Supporting Information for

Nonexponential Kinetics of Ion Pair Dissociation in Electrofreezing Water

Mohammad Alaghemandi,[†] Volkmar Koller,^{†,‡} and Jason R. Green^{†,§,¶}

[†]Department of Chemistry, University of Massachusetts Boston, Boston, MA 02125, USA

[‡] Department of Chemistry, Justus-Liebig-Universität Gießen, 35390 Gießen, Germany

[§] Department of Physics, University of Massachusetts Boston, Boston, MA 02125, USA

[¶] Center for Quantum and Nonequilibrium Systems, University of Massachusetts Boston, Boston, MA 02125, USA

mohammad.alaghemandi@umb.edu jason.green@umb.edu



Figure S1: The average number of water-oxygen atoms within 2.9 Å of the positively charged ion over time (solid orange line). Green area shows the bounds of the fluctuations in this number prior to dissociation. The blue line indicates the average distance between the ions. Data are averaged over 150 simulation events with $F_m = 3.47$ nN. The time of each trajectory is shifted so that $\tau = 0$ corresponds to the dissociation event (3.5 Å).



Figure S2: Fitting S(t) data of ion dissociation in an electrofreezing environment with stretched exponential function of form $\exp\left(-\left(\frac{F_e}{b}\right)^a\right)$. Data points in gray significantly deviate from the fitted functions.



Figure S3: The time-dependent rate coefficients estimated (a) by calculating the regional slope of S(t) according to Eq. 2 in the main text, (b) by using time-dependent β_F data and using $k_F(t) = \beta_F S(t)$ relation, and (c) by fitting the S(t) data with stretched exponential function of form $\exp\left(-\left(\frac{F_e}{b}\right)^a\right)$.



Figure S4: $\ln\{-\ln[S(t)]\}$ versus $\ln t$ at different electric field values. The function in Eq. 4 used to fit the data point for a range of (a) 1-240 ps, (b) 10-30 ps, (c) 30-100 ps, and (d) 120-240 ps. Functions fit better to data for small range of data points.



Figure S5: (a) Estimated rate constant (k_F) and (b) variance of barrier height (σ^2) versus F_e for different time intervals. Estimated rate constants are smaller for later time domains, indicating the changes in k_F over time. Estimated σ^2 are larger for later time domains, indicating the time dependency of σ^2 .



Figure S6: Characteristic time, $1/k(t, F_e)$, versus time estimated (a) by calculating inverse values of the regional slope of S(t) according to Eq. 2, (b) by using time-dependent β_F data and the relation in Eq. 3, and (c) by fitting the S(t) data with stretched exponential function of form $\exp\left(-\left(\frac{F_e}{b}\right)^a\right)$.