

## Supplementary Information for:

### Diffusional effects on the reversible excited-state proton transfer.

#### From experiments to Brownian dynamics simulations

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#### **An attempt to fit the kinetic data with SSDP**

We have attempted to fit the experimental data of C\* and Z\* fluorescence decays using the straightforward approach offered by SSDP. As described in references 4-7, the Section 4 of the main text, and the following sections of the Supplementary Information, the only variables are the intrinsic association ( $\kappa_a$ ) and the dissociation ( $\kappa_d$ ) rate constants. In this model a proton diffuses around a negatively charged spherical molecule with the radius  $a = 6 \text{ \AA}$ ; their interaction is described by the Coulomb attraction. The mutual diffusion coefficient is taken equal to  $D_{\text{P-Z}^*} = 110 \text{ \AA}^2/\text{ns}$  – the sum of  $D_{\text{P}}$  and  $D_{\text{Z}^*}$  [23,24], and the Debye radius corresponds to that in butanol,  $R_D = 35.8 \text{ \AA}$ . The lifetimes of C\* and Z\* radiation decays are determined independently and are:  $1/k_0 = \tau_0 = 18 \text{ ns}$  and  $1/k'_0 = \tau'_0 = 1.25 \text{ ns}$ . The abovementioned references and text chapters justify the choice of these fixed kinetic and diffusion parameters.

Since the initial slope of C\* decay is governed mostly by  $\kappa_d$ , its value cannot be varied much, and is kept at its a maximal possible value,  $15 \text{ ns}^{-1}$ . The best fit value of  $k_a$  is  $1 \text{ \AA}/\text{ns}$ . One can see (Fig. S.1) that the “best fit” of the spherical symmetry approach with the set of fixed parameters derived independently results in the prediction of much higher recombination efficiency between the Z\* and the proton: the long-time decay tail is significantly higher than the experimental data. Further increasing  $\kappa_d$  or decreasing  $k_a$  lower both the long-time tail and the short-time kinetics (the latter effect is shown in the right panel of Fig. S.1).

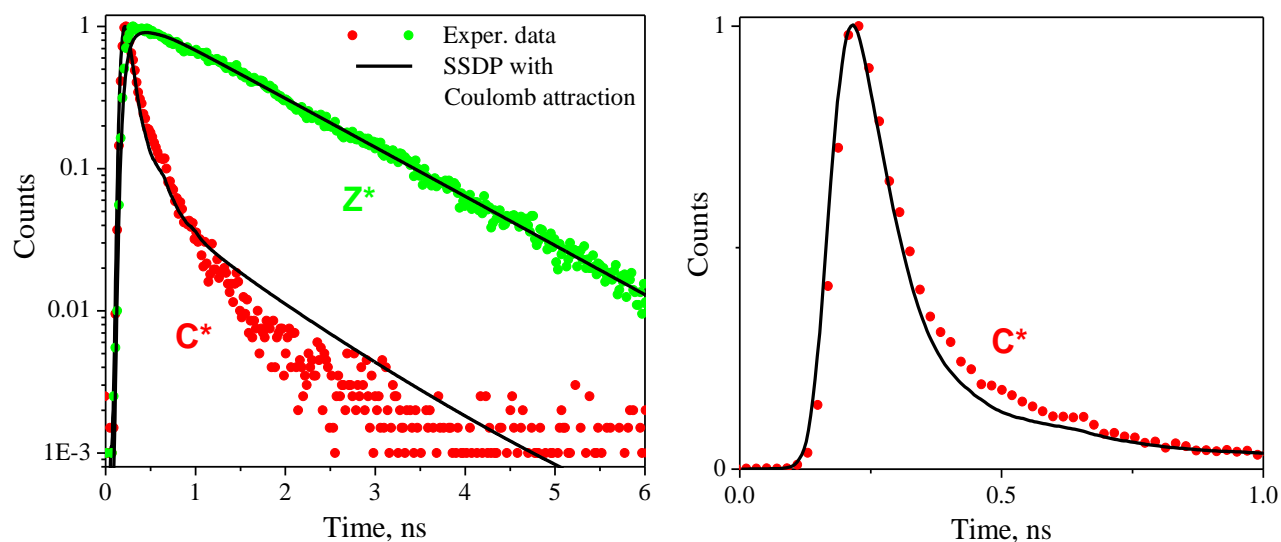


Fig. S.1. Left panel: filled symbols represent the fluorescence decay of MHQ, as in Fig. 2 of the main text. Solid lines are calculated with the help of SSDP package with the spherically-symmetrical Coulomb attraction. Right panel: the C\* fluorescence at small times (linear scale).

We argue that the unsatisfactory fit of the kinetic data using the SSDP package is caused by the breakdown of spherical-symmetric approach and by the complexity of the system. Clearly, the description of the recombination event has to take into account the anisotropic nature of the  $Z^*-H^+$  interaction, which is weaker than the spherical symmetric one. On the macroscopic level, this should lead to the  $\sim 1/r^2$  ion-dipole character of the  $Z^*-H^+$  interaction.

### ***Spherically-symmetric test simulations with BD***

To ensure the BD simulation method described above can reproduce known results in the spherically-symmetrical case, we compared the kinetics obtained during the simulations with those calculated with the help of the SSDP software which gives the accurate solution for such problems.

The results of comparison are depicted in Fig. S.2. In this model a proton diffuses around a negatively charged spherical molecule with the radius  $a = 6 \text{ \AA}$  [53]. The mutual diffusion coefficient is taken equal to  $D = 90 \text{ \AA}^2/\text{ns}$ , and the Debye radius corresponds to that in butanol,  $R_D = 35.8 \text{ \AA}$ .

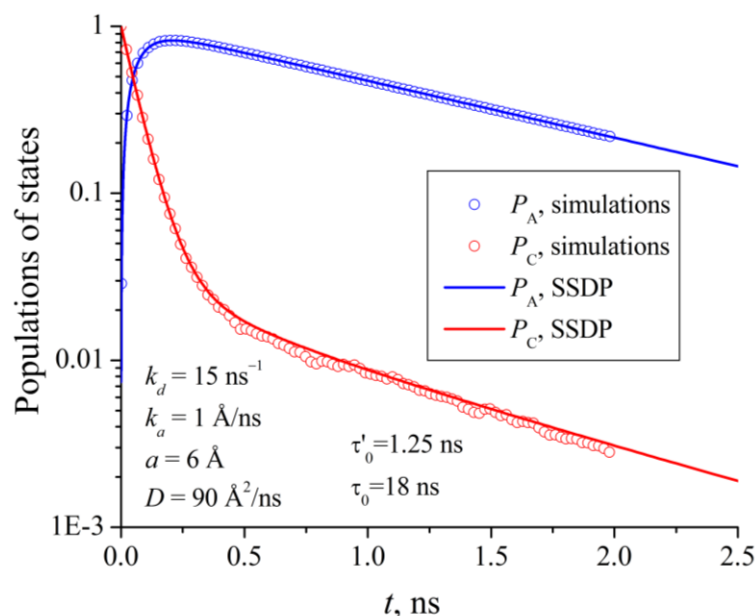


Fig. S.2. Fluorescence decay of the model system with the spherically-symmetrical Coulomb attraction. Circles are the results of BD simulation; solid lines are calculated with the help of SSDP package.

The width of the reaction zone in this case has been chosen to be extremely narrow,  $\Delta = 0.01 \text{ \AA}$ , to mimic the contact reaction embedded into the SSDP. In the limit where the reaction zone becomes infinitely thin, *i.e.*, the sink term is represented by the  $\delta$ -functions, the product,  $k_a \equiv \kappa_a \cdot \Delta$ , remains constant to maintain a limited action of the contact reaction.

The intrinsic association rate is chosen to be  $\kappa_a = 100 \text{ ns}^{-1}$ ; the dissociation rate constant is  $\kappa_d = 15 \text{ ns}^{-1}$ . The lifetimes are taken as they are in the real system under investigation:  $\tau_0 = 18 \text{ ns}$  and  $\tau'_0 = 1.25 \text{ ns}$ . These parameters are used in the SSDP with  $k_a = \kappa_a \cdot \Delta = 1 \text{ \AA/ns}$ . The agreement between the SSDP calculations and the BD simulations is perfect, so we applied our BD algorithm to more complicated anisotropic case of MHQ excited-state reversible proton transfer.

### **Other results of BD simulations and SSDP calculations**

The figures below show the kinetics calculated for all the reaction distances,  $R_{\text{reac}}$ . The residual plots correspond to the differences between BD simulations and experimental data.  $\langle |\text{Resid.}| \rangle$  is the average of the absolute values of the residuals which indicates the accuracy of fitting for each case.

