	0.077	0.047
8	0.120	2.744	9.126	0.070	0.050
9	0.136	2.968	8.961	0.083	0.053
10	0.113	2.402	9.305	0.066	0.047

Table S3:  $^1\text{H}$  relaxation results from individual 25 ps water simulations (revPBE,NVT,300K)

	$\frac{1}{T_1}$ (Hz)	$\tau_c$ (ps)	$\langle F(0)^2 \rangle (10^9 \text{au}^{-6})$	$\frac{1}{T_1}$ intra(Hz)	$\frac{1}{T_1}$ inter(Hz)
1	0.125	2.571	9.128	0.078	0.046
2	0.117	2.534	9.261	0.070	0.047
3	0.118	2.552	9.054	0.070	0.049
4	0.121	2.729	9.016	0.075	0.047
5	0.109	2.341	8.902	0.067	0.042
6	0.136	2.824	9.033	0.087	0.049
7	0.127	2.696	8.965	0.073	0.054
8	0.109	2.420	8.949	0.065	0.044
9	0.098	2.241	9.116	0.056	0.042
10	0.101	2.201	8.983	0.057	0.044

Table S4:  $^1\text{H}$  relaxation results from individual 20 ps acetonitrile simulations (PBE,NVE,350K)

	$\frac{1}{T_1}$ (Hz)	$\tau_c$ (ps)	$\langle F(0)^2 \rangle (10^9 \text{au}^{-6})$	$\frac{1}{T_1}$ intra(Hz)	$\frac{1}{T_1}$ inter(Hz)
1	0.019	0.637	5.820	0.015	0.004
2	0.015	0.482	5.996	0.010	0.004
3	0.019	0.644	6.032	0.014	0.005
4	0.016	0.541	5.882	0.011	0.005
5	0.016	0.505	5.953	0.012	0.004
6	0.016	0.505	5.906	0.011	0.005
7	0.021	0.719	5.809	0.015	0.006
8	0.017	0.549	6.048	0.013	0.005
9	0.020	0.630	6.075	0.015	0.005
10	0.018	0.573	6.085	0.013	0.004

Table S5:  $^1\text{H}$  relaxation results from sampling varying lengths from acetonitrile FFMD with constant sampling rate (0.5 ps)

	$\frac{1}{T_1}$ (Hz)	$\frac{1}{T_1}$ intra(Hz)	$\frac{1}{T_1}$ inter(Hz)
100 ps	0.029	0.020	0.009
250 ps	0.032	0.022	0.009
1000 ps	0.032	0.022	0.009
2000 ps	0.030	0.021	0.009

Table S6:  $^1\text{H}$  relaxation results from sampling at varying frequencies from acetonitrile FFMD at constant simulation length (250 ps)

	$\frac{1}{T_1}$ (Hz)	$\tau_c$ (ps)	$\langle F(0)^2 \rangle (10^9 \text{ au}^{-6})$	$\frac{1}{T_1 \text{ intra}}$ (Hz)	$\frac{1}{T_1 \text{ inter}}$ (Hz)
0.5 ps	0.032	1.002	6.314	0.022	0.009
1 ps	0.039	1.221	6.300	0.029	0.010
2 ps	0.058	1.898	6.293	0.046	0.012
3 ps	0.080	2.543	6.333	0.066	0.013
4 ps	0.107	3.554	6.266	0.090	0.017

Table S7: Acetonitrile dimer binding energies<sup>a</sup> for two primary dimer structures, calculated at ab initio and FF levels of theory

Dimer	QE PBE	OPLS-AA	MP2 <sup>1</sup>
Cyclic	4.8	5.9	4.5
Linear	3.3	3.1	2.1

<sup>a</sup> Levels of theory used are the same as dynamics in main text. MP2 values are taken from the basis set superposition error corrected results from reference 1. Values are reported in kcal/mol.

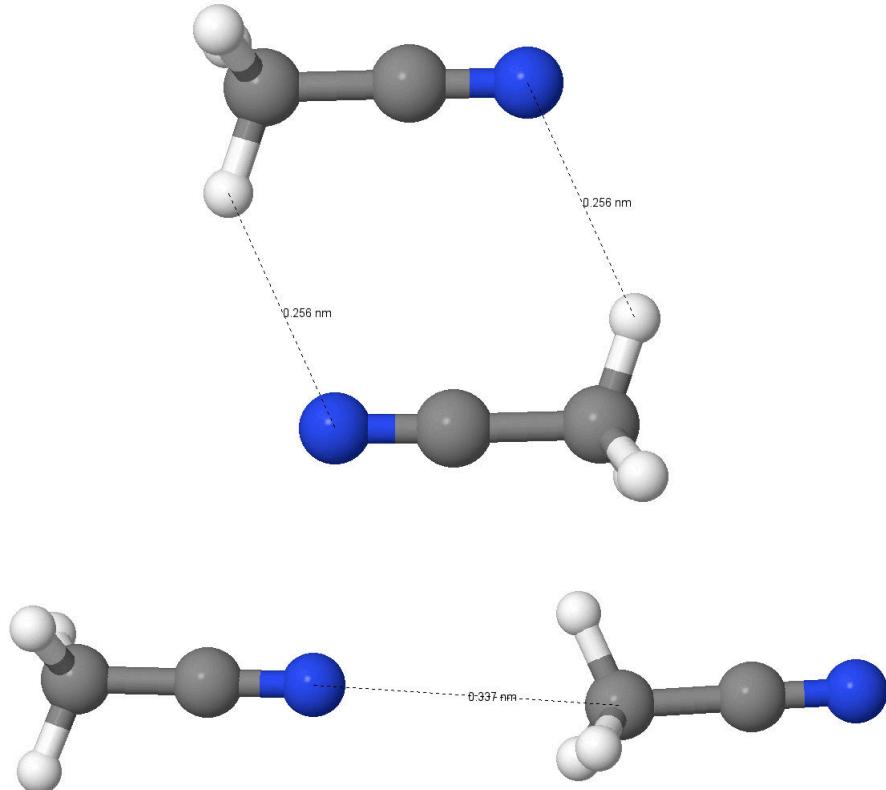


Figure S1: Optimized dimer structures corresponding to data in Table S7. **Top:** Cyclic, **Bottom:** Linear.

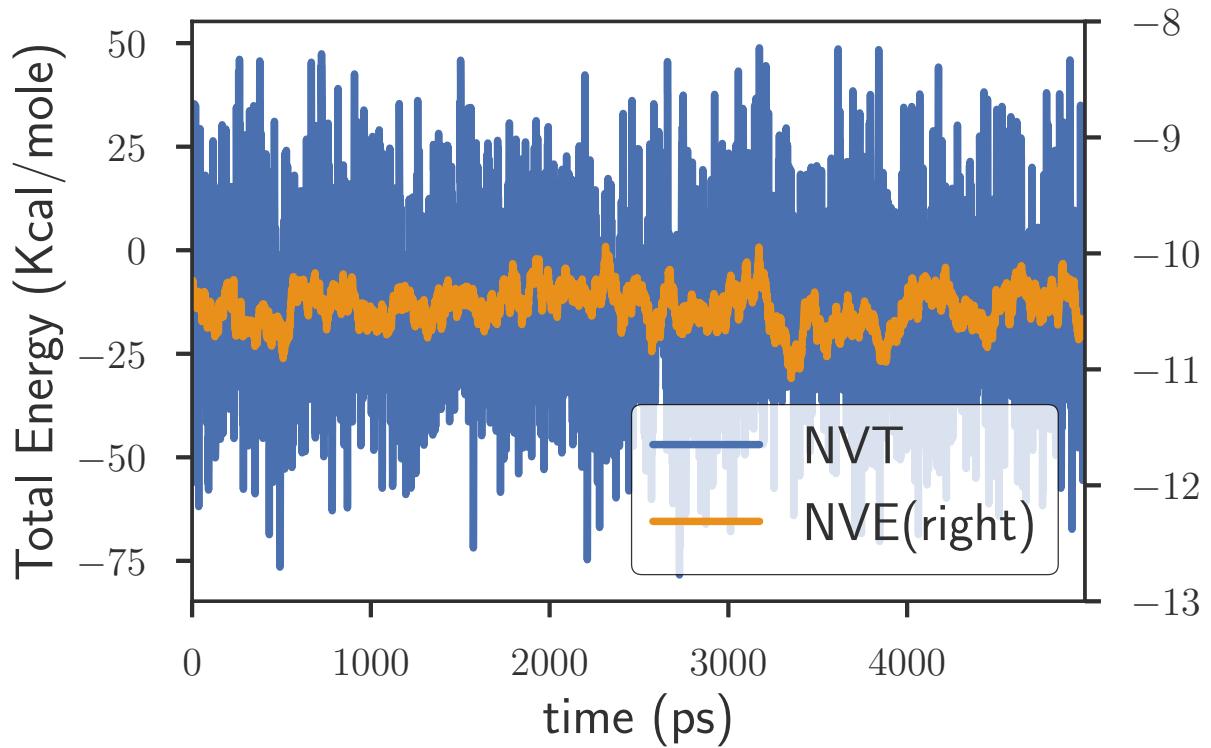


Figure S2: Total Energy plotted for FFMD acetonitrile simulations at 300K in NVE and NVT ensembles

Table S8: Intermolecular  $^1\text{H}$  relaxation results from acetonitrile FFMD (NVE,300K,64 mol.) using increasing cut-off radius for dipole-dipole calculations

$r_{\text{cut}}(\text{au})$	$\frac{1}{T_1 \text{ inter}}(\text{Hz})$	$\langle F(0)^2 \rangle(\text{au}^{-6})$	$\tau_c(\text{ps})$
12	0.041	620603380.471	12.844
15	0.023	649694064.324	7.068
17	0.017	652652121.468	5.085
19	0.013	662142240.981	3.749
21	0.011	661290613.993	3.070
23	0.009	662943675.558	2.683

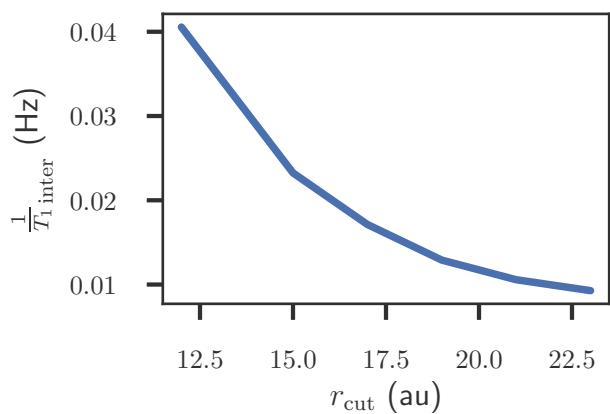


Figure S3: Convergence of computed intermolecular dipolar relaxation rate with distance cut-off used for the dipolar interaction calculation. Simulation is 64 molecule FFMD acetonitrile at 300K in NVE ensemble.

Spin-rotation quantities for water from 50 ps aiMD and single point calculations for nuclear SR coupling tensor:

Rotational correlation time about axis which passes through both O-H bonds,  $\tau_c = 3.96$  ps

Molecular moment of inertia about axis which passes through both O-H bonds,  $\Theta = 1.0 \times 10^{-40}$  g cm<sup>2</sup>

SR coupling tensor components calculated in Dalton with B3LYP functional and IGLO-III basis:  
 $C_x = 232086$  Hz,  $C_y = 210236$  Hz,  $C_z = 223342$  Hz

Computed SR contribution to longitudinal <sup>1</sup>H relaxation rate,  $1/T_{1,\text{SR}} = 3.73 \times 10^{-5}$  Hz

## References

- (1) J. R. Reimers and L. E. Hall, *J. Am. Chem. Soc.*, 1999, **121**, 3730–3744.