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MD studies of electron transfer at ambient and elevated pressures

ALEX GILES, University of the Fraser Valley, JACOB SPOONER, Simon Fraser University, NOHAM WEINBERG, University of the Fraser Valley; Simon Fraser University — The effect of pressure on the rate constants of outer-sphere electron transfer reactions has often been described using the Marcus-Hush theory.¹ This theory agrees well with experiment when internal reorganization of the ionic system is negligible,² however it does not offer a recipe for calculation of the effects that result from significant solute restructuring. We have recently developed a molecular dynamics technique that accurately describes structural dependence of molecular volumes in non-polar and weakly polar systems. We are now extending this approach to the case of highly polar ionic systems where both solvent and solute restructuring components are important. For this purpose we construct pressure-dependent two-dimensional surfaces for electron transfer reactions in coordinate system composed of interionic distance and Marcus-type solvent polarization coordinate, and use these surfaces to describe pressure effects on reaction kinetics.

¹R.A. Marcus. *J. Chem. Phys.* **24**, 966 (1956); **24**, 979 (1956); **26**, 867 (1957). *Discuss. Faraday Soc.* **29**, 21 (1960). *Faraday Discuss. Chem. Soc.* **74**,7 (1982); N.S. Hush. *Trans. Faraday Soc.* **57**, 557 (1961).

²T.W. Swaddle. *Inorg. Chem.* **29**, 5017 (1990).

Alex Giles
University of the Fraser Valley

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