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Electric Field Fluctuations in Water DAYTON THORPE, DAVID LIMMER, DAVID CHANDLER, University of California, Berkeley — Charge transfer in solution, such as autoionization and ion pair dissociation in water, is governed by rare electric field fluctuations of the solvent. Knowing the statistics of such fluctuations can help explain the dynamics of these rare events. Trajectories short enough to be tractable by computer simulation are virtually certain not to sample the large fluctuations that promote rare events. Here, we employ importance sampling techniques with classical molecular dynamics simulations of liquid water to study statistics of electric field fluctuations far from their means. We find that the distributions of electric fields located on individual water molecules are not in general gaussian. Near the mean this non-gaussianity is due to the internal charge distribution of the water molecule. Further from the mean, however, there is a previously unreported Bjerrum-like defect that stabilizes certain large fluctuations out of equilibrium. As expected, differences in electric fields acting between molecules are gaussian to a remarkable degree. By studying these differences, though, we are able to determine what configurations result not only in large electric fields, but also in electric fields with long spatial correlations that may be needed to promote charge separation.

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