Electronic Supplementary Information

Excited state hydrogen transfer dynamics in phenol–(NH$_3$)$_2$ studied by picosecond UV-near IR-UV time-resolved spectroscopy

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1. Solution of the differential equation for the proposed reaction scheme

Here we define amounts of species concerning to the ESHT reaction of the PhOH–$(NH_3)_2$ cluster as follows,

$[R] \equiv \left[PhOH^* - (NH_3)_2\right](t),$

$[P] \equiv \left[\cdot NH_4NH_3\right](t),$

$[X] \equiv [Intermediate, X](t).$

When the ESHT reaction proceeds according to the reaction scheme proposed in the main text, time-changes in the related species are represented by the following differential equations:

$$\frac{d[R]}{dt} = -\left(k_1 + k_2\right)[R] \qquad (S1),$$

$$\frac{d[X]}{dt} = k_2[R] - k_3[X] \qquad (S2),$$

$$\frac{d[P]}{dt} = k_1[R] + k_3[X] \qquad (S3).$$

The Laplace transformation of equation (S1)–(S3) transforms them into equations (S4)–(S6) as follows:

$$sL\{[R]\} - [R]_0 = -\left(k_1 + k_2\right)L\{[R]\} \qquad (S4),$$

$$sL\{[X]\} - [X]_0 = k_2L\{[R]\} - k_3L\{[X]\} \qquad (S5),$$

$$sL\{[P]\} - [P]_0 = k_1L\{[R]\} + k_3L\{[X]\} \qquad (S6),$$

where $L\{[\Omega]\}$ and $[\Omega]_0$ represent the Laplace transformation and initial amount of $[\Omega]$, respectively. Since $[X]_0 = 0$ and $[P]_0 = 0$, the equations (S4)–(S5) reduce to

$$sL\{[R]\} - [R]_0 = -\left(k_1 + k_2\right)L\{[R]\} \qquad (S4)',$$

$$sL\{[X]\} = k_2L\{[R]\} - k_3L\{[X]\} \qquad (S5)',$$

$$sL\{[P]\} = k_1L\{[R]\} + k_3L\{[X]\} \qquad (S6)'.$$

The equations (S4)′–(S6)′ can be solved about $L\{[\Omega]\}$ as follows:

$$L\{[R]\} = \frac{[R]_0}{(k_1 + k_2 + s)} \qquad (S7),$$

$$L\{[X]\} = \frac{k_2[R]_0}{(k_1 + k_2 + s)(k_3 + s)} \qquad (S8),$$

$$L\{[X]\} = \frac{((k_1 + k_2)k_3 + k_1s)k_2[R]_0}{s(k_1 + k_2 + s)(k_3 + s)} \qquad (S9).$$

Partial fraction decomposition of equations (S7)–(S9) gives:

$$L\{[R]\} = \frac{[R]_0}{(k_1 + k_2 + s)} \qquad (S7)',$$

$$L\{[X]\} = \frac{k_2[R]_0}{(k_1 + k_2 - k_3)}\left(\frac{1}{(k_3 + s)} - \frac{1}{(k_1 + k_2 + s)}\right) \qquad (S8)',$$

$$L\{[X]\} = [R]_0\left(\frac{1}{s} - \frac{(k_1 - k_3)k_2}{(k_1 + k_2 - k_3)(k_1 + k_2 + s)} - \frac{k_2}{(k_1 + k_2 - k_3)(k_3 + s)}\right) \qquad (S9)'.$$

The inverse Laplace transformation of equations (S7)′–(S9)′ recovers $[\Omega]$ as follows:

$$[R] = [R]_0 e^{-(k_1 + k_2)t} \qquad\qquad (S10),$$

$$[X] = [R]_0 \frac{k_2}{(k_1 + k_2 - k_3)}(e^{-k_3 t} - e^{-(k_1 + k_2)t}) \qquad (S11),$$

$$[P] = [R]_0 \left(\frac{k_1 - k_3}{k_1 + k_2 - k_3}(1 - e^{-(k_1 + k_2)t}) + \frac{k_2}{k_1 + k_2 - k_3}(1 - e^{-k_3 t}) \right) \quad (S12).$$

Thus, the time evolutions are expressed in double exponential functions. The equation (S12) is used as the equation (1) in the main text, where $[R]_0$ is replaced by A to change the absolute amount of $[R]_0$ to the signal intensity. In the fitting procedure, convoluted forms of the functions by a Gaussian function that represents the instrumental function were used.