Supporting Information

Photo-Induced Degradation of PFASs: Excited-State Mechanisms from Real-Time Time-Dependent Density Functional Theory

Sharma S.R.K.C. Yamijala,1,2 Ravindra Shinde,1 Kota Hanasaki,1 Zulfikhar A. Ali,1 and Bryan M. Wong1,*

1Department of Chemical & Environmental Engineering, Materials Science & Engineering Program, Department of Chemistry, and Department of Physics & Astronomy, University of California, Riverside, Riverside, CA 92521, United States

2Department of Chemistry and Center for Atomistic Modelling and Materials Design, Indian Institute of Technology Madras, Chennai - 600036, India

*Corresponding author. E-mail: bryan.wong@ucr.edu. Web: http://www.bmwong-group.com

Contents

p. S2: Density of states of PFOA calculated at various real-space grid spacings.
p. S3: PFOS molecule surrounded with 43 explicit water molecules, optical absorption spectra of PFOS + 43 H2O molecules, and temporal dependence of the electric field of the applied optical pulse.
p. S4: Variations in the dissociation dynamics of PFOS + 43 H2O molecules as a function of time.
p. S5: Variation of selected C–F bond lengths in PFOS as a function of time.
**Figure S1.** Electronic density of states (DOS) of PFOA calculated at various real-space grid spacings.
Figure S2. (a) PFOS molecule surrounded with 43 explicit water molecules (depicted as thin sticks for visual clarity). (b) Optical absorption spectra of PFOS + 43 H$_2$O molecules. (c) Temporal dependence of the electric field of the applied optical pulse used in our calculations.
Figure S3. Variations in the dissociation dynamics of PFOS + 43 H₂O molecules as a function of time. The encircled C21–F24 bond in PFOS dissociates at the end of 32 fs.
Figure S4. Variation of selected C–F bond lengths in PFOS as a function of time (see Fig. S1(a) for atom numbering). After 5 fs, an irreversible elongation of the C21–F24 bond in PFOS occurs.