Supporting Information for "Heterogeneous Reaction Rates in an Ionic Liquid: Quantitative Results from 2D-MUPPETS"

Kalyanasis Sahu, Sean J. Kern and Mark A. Berg

2D-MUPPETS PHASE RESULTS

Figure S1 shows phase results for 2D-MUPPETS (see Figure 8 for the magnitudes). The theoretical predictions (Figure S1A) are based on Model D. The phase difference $\Phi_1 - \Phi_0$ is the same as in the 1D calculations (Figure 5), but there is an unexplained overall shift of −24°. A phase drop is predicted, which should be delayed as t_1 is increased.

The experimental results are shown in Figure S1B. After 200 ps, the phase becomes irreproducible due to the small magnitude of the signal. The early part of the predicted phase drop is seen, but the results are not reliable enough either to confirm the predicted change in half point of the phase drop or to distinguish among the proposed models.

AURAMINE RELAXATION IN VARIOUS SOLVENTS

The complete set of pump-probe data for auramine in various solvents is shown in Figure S2. The half-lives used to construct Figure S3 are collected in Table S1. All the decays on a time axis scaled to these half-lives are plotted in Figure S3. The decays shapes vary significantly with solvent. A selection of these decays were presented in Figure 13.

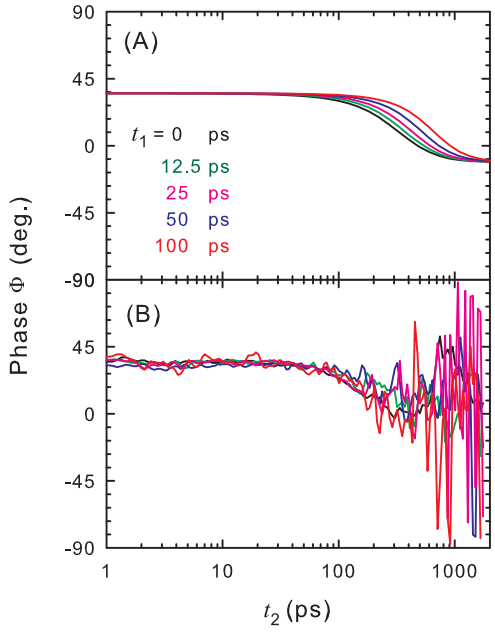

Figure S1. Phase of MUPPETS signal: t_1 = 0 ps (black), 12.5 ps (green), 25 ps (pink), 50 ps (blue) and 100 ps (red). (A) Predictions of model D. (B) Experimental results.

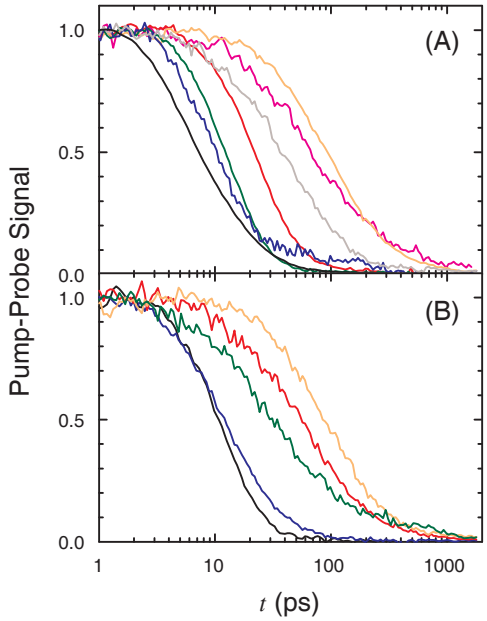

Figure S2. Pump-probe signal of auramine in different solvents: (A) acetonitrile (black), propylene carbonate (blue), dimethyl sulfoxide (green), ethanol (red), benzyl alcohol (grey), glycerol (pink), decanol (orange); (B) methanol (black), ethylene glycol (blue), glycerol triacetate (green), 1,3-butanediol (red), cyclohexanol (orange).

Table S1. Half-lives $\tau_{1/2}$ of auramine in various solvents with different viscosities η.

	η (cP)	$\tau_{1/2}$ (ps)
Acetonitrile	0.4	7.2
Methanol	0.6	10.8
Ethanol	1.1	21.9
Dimethyl sulfoxide	2.0	12.3
Propylene carbonate	2.5	10.4
Decanol	10.9	93
Ethylene glycol	16.1	12
Glycerol triacetate	28	31
Cyclohexanol	57.5	87
1,3-Butanediol	96.8	56.1
Glycerol	934	67

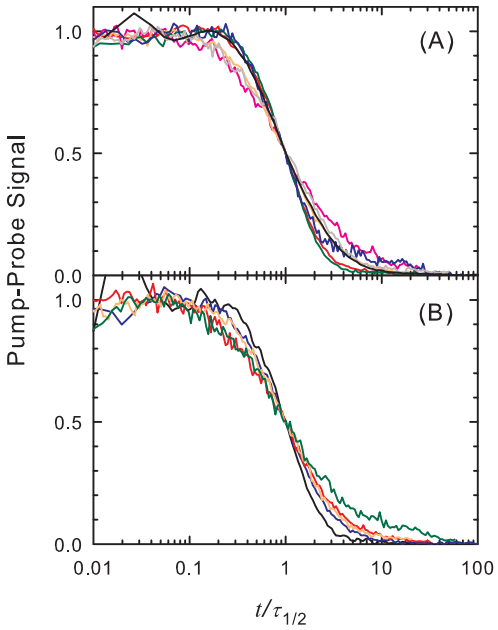

Figure S3. Pump-probe data of auramine (Figure S2) in different solvents presented on a time scale normalized by the half-life $\tau_{1/2}$. For clarity, the data are shown in two panels: (A) acetonitrile (black), propylene carbonate (blue), dimethyl sulfoxide (green), ethanol (red), benzyl alcohol (grey), glycerol (violet), decanol (orange); (B) methanol (black), ethylene glycol (blue), glycerol triacetate (green), 1,3-butanediol (red), cyclohexanol (orange).