

Heterogeneous Solvation Dynamics in an Ionic Liquid: Multidimensional Rate Spectra Yield Quantitative Measurements

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Multidimensional correlation functions have been applied to simulations of solvation dynamics in an ionic liquid. Heterogeneity is found in both the rate of diffusive solvation and in the amplitude of inertial solvation. New methods for analyzing multidimensional kinetics have been developed to quantify these phenomena.

Solvation dynamics have a complex form that becomes even more exaggerated in ionic liquids. The inertial phase is subpicosecond and steeper than exponential. In ionic liquids, the diffusive phase is more clearly distinguished from the inertial phase and has increased rate dispersion (shallower than an exponential). To understand the role of heterogeneity in these phenomena, multidimensional kinetics have been extended to the analysis of an equilibrium fluctuations from computer simulations [1].

To visualize the complex phenomena involved, rate–rate correlation spectra have been developed that parallel the frequency–frequency correlation spectra used in multidimensional spectroscopy (Fig. 1). A new non-parametric (without fitting functions) method (unpublished) has been used to quantify these spectra.

In simulations of coumarin 153 in 1-ethyl-3-methylimidazolium tetrafluoroborate [2], heterogeneity accounts for 55% of the rate dispersion in the diffusive phase. This dispersion can explain the failure of dielectric-continuum theories in ionic liquids [3]. This heterogeneity exchanges with a time of 40 ps, which is in the intermediate-exchange case. An unexpected heterogeneity was found in the amplitude of the inertial solvation. The amplitude–exchange time is close to rate–exchange time, even though there is no correlation between the rates and amplitudes themselves.

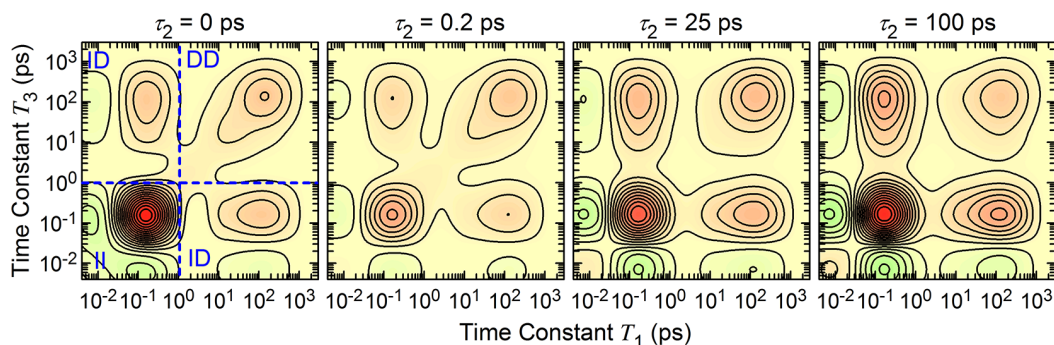


Fig. 1. Rate-rate correlation spectra of solvation dynamics. The ellipticity of the DD peak at $\tau_2 = 0$ is due to rate heterogeneity, and its loss at longer times is due to rate exchange. The loss of II peak volume at $\tau_2 = 0.2$ ps is due to amplitude heterogeneity, and its recovery at longer times is due to amplitude exchange. The ID peaks show no correlation between amplitude and rate heterogeneity. Adapted from [1].

Based upon work supported by the National Science Foundation under grant number 1403027.

[1] S. D. Verma, S. A. Corcelli, and M. A. Berg, *J. Phys. Chem. Lett.* 7 (2016).

[2] Z. L. Terranova, and S. A. Corcelli, *J. Phys. Chem. B* 117 (2013).

[3] X.-X. Zhang, M. Liang, N. P. Ernsting, and M. Maroncelli, *J. Phys. Chem. Lett.* 4 (2013).