Electronic Supplementary Information

Real-Time Degradation Dynamics of Hydrated Per- and Polyfluoroalkyl Substances (PFASs) in the Presence of Excess Electrons

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Figure S1. Final geometries of hydrated PFOA molecules obtained with six different initial BOMD conditions (positions and velocities). All NVE simulations were performed with 2 excess electrons, and all simulations were propagated for 150 fs or longer. For each of the different initial conditions, we observe a defluorination in the presence of excess electrons. All of these six initial conditions were obtained from an NVT simulation with a separation of 500-1000 fs between each initial condition.



Figure S2. Final geometries of hydrated PFOS molecules obtained with six different initial BOMD conditions (positions and velocities). All NVE simulations were performed with 2 excess electrons, and all simulations were propagated for 150 fs or longer. For each of the different initial conditions, we observe a defluorination in the presence of excess electrons. All of these six initial conditions were obtained from an NVT simulation with a separation of 500-1000 fs between each initial condition.



Figure S3. Evolution of the spin-density in a hydrated PFOS molecule with one excess electron during an NVE simulation.



Figure S4. Atoms exhibiting the largest changes in Mulliken charges (left) and spin (right) during the initial stages of the simulation (i.e., during C-F bond dissociation). The top (bottom) panel depicts results for a PFOA (PFOS) molecule with one excess electron. In both cases, after the C-F bond dissociation, negative charges (left panels) were localized on the fluorine atoms, and spins (right panels) were localized on the carbon atoms. In the inset of the left panels, we show the atom numbering scheme used in our simulations.



Figure S5. Formation of an HF molecule (bond length ~0.99 Å, circled in pink) in the NVE simulations of (a) PFOA and (b) PFOS with a -2 electronic charge. In both simulations, an H-F bond is formed after 2 ps. In panel (a), the formation of a C=C bond (~1.29 Å, circled in black) can also be seen.

Apart from the *trans*-type intermediate discussed in the main text, we also found that an HF molecule was formed during our simulations (see **Figure S5**). Specifically, one of the dissociated fluorine atoms from the PFAS molecule combines with a proton from the solvent (which originates from PFOA/PFOS releasing its carboxylic/sulfonic acid proton into the solvent) to form an HF molecule. In addition, we observed the formation of an HF molecule in our other NVE simulations as well; as such, we suggest that an HF molecule could also be a significant intermediate or end product of the PFAS degradation process.

Computational Details

All Born-Oppenheimer Molecular Dynamics (BOMD) simulations were performed in a microcanonical (NVE) ensemble using the Quick-Step method as implemented in the CP2K software package.¹ The BOMD equations of motion were integrated with a 0.5 fs time step, and initial velocities and coordinates for all NVE runs were obtained by first running an NVT simulation at 300 K. For the NVT simulations, we used the Nosé-Hoover thermostat of the chain length three. In all the NVT and NVE runs, Grimme's D3 dispersion² correction was employed. To calculate the electronic energies and gradients at each nuclear step, we used density functional theory with a self-interaction corrected PBE³ exchange-correlation functional. Specifically, we have included a self-interaction correction (SIC) for all orbitals in our BOMD simulations using the average density SIC, as implemented in the CP2K package.⁴ Following earlier work,⁵ we tuned the scaling parameters 'a' (=0.2) and 'b' (=0.25) to reproduce the vertical electron affinities of PFOA and PFOS obtained with a non-empirically tuned range-separated LC-BLYP functional (which typically gives energies that match experiment or highlevel wavefunction-based benchmarks^{6,7}). To solve the self-consistent Kohn-Sham equations, we used the molecularly optimized double-zeta quality (DZVP) basis-sets,⁸ which are compatible with the employed Goedecker–Teter–Hutter (GTH) pseudopotentials.^{9,10} For the auxiliary plane-wave (PW) basis used in the Gaussian-and-Plane-Waves method of CP2K,¹¹ we used 600 Ry for the PW energy cutoff and 60 Ry for the reference grid cutoff.

Calculations with Other Exchange-Correlation Functionals

Since prior studies on hydrated electrons have shown that the results are not sensitive to the choice of semi-local functional (particularly PBE vs. BLYP),^{12,13} we omitted additional calculations with the BLYP functional. However, to verify the robustness of our results, we performed additional calculations with the B3LYP hybrid functional and found qualitatively similar results for some of our initial studies. Due to the immense computational cost of hybrid functionals, we did not pursue

additional BOMD calculations with the B3LYP functional, but we anticipate the results to be qualitatively similar to our self-interaction corrected PBE calculations.

Tuning the Scaling Parameters

Following earlier studies,⁵ we tuned the scaling parameters '*a*' and '*b*' to reproduce the vertical electron affinities of PFOA and PFOS, which we obtained with the non-empirically tuned rangeseparated LC-BLYP functional. We found that the values of a = 0.2 and b = 0.25 reproduce these benchmark electron affinities, which we subsequently used in our calculations. We also performed additional calculations with a = 0.2 and b = 0.0, as used in prior studies;⁴ however, even with these different parameters, we observed PFAS defluorination in the presence of excess charges, indicating the robustness of our results.

Number of Explicit Water Molecules Considered in the Present Study

To mimic the surrounding water environment, we solvated each of these PFAS species with 43 explicit water molecules that were treated quantum mechanically. It is important to note that earlier studies have already demonstrated that 31 water molecules are sufficient to reproduce the quantum mechanical behavior of a hydrated electron.⁴ Considering the number of MD simulations performed in this work and the substantial computational demand for each of these *ab initio* MD calculations, the present choice of 43 water molecules was optimal for capturing all the necessary PFAS degradation dynamics without sacrificing accuracy.

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