

Supporting Information

Degradation of Per- and Polyfluoroalkyl Substances with Hydrated Electrons: A New Mechanism from First-Principles Calculations

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Cavity preparation for hydrated electron simulations: The cavity of the hydrated electron was prepared in several stages. First, an NVT calculation of a periodic cell containing 81 water molecules, one PFOA or PFOS molecule, and one Cl⁻ ion was equilibrated using classical force field simulations for 1 ns (the approximate length of a PFOA/PFOS molecule is around 12 Å). The resulting system was then integrated for over 10 ps without periodic boundary conditions with a time step of 1 fs at the PBE level of theory. The chloride ion was subsequently removed from the simulation, and the system was then initialized with an extra negative charge to generate the desired hydrated electron. The entire system was then integrated for another 6 ps with a 0.5 fs time step in an NVT ensemble. We found that the resulting cavity was surrounded by four to five water molecules, and we analyzed five trajectories with different initial conditions for our solvated PFOA and PFOS systems.

Excess electron simulations: A periodic cell containing 81 water molecules and one PFOA or PFOS molecule was equilibrated for 1 ns using a classical force field in an NVT ensemble. Another 20 ps (with a 1 ps time step) of an NVT simulation was performed without periodic boundary conditions at the PBE level of theory. An excess electron was then added by simply initializing the system with an overall negative charge without preparing a cavity, and 3 ps of an NVT simulation was carried out. A total of 13 and 12 trajectories for solvated PFOA and PFOS, respectively, were propagated from different initial conditions.

Metadynamics calculations: Metadynamics simulations were harnessed to obtain the free energy profile of the C–F bond dissociation. In metadynamics simulations, the free energy profile is constructed from a biasing potential, which depends on a set of pre-defined collective variables (CVs). In this work, we used the coordination number as the CV using the following expression:

$$\text{CV or CN} = \frac{1 - \left(\frac{d_{AB}}{d_0}\right)^p}{1 - \left(\frac{d_{AB}}{d_0}\right)^{p+q}}$$

where, d_{AB} is the distance between any atoms A and B , and d_0 is the reference distance or fixed cutoff parameter. We chose the distance between the C and F atoms in the C–F bond of a PFOA or PFOS molecule as a collective variable. In the previous equation, p and q were both set to 6 to differentiate between the bonded and non-bonded states. For a pair of C and F atoms, the CN value is close to one when they are bonded and approaches zero when they are in a non-bonded state. In this work, well-tempered metadynamics^{1,2} simulations were carried out by depositing Gaussians with a height of 0.00001 Hartree (0.00627 kcal/mol). The width of the Gaussian was set to 0.1 for the collective variable, and the deposition rate of the Gaussian hill was set to 10 steps. The well-tempering was implemented using a Gaussian height damping factor 6. The collective variable for each of the trajectories is shown in Figure S6. Free energy profiles are shown in Figures S7 and S8 for solvated PFOA and PFOS, respectively.

Volumetric data analysis

Calculations for the radius of gyration: To calculate the radius of gyration, we performed spin density analyses on volumetric grid data obtained from cube files created during our molecular dynamics simulations.^{3,4} The cube files were collected every 5 fs for each of the trajectories. The following equation defines the center of the spin density distribution $\rho(\mathbf{r})$ (the number density of particles at position \mathbf{r}):

$$\mathbf{r}_c = \int \rho(\mathbf{r}) \mathbf{r} d\mathbf{r},$$

which is computed numerically on a real-space grid as follows:

$$\mathbf{r}_c = \sum_{i=1}^N \rho(\mathbf{r}_i) \mathbf{r}_i,$$

where the summation runs over all N grid points. The second-moment tensor, \mathbf{S} , for the spin density is given by:

$$\mathbf{S} = \int (\mathbf{r} - \mathbf{r}_c)(\mathbf{r} - \mathbf{r}_c)\rho(\mathbf{r}) d\mathbf{r}.$$

Since the gyration tensor is a symmetric 3×3 matrix, a coordinate transformation can be found in which it is diagonal

$$\mathbf{S} = \begin{bmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{yz} & S_{zz} \end{bmatrix} \rightarrow \begin{bmatrix} \lambda_x^2 & 0 & 0 \\ 0 & \lambda_y^2 & 0 \\ 0 & 0 & \lambda_z^2 \end{bmatrix},$$

where λ_x^2 , λ_y^2 , and λ_z^2 are the eigenvalues of \mathbf{S} , and the radius of gyration is calculated as

$$r_g^2 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2.$$

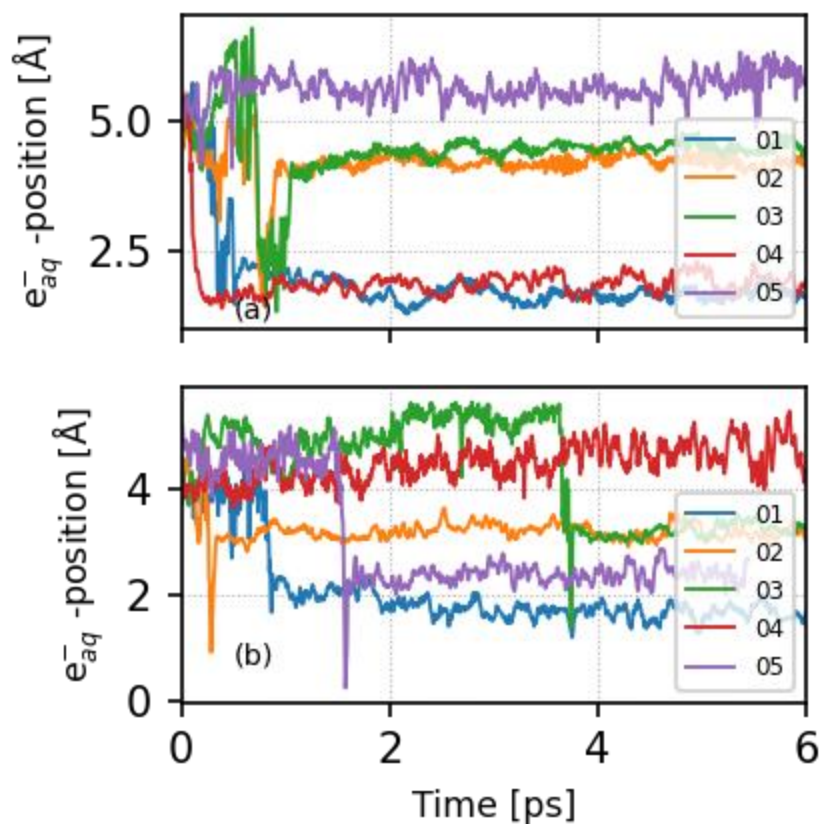


Figure S1. Time evolution of the average distance between the hydrated electron and the center of mass of the aqueous cluster. Panels (a) and (b) represent different trajectories of solvated PFOA and PFOS systems, respectively.

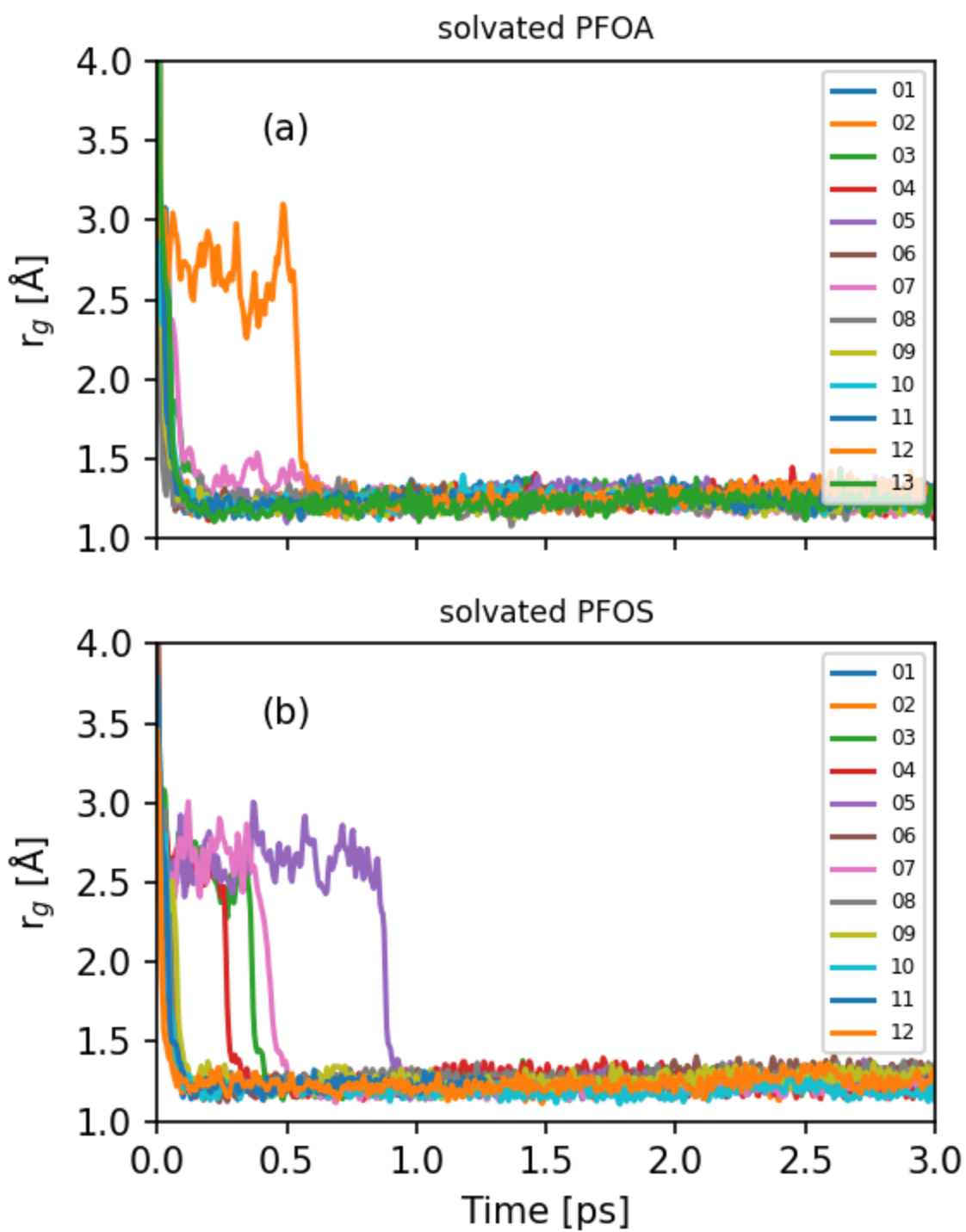


Figure S2. Time evolution of the radius of gyration of the excess electron in solvated (a) PFOA and (b) PFOS systems.

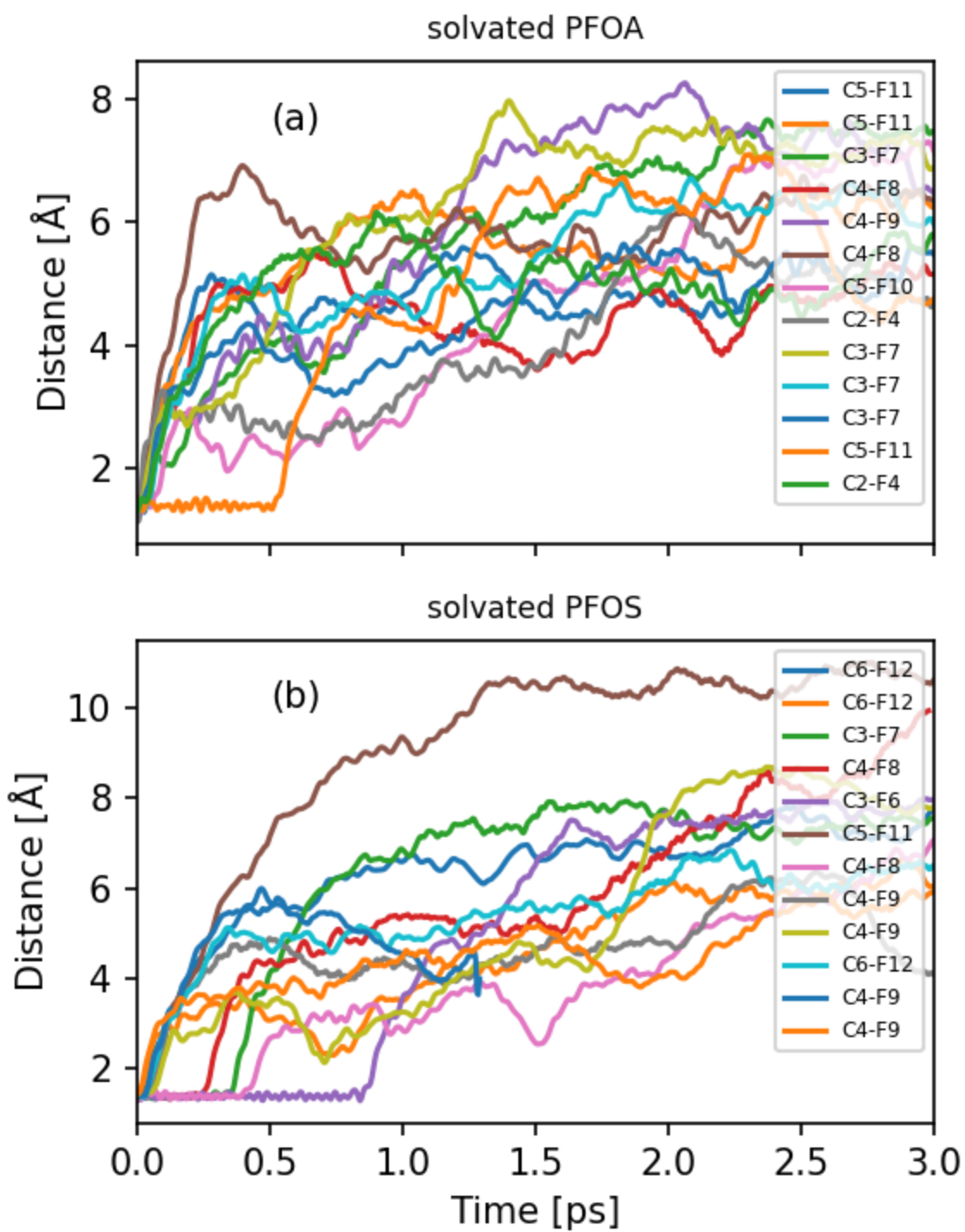


Figure S3. Evolution of C–F bond distances for the defluorination of PFOA and PFOS by an excess electron.

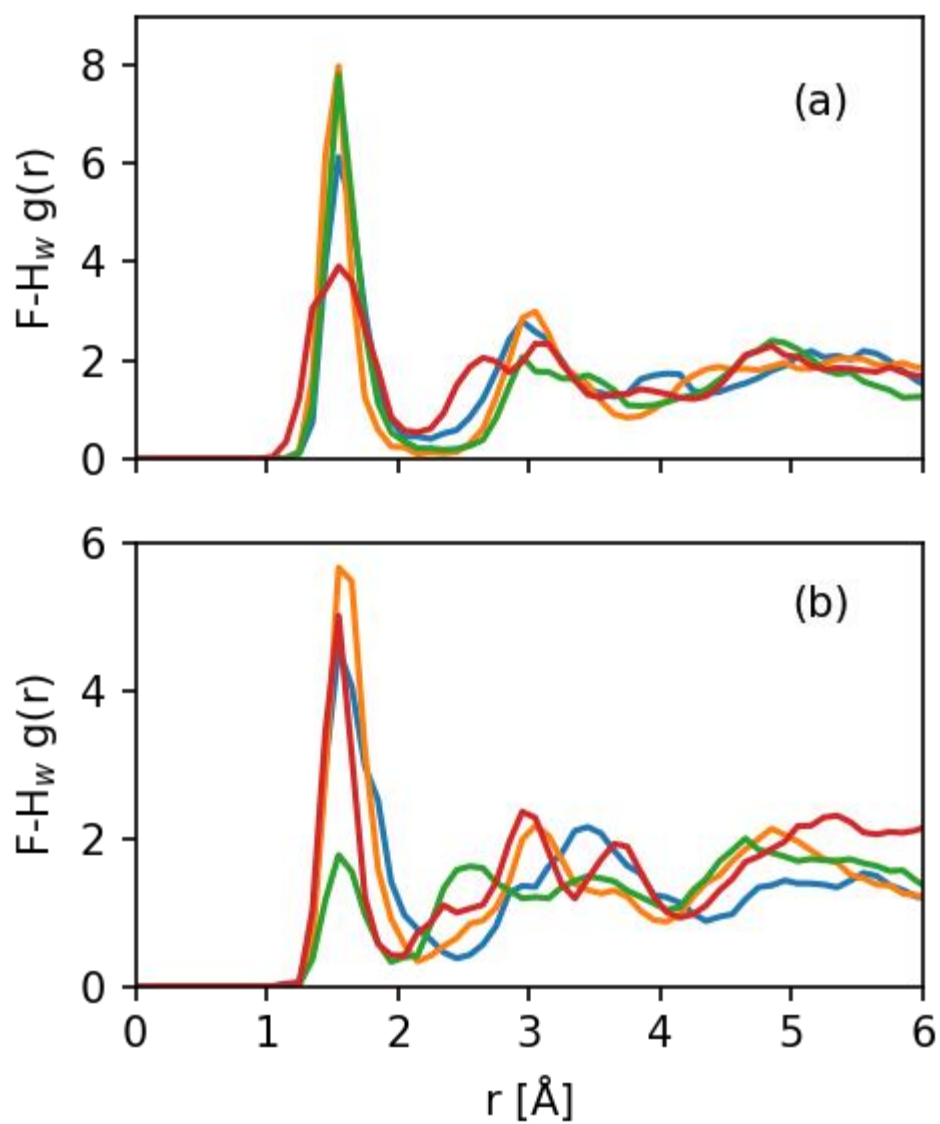


Figure S4. Radial distribution functions (RDFs), $g(r)$, between the defluorinated F atom and the H atom of surrounding water molecules from pre-created cavity simulations for the hydrated electron. Panels (a) and (b) represent RDFs from solvated PFOA and PFOS systems, respectively.

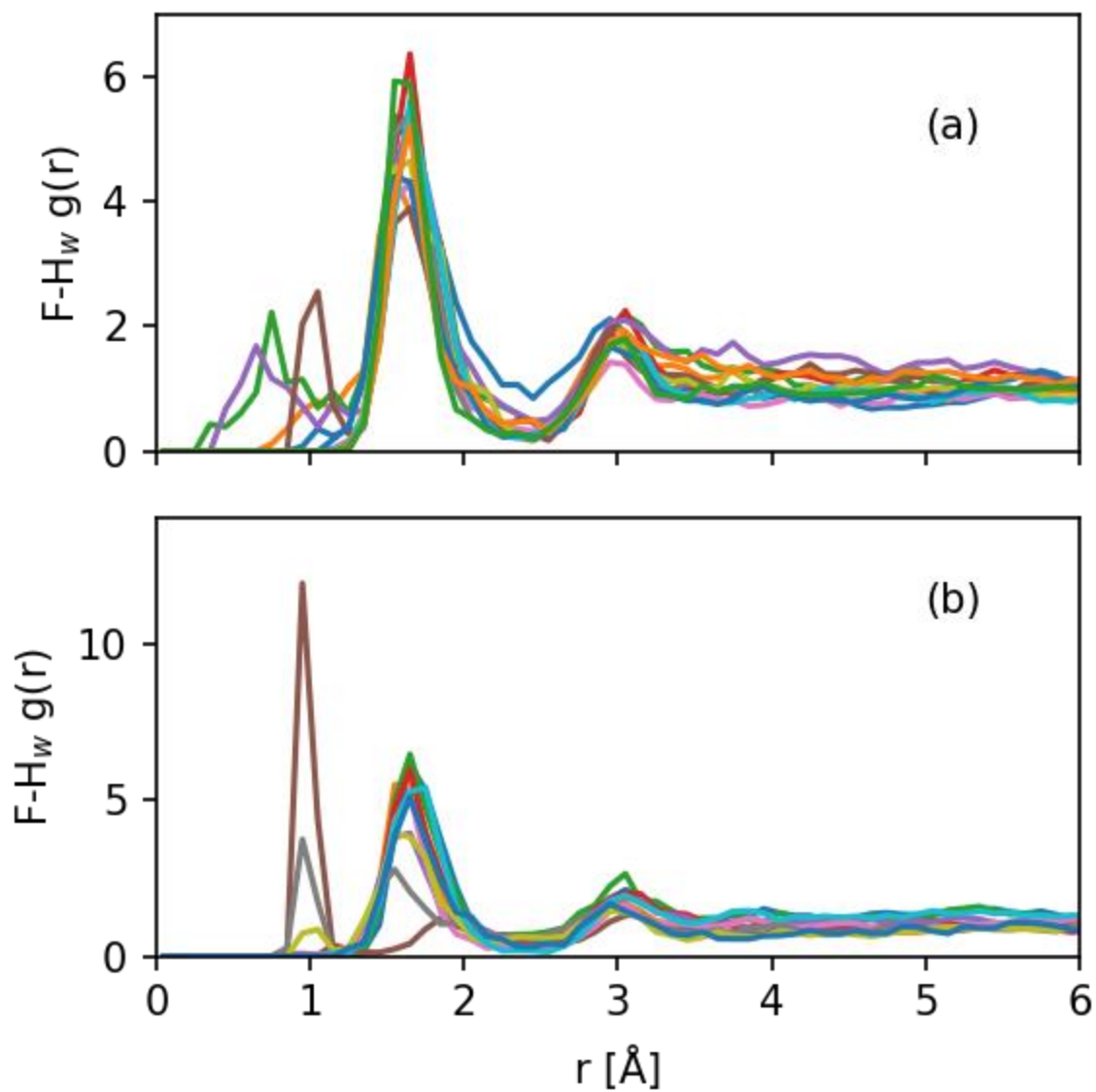


Figure S5. Radial distribution functions (RDFs), $g(r)$, between the defluorinated F atom and the H atom of surrounding water molecules for an excess electron in solvated (a) PFOA and (b) PFOS systems.

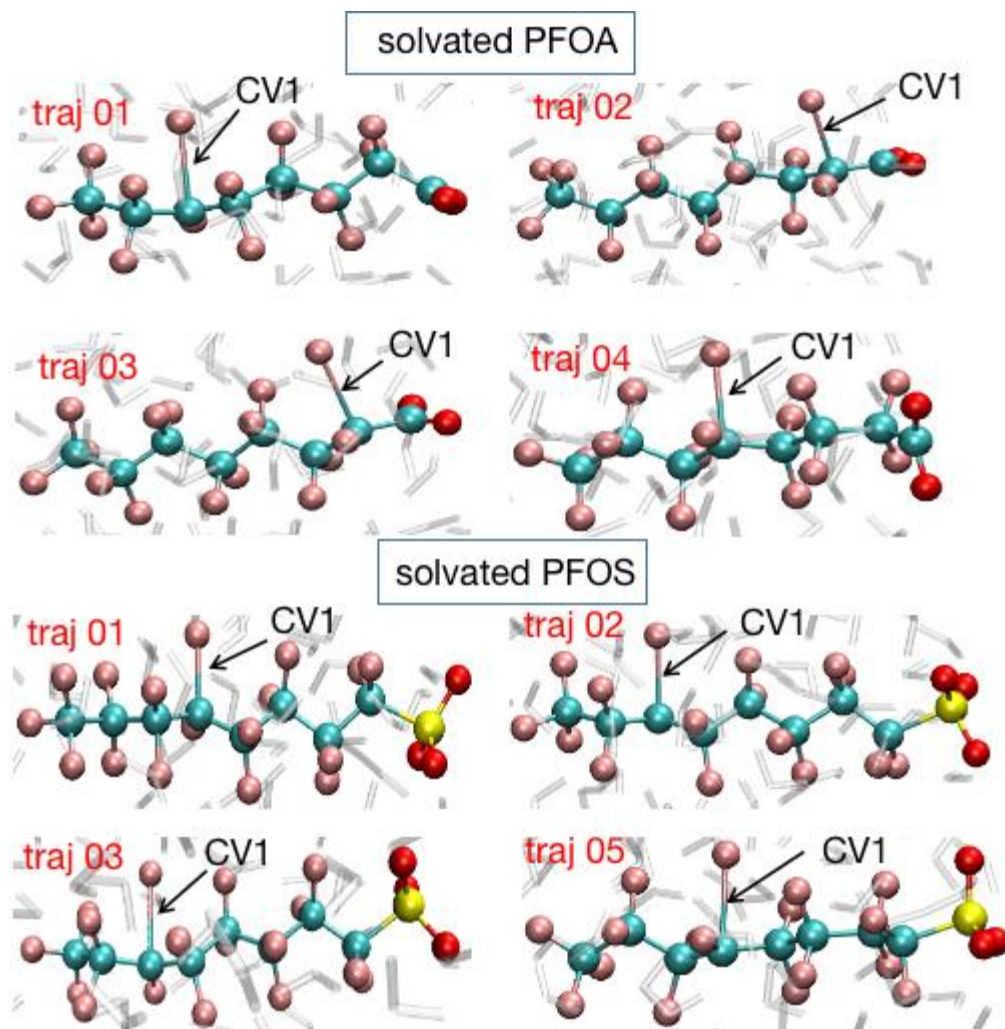


Figure S6. Snapshots illustrating the collective variables used in our well-tempered metadynamics simulations.

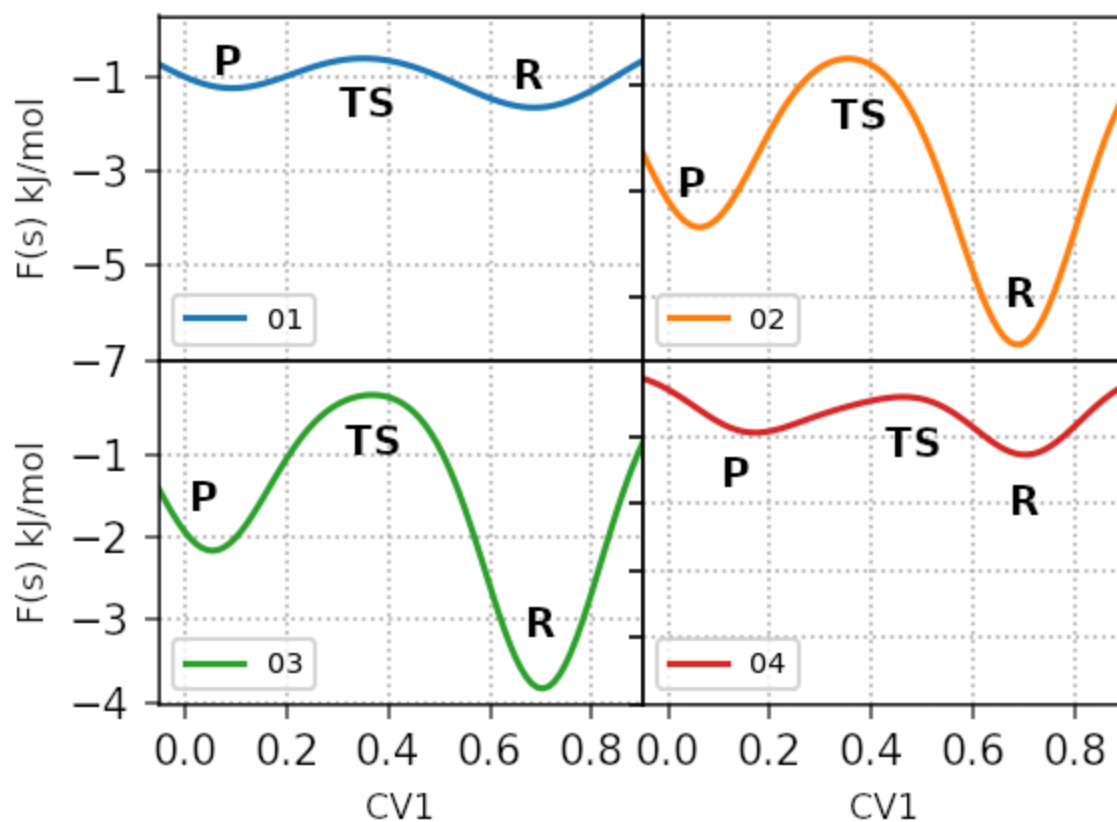


Figure S7. Free energy landscapes of PFOA defluorination by a hydrated electron obtained from our well-tempered metadynamics simulations. R, TS, and P represent the reactant, transition state, and product, respectively.

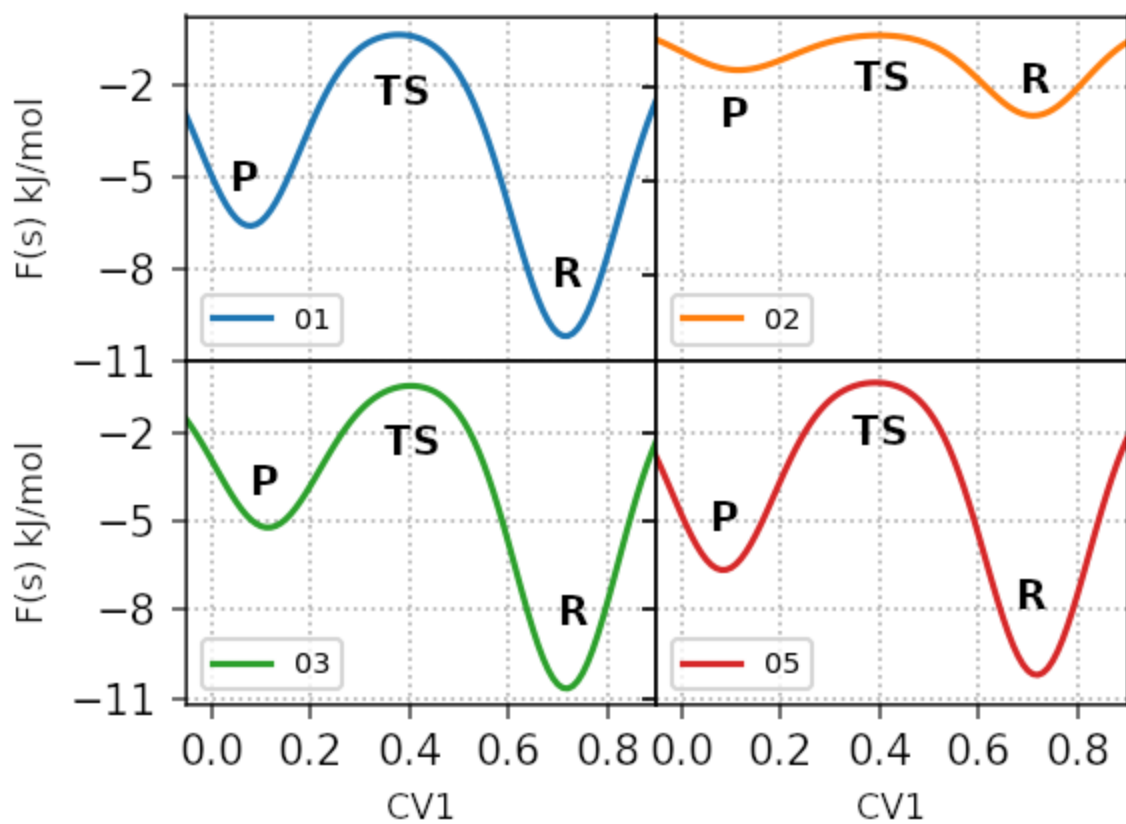


Figure S8. Free energy landscape of PFOS defluorination by a hydrated electron obtained from our well-tempered metadynamics simulations. R, TS, and P represent the reactant, transition state, and product, respectively.

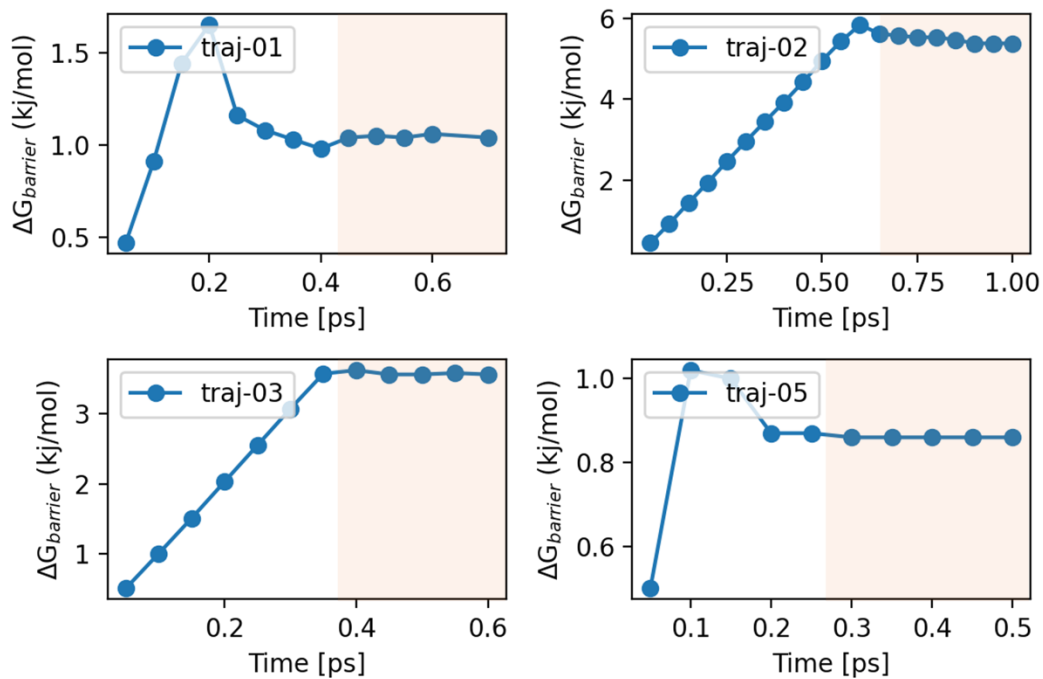


Figure S9. Free energy difference between the transition state and reactant as a function of time for solvated PFOA trajectories. The pale orange region in each plot indicates the convergence area.

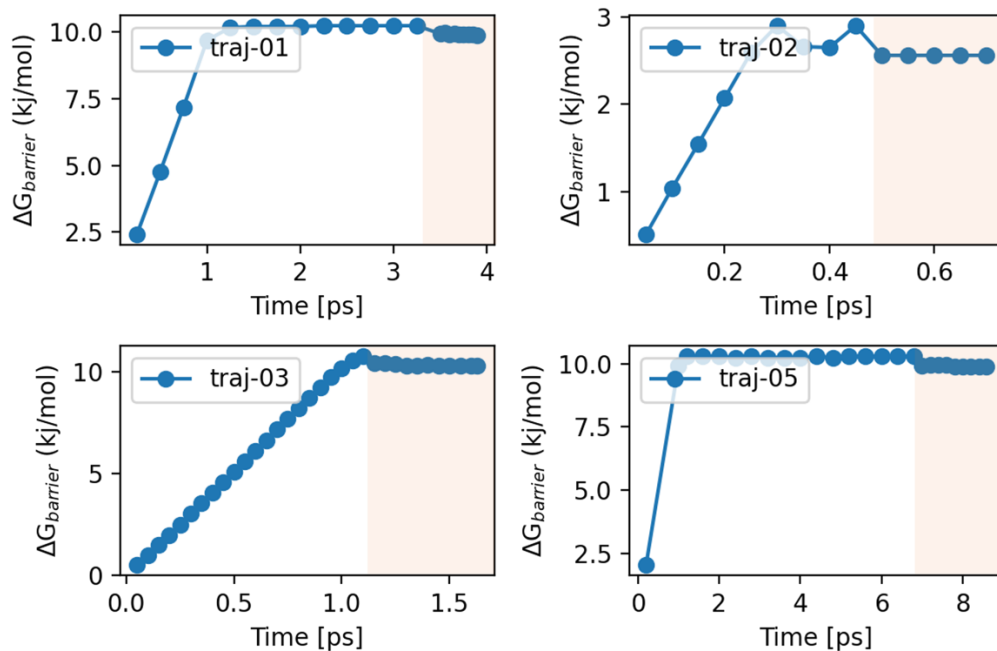


Figure S10. Free energy difference between the transition state and reactant as a function of time for solvated PFOS trajectories. The pale orange region in each plot indicates the convergence area.

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