Supporting Information

Driving force dependence of rates for nonadiabatic proton and proton-coupled electron transfer: Conditions for inverted region behavior

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Figure S1

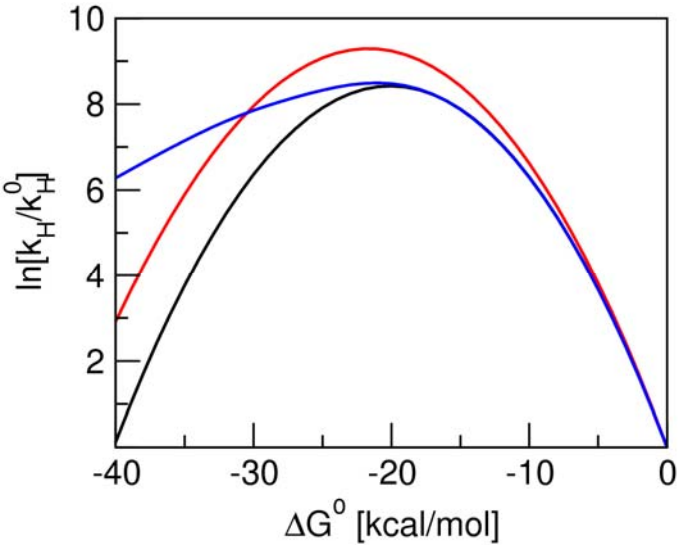

Figure S1: Driving force dependence of the vibronically nonadiabatic rate constant for three models with λ = 20 kcal/mol and (1) ω = 400 cm^{-1} and δx = 0.1 Å (black); (2) ω = 400 cm^{-1} and δx = 0.5 Å (blue); (3) ω = 3000 cm^{-1} and δx = 0.1 Å (red). The first model corresponds to the ET model discussed in the main part of the paper. The temperature is 300 K, and k_H^0 is the rate constant for ΔG^0 = 0. The reduced mass of the vibrational mode is 1 amu for all of these models.

Figure S2

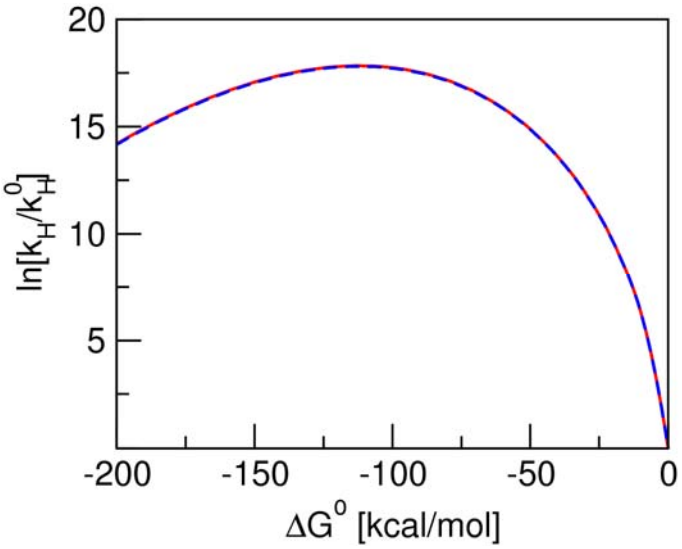

Figure S2: Driving force dependence of the vibronically nonadiabatic rate constant for the PCET model with two uncoupled modes, where λ = 20 kcal/mol, ω = 3000 cm^{-1} and δx = 0.5 Å for the first mode, and ω = 400 cm^{-1} and δx = 0.1 Å for the second mode. The red curve corresponds to this model with two uncoupled modes, and the blue curve corresponds to the original PCET model with only the first mode. The proton transfer is assumed to be electronically nonadiabatic, the temperature is 300 K, and k_H^0 is the rate constant for $\Delta G^0 = 0$. The reduced mass of both vibrational modes is 1 amu.

Figure S3

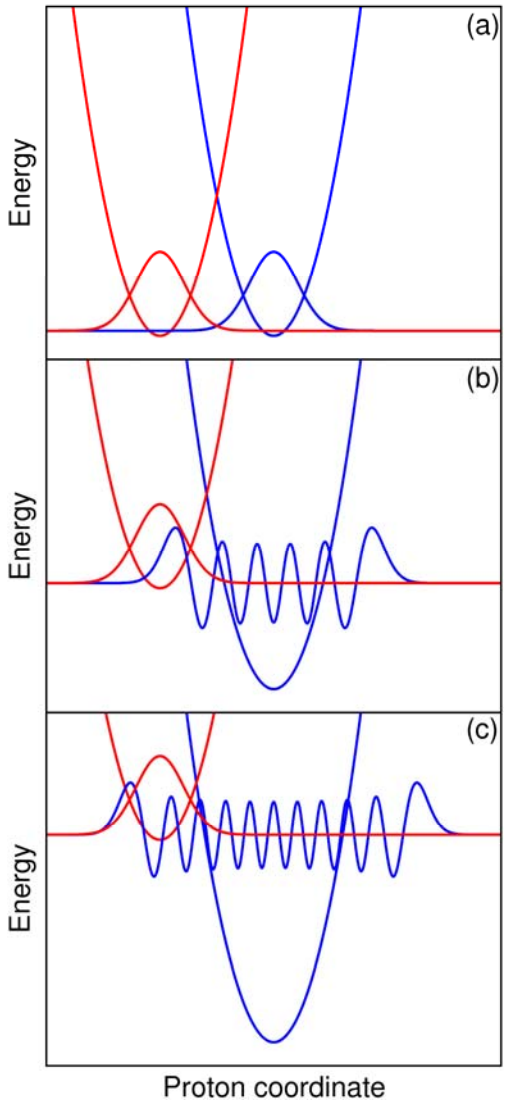

Figure S3: Proton potential energy curves and associated proton vibrational wavefunctions for the PCET model, where λ = 20 kcal/mol, ω = 3000 cm^{-1} and δx = 0.5 Å, with (a) the ground reactant and product vibrational states degenerate, (b) the ground reactant and tenth excited product vibrational states degenerate, and (c) the ground reactant and twentieth excited product vibrational states degenerate. The overlap integral is largest for (b), and the overlap is smallest for (c) because of cancellation effects due to the oscillations of the excited proton vibrational wavefunctions.