Supporting Information to Time-Resolved Probing of the Nonequilibrium Structural Solvation Dynamics by the Time-Dependent Stokes Shift

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Calculation of the first term in Eq. (8)

For the first term in Eq. (8) of the main text, we follow the back transform given in Ref.[1] We obtain

$$\Delta E_0(t) = \frac{-\Delta\mu^2}{2\pi a_0^3} \int_C dz \frac{\chi(z)}{iz} e^{izt} \tag{S1}$$

$$= -\frac{-\Delta\mu^2}{2\pi a_0^3} \int_C dz \frac{\chi(z) - \chi(0)}{iz} e^{izt} - \frac{-\Delta\mu^2}{2\pi a_0^3} \int_C dz \frac{\chi(0)}{iz} e^{izt}, \tag{S2}$$

where C is the contour parallel to but slightly below the real axis. By means of the theorem of residues, the second term is equal to $-\frac{\Delta\mu^2}{a_0^3}\chi(0)\Theta(t)$. $\chi(z)$ is analytic on the real axis and $\chi(0)$ is a real number. Since $\frac{\chi(z)-\chi(0)}{z} = [\frac{d\chi(z)}{dz}]_{z=0} + O(z)$ for $z \to 0$ and since $d\chi(z)/dz$ has no singularity at $z = 0$, the term does not possess a pole at $z = 0$.

Therefore, the contour C may now coincide with the real axis. Moreover, we decompose $\chi(\omega) = \Re[\chi(\omega)] + i\Im[\chi(\omega)]$ and use the fact that $\chi(-\omega) = \chi^*(\omega)$ because $\chi(t)$ is real. With this, we find that

$$\int_C dz \frac{\chi(z) - \chi(0)}{iz} e^{izt} = 2\int_0^\infty d\omega \frac{\Im[\chi(\omega)]}{\omega} \cos(\omega t) + 2\int_0^\infty d\omega \frac{\Re[\chi(\omega)] - \chi_s}{\omega} \sin(\omega t). \quad \text{(S3)}$$

Thus, Eq. (S2) reads

$$\Delta E_0(t) = \frac{-\Delta\mu^2}{\pi a_0^3} \left[\int_0^\infty d\omega \frac{\Im[\chi(\omega)]}{\omega} \cos(\omega t) + \int_0^\infty d\omega \frac{\Re[\chi(\omega)] - \chi_s}{\omega} \sin(\omega t) + \pi \chi_s \Theta(t) \right]. \quad \text{(S4)}$$

Since $\Delta E_0(t) = 0$ for $t < 0$ and the first and second integrand are equal for positive t, Eq. (S4) yields

$$\Delta E_0(t) = \frac{-2\Delta\mu^2}{\pi a_0^3} \int_0^\infty d\omega \frac{\Im[\chi(\omega)]}{\omega} \cos[\omega t] - \frac{\Delta\mu^2}{a_0^3} \chi_s \Theta(t). \quad \text{(S5)}$$

References

(1) Hsu, C.-P.; Song, X.; Marcus, R. A. Time-Dependent Stokes Shift and Its Calculation from Solvent Dielectric Dispersion Data. *J. Phys. Chem. B* **1997**, *101*, 2546-2551.