

## Supporting Information

# Solvent-Hindered Intramolecular Vibrational Redistribution

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**S1.  $T_1$  Relaxation**

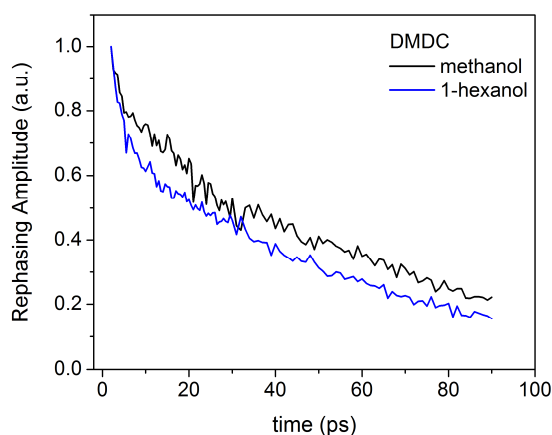
**S2. Molecular Dynamics Simulations**

**S3. Hydrogen Bond Number**

**S4. Movies of Filtered 50-ps Trajectories**

## S1. $T_1$ Relaxation

The cross peak growth at early times (0-20 ps) that was analyzed in this work is attributed purely to the IVR process. Other possible components to this signal would be orientational relaxation and population relaxation, which would compete with IVR, where increases in orientational and population relaxation times would be observed as slowing in the growth of the cross peak, attributed to IVR. Orientational relaxation of nanoscale molecules in viscous, hydrogen bonding solvents has been shown to be on the 100-1000 ps timescale, which is clearly separated from the early time growth of the nonrephasing cross peak analyzed in this work. The overall population relaxation could also contribute to this peak, where stronger coupling, i.e. more hydrogen bonds, would lead to faster  $T_1$  relaxation observed as a slowing down of the IVR. To observe the influence of hydrogen bonds on  $T_1$  relaxation we carried out  $T_1$  relaxation measurements by analyzing the decay of the main vibrational mode in the 2D rephasing spectra. In particular, we studied the two solvents that showed significant differences in their IVR rates. Figure S1 shows the decay in rephasing signal at waiting times approaching 100 ps, roughly the population relaxation time for DMDC in non-polar solvents like hexane. It is clearly seen that at early times DMDC in 1-hexanol shows a faster decay, reflecting the already observed trend that DMDC in 1-hexanol undergoes faster IVR on the 0-20 ps timescale. After the initial decay due to IVR, it is clear that the overall  $T_1$  relaxation occurs not only on a much longer timescale, but is also not influenced to any significant amount by the change in solvent. This data makes it clear that any small changes in the overall  $T_1$  relaxation could not be responsible for the large changes in IVR timescales that is seen through the alcohol series.

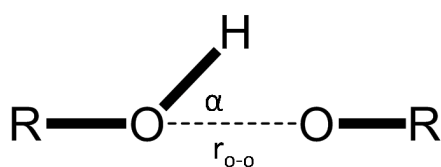


**Figure S1.**  $T_1$  relaxation for DMDC in methanol and 1-hexanol, which show significant differences in the observed IVR timescales.

## S2. Molecular Dynamics Simulations

Molecular Dynamics (MD) simulations were used to determine the average number of hydrogen bonds between the vibrational probe and the solvent. For each simulation, DMDC was placed in a cubic box containing between 500 and 520 solvent molecules, with periodic boundary conditions in all directions. The simulations were carried out using the NPT ensemble, where temperature and pressure were held constant at 298 K and 1 bar using the Berendsen coupling scheme. The particle-mesh Ewald summation method was used to account for long range electrostatic interactions. Simulations were carried out for 50 ps with 1 fs step sizes. The force field of DMDC was constructed using DFT calculations, carried out using the B3LYP functional and the 6-31+G(d) basis set for the oxygen and carbon atoms and the LANL2DZ pseudopotential for the manganese atoms. The general AMBER force field was used to describe the solvent molecules, ranging from methanol to 1-hexanol, where optimized structures were found from DFT calculations using the B3LYP functional and the 6-31+G(d) basis.

The hydrogen bonding statistics were determined using the `g_hbond` function of the GROMACS package, where the default and most commonly implemented criteria for a hydrogen bond were used. These criteria are an oxygen to oxygen distance ( $r_{o-o}$ ) of 3.5 Å or less, and an angle ( $\alpha$ ) between the oxygen-oxygen bond and the oxygen-hydrogen bond of 30° or less (Fig S2). The `g_hbond` function will characterize the hydrogen bonding environment based on these criteria, where the presence of hydrogen bonds between selected groups (in this case the solute and the solvent) are counted during each time step of the simulation. Therefore, for each step in the simulation, the `g_hbond` function counts the number of solvent molecules that satisfy the hydrogen bond criterion described above and shown in Figure S2. For this study, we used a simple measure of the total number of hydrogen bonds between bath and solute per time step, averaged over the entire MD trajectory.

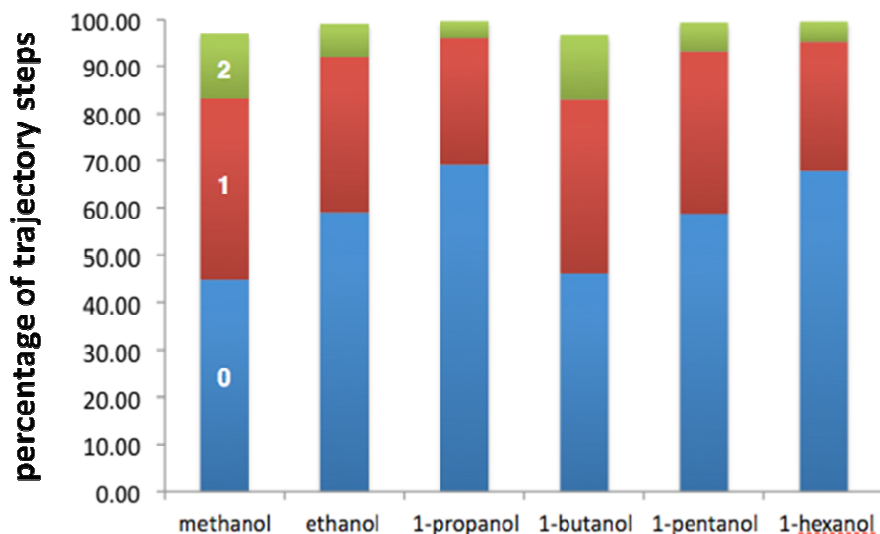


**Figure S2.** Criteria used for counting hydrogen bonds.  $\alpha \leq 30^\circ$ ,  $r_{o-o} \leq 3.5 \text{ \AA}$ .

## S3. Hydrogen Bond Number

Here we provide a more detailed breakdown of the hydrogen bonding environment in DMDC/alcohol solutions. Figure S3 shows the percentage of steps in the molecular dynamics simulation where the corresponding number of hydrogen bonds is observed. It can be seen that

for all of the solvents, the solute is only participating in a hydrogen bond with a solvent molecule for roughly half of the steps. The steps in which the solute is hydrogen bonding with the solvent are further broken down into percentage of the steps in which one hydrogen bond is formed and the percentage of the steps in which two hydrogen bonds are formed. The differences in hydrogen bonding number can also be seen from this graph, where methanol and 1-butanol clearly show the largest degree of hydrogen bonding.



**Figure S3.** Breakdown of the hydrogen bond statistics for this system. The number of hydrogen bonds formed between solute and solvent, shown are 0-2, and the percentage of steps in the MD simulation in which this number of hydrogen bonds is found.

#### S4. Movies of Filtered 50-ps Trajectories

To illustrate the time scale of both the solvent dynamics and the slow orientational diffusion of the DMDC solute, we have provided two animations of 50 ps long trajectories that have had their high-frequency dynamics filtered. The file “dmcdc\_butanol\_new\_1080p.mov” shows the case of butanol, and “dmcdc\_methanol\_new\_1080p.mov” shows the case of methanol. In methanol, it is clear that the solute molecule barely reorients on the 50-ps timescale depicted in the movie. In butanol, which has higher viscosity, the solute appears to be virtually motionless on this short timescale. Similar slow orientational dynamics have been reported previously for dye molecules of comparable size in alcohol solution.