

# Advanced Experimental and Computational Approaches for Advanced Reduction of PFAS Contaminants

Sohag Biswas, Xian Wang, and Bryan M. Wong\*

<sup>a</sup>Materials Science & Engineering Program, Department of Physics & Astronomy, and Department of Chemistry, University of California-Riverside, Riverside, California 92521, USA

\*E-mail: [bryan.wong@ucr.edu](mailto:bryan.wong@ucr.edu) Website: <http://www.bmwong-group.com>

## Abstract

The elimination of per- and polyfluoroalkyl substances (PFAS) in water continues to garner significant attention due to their enduring presence in the environment and associated health concerns. The emergence of advanced reduction processes (ARPs) holds significant promise in reducing persistent PFAS in water, primarily due to its ability to produce short-lived yet highly reductive hydrated electrons. This concise review offers insights into the latest developments in ARP-based PFAS degradation, encompassing both experimental and theoretical investigations conducted within the last 2 - 5 years. We conclude with an outlook on potential research avenues in this dynamic field and suggest future experimental and computational strategies to enhance ARP capabilities.

## Introduction:

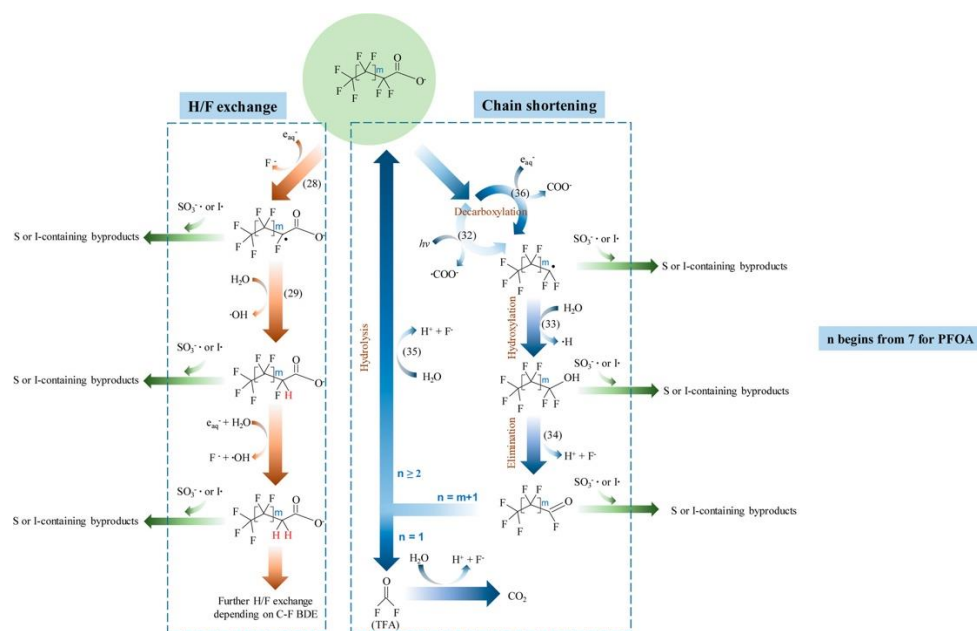
Per- and polyfluoroalkyl substances (PFAS) represent a substantial group of organic fluorine compounds that have accumulated in soil, sediment, and aquatic environments due to their extensive utilization in various industries. These artificially-made compounds also find widespread application as surfactants [1] and coatings in sectors such as textiles,[2] paper manufacturing,[3] fire-suppressing foams,[4–6] cosmetics,[7] and cookware.[8,9] Nevertheless, apprehensions regarding PFAS have steadily increased due to their persistence, tendency to accumulate in organisms, and harmful health effects. Numerous PFAS

compounds have been shown to accumulate in biological tissues, attach to blood proteins, and exhibit extended lifespans within the human body.[10] Human exposure to PFAS has been associated with conditions such as cancer,[11] obesity,[12] heightened cholesterol levels,[13] immune system suppression, and disturbances in hormonal functions.[14] Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are commonly found in surface freshwater,[15] groundwater,[16] drinking water,[17] and landfill leachate.[18,19] These emerging pollutants pose a significant challenge for water treatment due to the absence of practical and efficient removal methods. Given their environmental persistence and harmful effects, developing effective strategies for PFAS elimination is imperative.

Among the limited options available, advanced reduction processes (ARPs) have emerged as a promising solution. ARPs are a form of chemical degradation that generates powerful and highly reductive radicals to eliminate waterborne contaminants. These reductive radicals commonly encompass hydrated electrons and hydrogen radicals and, depending on the specific activation techniques and solutes employed, may also include sulfite radical anions, sulfur dioxide radical anions, or certain organic compounds. While ARPs for treating water and wastewater have only recently gained prominence, research into the interactions of these reductive radicals with various waterborne chemicals commenced several decades ago.

Unlike advanced oxidation processes (AOPs), ARPs degrade oxidized contaminants by generating reducing radicals. ARPs, especially those using hydrated electrons, show superior PFAS degradation and detoxification in wastewater, while AOPs convert PFAS into more toxic short-chain perfluoro-carboxylic acids. These promising results underscore the potential of ARPs as a viable approach for mitigating the environmental impact of PFAS in aqueous media. This short review article presents an update on the chemical mechanisms involved in the

reductive degradation of PFAS with ARPs by experimental and computational techniques within the past 2-5 years. Our review also addresses factors influencing PFAS degradation and defluorination efficiency and explores the environmental ramifications of these effects for the water industry while identifying areas requiring further research.

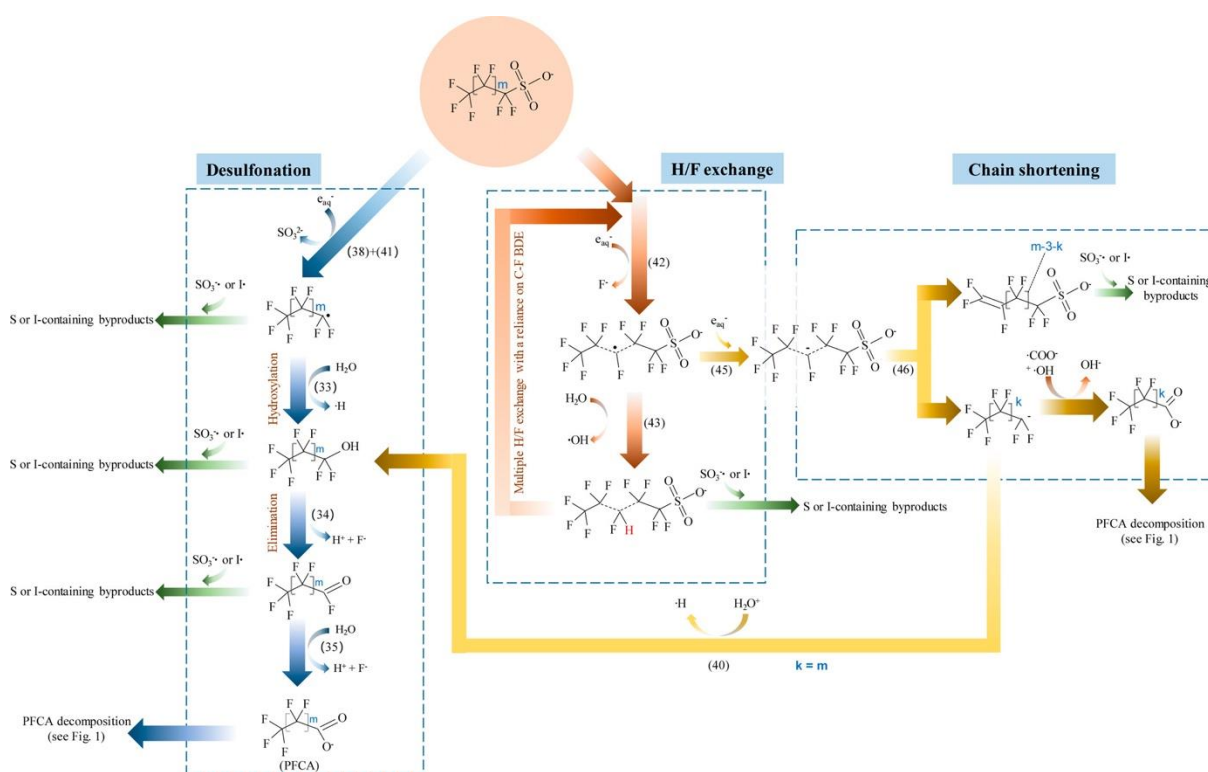


**Figure 1.** Proposed major pathways of advanced reductive degradation of PFOA. Adapted from reference [20]. Copyright American Chemical Society.

### Hydrated Electrons: Generation and Their Role in PFAS Destruction

The primary reason for successfully eliminating PFAS molecules with ARPs can be attributed to the production of hydrated electrons, as indicated by the outcomes of scavenging experiments.[21] ARPs employ electromagnetic radiation to produce highly reducing agents, including hydrated electrons, hydrogen radicals, or radicals originating from the catalyst itself, all of which play a role in initiating the degradation of PFAS.[22,23]

Hydrated electrons stand out as a powerful reducing agent characterized by an exceptionally negative standard reduction potential of  $-2.9\text{ V}$ .<sup>[24]</sup> Despite their brief existence, they exhibit a half-life exceeding  $300\ \mu\text{s}$ .<sup>[25]</sup> Conventionally, their mode of interaction with chemical species is thought to involve a one-electron transfer mechanism. The rate constants for these reactions display considerable variation, spanning from approximately  $10\ \text{M}^{-1}\text{s}^{-1}$  to a diffusion-controlled limit. Remarkably, the activation energies for these reactions fall within a relatively narrow range of  $6$  to  $30\ \text{kJ/mol}$ .<sup>[20]</sup> Numerous methods are available for the efficient degradation of PFAS in water, including UV/sulfite, UV/iodide, UV/diamond, UV/ $\text{Fe}(\text{CN})_6$ , and UV-based treatments with various compounds such as amino polycarboxylic acids and indole derivatives.<sup>[20,21,26–28]</sup> In the following section, we describe the degradation of PFAS using UV/sulfite and UV/iodide ARPs.



**Figure 2.** Proposed major pathways of advanced reductive degradation of PFOS. Adapted from reference [20]. Copyright American Chemical Society.

### Degradation of PFAS using UV-sulfite and UV-iodide ARPs

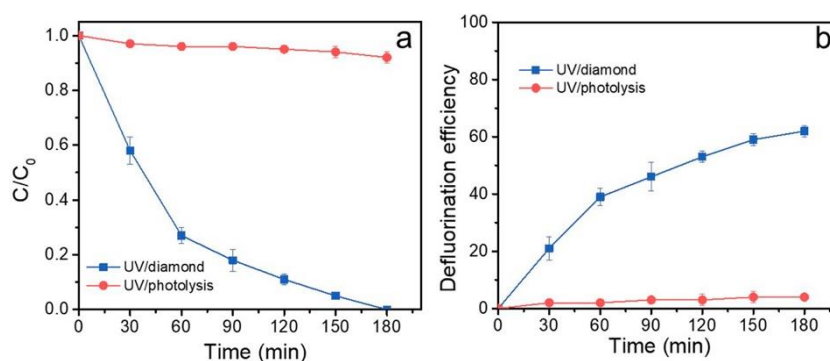
UV/sulfite-based processes for reducing PFAS primarily operate in alkaline environments.[29] Notably, in PFAS treatment, the predominant sulfite species is  $\text{SO}_3^{2-}$  rather than  $\text{HSO}_3^-$ . When exposed to UV light in water, sulfite undergoes photoionization, generating hydrated electrons and an equimolar amount of  $\text{SO}_3^-$ . [20] These hydrated electrons possess remarkable reactivity, enabling them to cleave the carbon-fluorine bonds present in PFAS molecules. The pH level plays a critical role in determining the composition of hydrated electrons as they interact with protons and other scavenging agents.

The photochemical behavior of iodide in water has also been subject to investigation.  $\text{I}^-$  is initially excited in water, forming the  $\text{I}^-\text{H}_2\text{O}^*$  excited species. This complex then thermally decomposes into an intermediate cage complex ( $\text{I}^-, \text{e}^-$ ), allowing electrons to diffuse freely near the  $\text{I}^-$  atom amid water molecules. Ultimately, the caged complex dissociates, yielding hydrated electrons ( $\text{e}_{\text{aq}}^-$ ) and the production of  $\text{I}^-$ .

The degradation of perfluorooctanoic acid (PFOA) through the action of hydrated electrons adheres to a second-order kinetics reaction. In ARPs, PFOA degradation can achieve remarkable efficiency, reaching up to 100%. [20,21,30–32] However, the extent of defluorination, a vital aspect of the process, tends to exhibit significant variability, with maximum efficiencies ranging from 55% to 96% in most investigations. [20,21,30–32] For PFOA degradation, two significant concurrent reactions (**Figure 1**) involving hydrated electrons have been identified: H/F exchange, which signifies the cleavage of C–F bonds, and chain shortening, implying the breaking of C–C bonds. [29,33] Notably, in the PFOA molecule,

the  $-CF_2-$  unit at the alpha position adjacent to the carboxyl group displays increased reactivity. This enhanced reactivity is likely attributed to the inductive effect of the head group, making it a favored site for reactions.[26]

Regarding PFOS, three reaction pathways (**Figure 2**) have been proposed to enable reductive degradation by hydrated electrons. These pathways include desulfonation, H/F exchange, and chain shortening through C–C bond cleavage. In the desulfonation process, the hydrated electron attaches to the molecule, resulting in the dissociation of the C–S bond and the formation of  $C_8F_{17}OH$ . This compound can subsequently undergo a transformation, leading to the degradation of PFOA.[20]



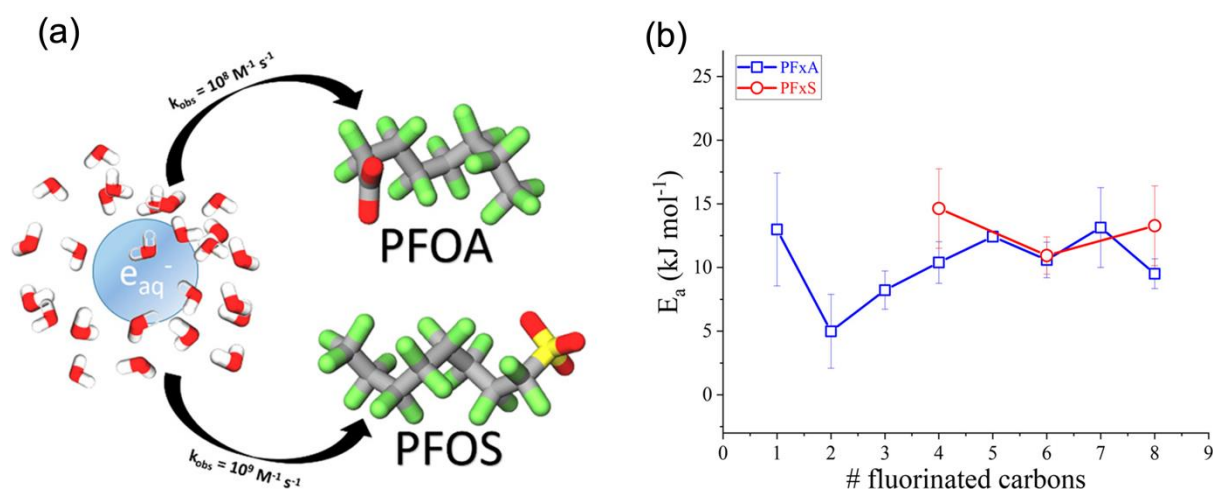
**Figure 3.** PFOA removal efficiency by (a) UV/diamond and (b) corresponding defluorination efficiency with a PFOA concentration of  $20 \mu\text{mol L}^{-1}$ . Adapted from reference [34]. Copyright American Chemical Society.

### Degradation of PFOA using UV/diamond ARPs

Although the generation of hydrated electrons in the UV/sulfite process has been recognized as an effective activation method for degrading target pollutants, the ARP water treatment technology associated with the UV/sulfite process faces two significant

challenges.[35,36] First, there is potential secondary pollution in the homogeneous process when sulfite is added. Second, the generation of hydrated electrons in the UV/sulfite process is pH-dependent, making it less efficient under acidic conditions.[37] Consequently, there is a pressing need to develop an efficient and environmentally friendly heterogeneous catalyst for producing hydrated electrons, particularly for PFAS treatment in water.

Recently, a UV/diamond system was employed to generate hydrated electrons for decomposing PFOA.[34] Diamond, a wide-bandgap semiconductor catalyst with a 5.5 eV bandgap, has been shown in various studies to produce photogenerated electrons when exposed to UV light.[38,39] The unique properties of diamond include a negative conduction band maximum (CBM) of -4.9 V and an electron affinity (EA) of -0.5 eV.[40] Unlike most semiconductors, the CBM of diamond is positioned 0.8 – 1.3 eV above the vacuum level, efficiently emitting electrons when illuminated with UV light.[39] Recent studies have explored the potential for PFOA degradation using in situ-generated hydrated electrons on the surface of a diamond catalyst across a broad pH range. **Figure 3** illustrates that direct UV photolysis alone led to minimal PFOA degradation after 180 minutes of irradiation.[34] In sharp contrast, rapid PFOA removal occurred when a diamond catalyst was introduced with UV irradiation. Within 180 minutes, nearly all of the initial PFOA concentration was decomposed. The UV/diamond ARP revealed a stepwise reaction process in which PFOA was decomposed into shorter perfluorinated small molecules, consistent with earlier findings.[41,42]



**Figure 4.** (a) Schematic representation of ARP approaches using hydrated electrons for degradation of PFAS. (b) Activation energies for the reduction of PFxA (blue squares) and PFxS (red circles) as a function of the number of the fluorinated carbons comprising the fluoroalkyl backbone. Adapted from reference [28]. Copyright American Chemical Society.

### Reaction Kinetics for PFAS Degradation Using ARPs

Although ARPs enable degradation pathways for PFAS with hydrated electrons, recent research has focused on time-resolved kinetic analyses of PFAS with hydrated electrons.[28,43] Recently, Maza *et al.*[28] generated hydrated electrons by exciting a  $K_4Fe(CN)_6$  solution with UV radiation at 266 nm under  $N_2$  and measured the rate constants and activation energies for the initial reduction of PFOA and PFOS. Interestingly, the reduction of both PFOA and PFOS showed little dependence on the number of carbon atoms in the molecules. The reduction occurred with apparent rate constants ranging from  $10^8$  to  $10^9 M^{-1} s^{-1}$ , with the rate constant of PFOA being roughly half that of PFOS. **Figure 4** illustrates the activation energies for PFOA and PFOS in the presence of hydrated electrons, showing no



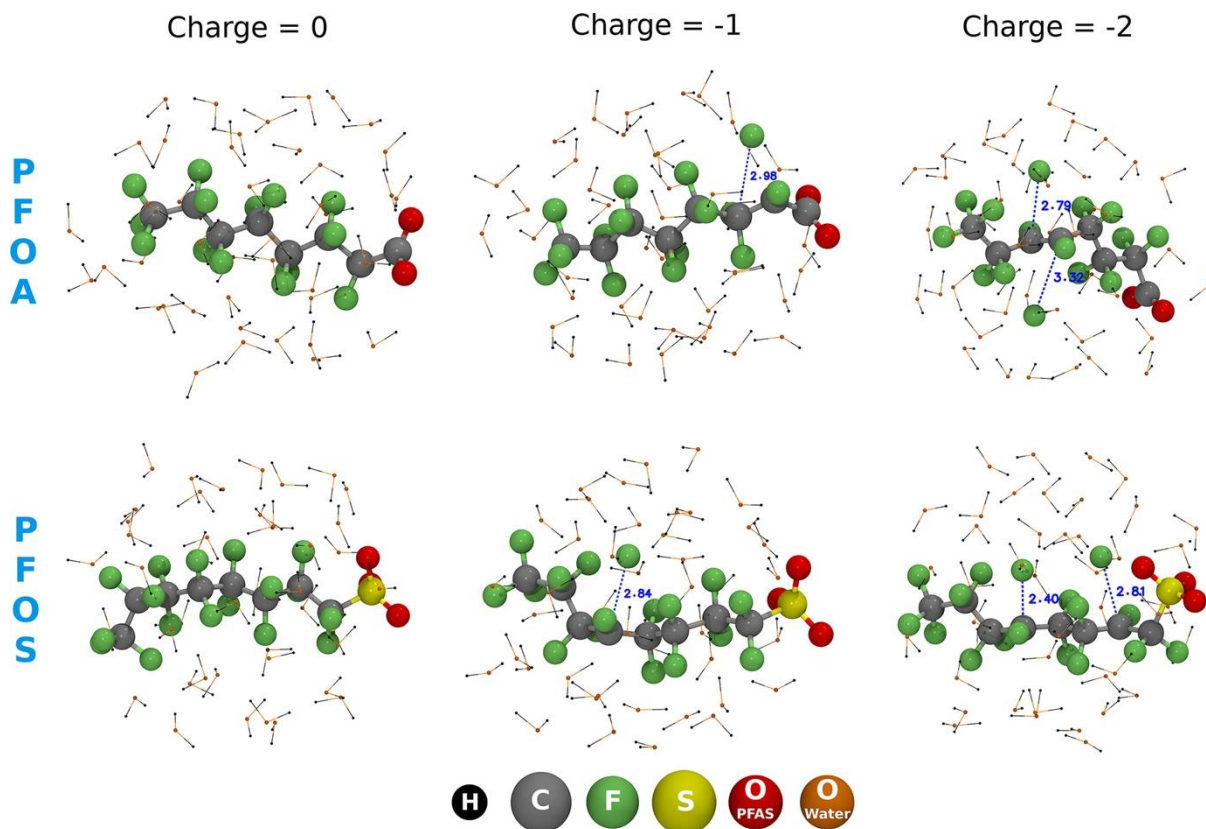
significant difference between the two. The magnitude of the activation energy (~11 kJ/mol) suggests that the reduction of both PFOA and PFOS operates in a diffusion-controlled regime.

### ***Ab Initio* Molecular Dynamics (AIMD): PFAS Degradation Dynamics Using Excess and Hydrated Electron**

While experimental studies on ARPs and PFAS degradation are abundant, computational and theoretical research on time-resolved dynamic studies of ARPs is scarce.[44] Most computational ARP investigations have focused on static, time-independent properties near stationary points on the PFAS potential energy surface, which neglects dynamical effects and does not give direct information on defluorination time scales or kinetics.

To shed mechanistic insight into these time-resolved degradation events, our group conducted pioneering AIMD simulations of PFOA and PFOS in charged aqueous environments to elucidate PFAS degradation dynamics using ARP. In this study, each PFAS molecule was solvated by 43 explicit water molecules with excess charges using a self-interaction corrected PBE functional.[45] **Figure 5** illustrates solvated PFOA and PFOS snapshots after one ps of NVE (constant Number, Volume, and Energy) simulations. The left column shows their stability in neutral aqueous environments, consistent with experimental observations. In the middle and right columns, AIMD results with -1 and -2 charges for both PFOA and PFOS show a rapid dissociation of the strongest C–F bonds in PFAS (< 100 fs) due to the presence of excess electrons (the number of dissociated C–F bonds is directly related to the extra electrons). Moreover, defluorination in the presence of two excess electrons forms an intermediate with an alkene-type C=C bond, a critical step in PFAS degradation. These simulations also indicate the potential formation of H–F molecules. As such, this study showed that AIMD calculations

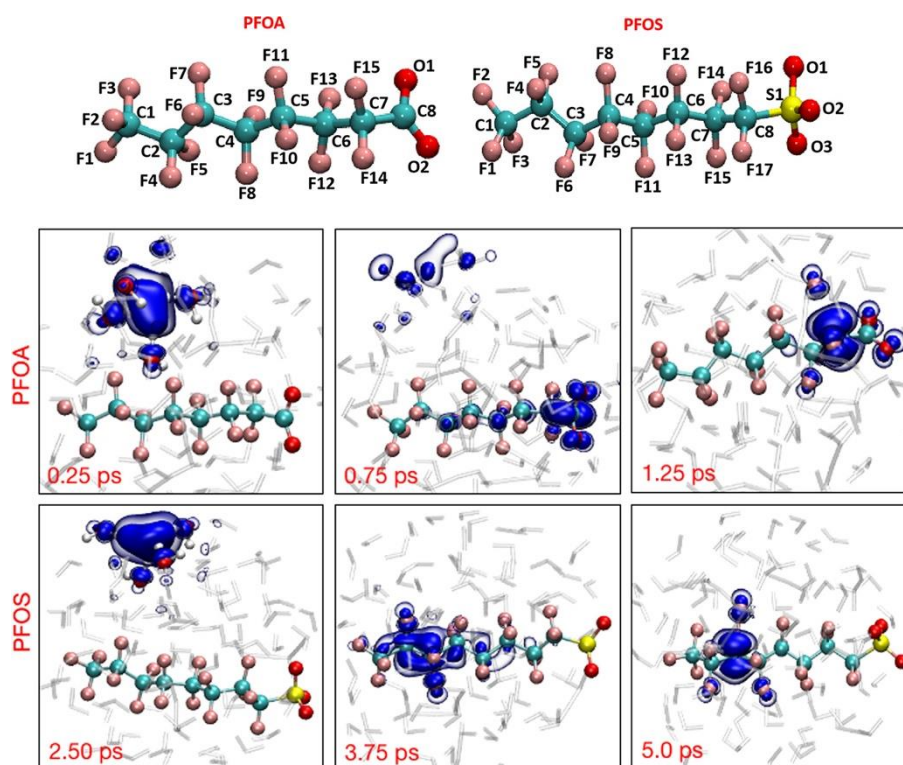
can shed mechanistic insight into real-time PFAS degradation dynamics in charged environments.



**Figure 5.** Geometries of solvated PFOA (top panel) and PFOS (bottom panel) anions after 1 ps of NVE simulations with 0 (left), 1 (middle), and 2 (right) excess electrons. PFOA and PFOS lose their acidic proton to the surrounding water molecules during the simulation and are found in their anionic forms. Both PFOA and PFOS are stable in neutral environments, whereas defluorination rapidly occurs in the presence of 1 and 2 excess electrons. Adapted from reference [44]. Copyright Royal Society of Chemistry.

Although the study described previously explored the dynamics of PFAS degradation under the influence of additional charges, it is crucial to highlight that simply adding an extra

electron in an AIMD simulation does not accurately replicate the behavior of hydrated electrons in ARP experiments. This discrepancy emerges because the surrounding water molecules fail to effectively polarize the extra electron, resulting in configurations of the hydrated electron that deviate from realistic experimental conditions. A hydrated electron can only manifest when the excess electron sheds enough energy to form a stable localized cavity firmly bound with water molecules. To correctly simulate the effects of a hydrated electron on PFAS, we employed DFT-based AIMD and metadynamics simulations to investigate its interaction with PFOA and PFOS.[46,47] **Figure 6** illustrates the time-dependent evolution of spin density for the hydrated electron and the subsequent C–F defluorination of PFOA/PFOS in the presence of 81 explicit water molecules. Additional information on the preparation of the hydrated electron can be found in reference [46]. Importantly, the defluorination process of PFAS by a hydrated electron shows significant differences compared to that involving an excess electron. In solvated PFOA, C–F bonds break within one picosecond, while C–F bond cleavage ranges from femtoseconds to a few picoseconds for PFOS. This time difference results from the more compact and tightly bound hydrated electron cavity, reducing its reactivity toward PFOS. In these scenarios, the hydrated electron targets either the C3 or C4 sites.



**Figure 6.** (Top panels) Chemical structure and atom numbering scheme of the PFOA and PFOS anions. Time-resolved evolution of the spin density of the hydrated electron for representative trajectories of PFOA (middle panels) and PFOS (bottom panels). Adapted from reference [47]. Copyright American Chemical Society.

In addition, we conducted metadynamics simulations to explore the free-energy profiles of various C–F bond cleavages in PFOA and PFOS. Notably, the free energy activation barrier for PFOS C–F bond dissociation is three times higher than PFOA. These calculations and other statistical analyses (detailed in reference [46]) demonstrate that the hydrated electron has a more rigid solvation shell, making it less reactive with PFOS, resulting in slower defluorination. Both PFOS and PFOA fall below the diffusion-controlled limit, which indicates that the degradation process is independent of the overall chemical rate constant.[28,46] Importantly, our AIMD simulations reveal that all C–F bonds in PFAS have a high probability

of dissociation in the presence of hydrated electrons. This kinetic/statistical process differs from a thermodynamic one: even though certain C–F bonds may be more thermodynamically reactive, all C–F bonds exhibit a high probability of dissociation, as shown by our AIMD simulations. These DFT-based metadynamics simulations represent the first *ab initio* dynamics study of PFAS degradation via hydrated electrons, a configuration previously overlooked in prior computational studies.

### Conclusions and Future Outlooks

In summary, recent advances in ARPs for PFAS degradation, explored experimentally and theoretically, hold promise for addressing PFAS contamination in water and wastewater treatment. ARPs effectively degrade various PFAS compounds, outperforming many other chemical methods. However, more research is needed to optimize the hydrated electron-based PFAS degradation process. The high reactivity of hydrated electrons with both PFAS and abundant water matrix components limits their availability for PFAS degradation, which reduces the efficiency of water treatment. Innovative strategies are needed to overcome this scavenging effect. Specifically, addressing the inhibitory effect of H<sup>+</sup> ions can reduce the reliance of ARPs on high pH levels, eliminating the need for costly pH adjustments. Additionally, factors such as total dissolved solids (TDS), incomplete defluorination, energy consumption, and dissolved oxygen influence PFAS degradation in ARPs, require further optimization for effective and environmentally conscious remediation technologies.

AIMD simulations can shed mechanistic insight into ARPs, but these predictive techniques have substantial computational costs. PFAS degradation often occurs in complex, heterogeneous systems with intricate interfaces and solvent interactions. Achieving realism in simulations requires larger system sizes to accurately mimic experimental conditions.

Extending both the length and time scales of these simulations is crucial for capturing the spatial and temporal dynamics of PFAS degradation experiments. Our research group is actively addressing these challenges by employing large-scale semiempirical techniques and cutting-edge hardware accelerators beyond current DFT capabilities.[48–50] As computational resources and new algorithms continue to improve, we recommend the environmental research community to use these advanced quantum dynamics simulations in concert with experimental efforts to gain deeper insight into PFAS degradation dynamics and other environmental processes.

### **Data Availability**

Data will be made available on request.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

### **Acknowledgements**

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### **References and recommended reading:**

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest

•• of outstanding interest

- [1] B.C. Crone, T.F. Speth, D.G. Wahman, S.J. Smith, G. Abulikemu, E.J. Kleiner, J.G. Pressman, Occurrence of per- and polyfluoroalkyl substances (PFAS) in source water and their treatment in drinking water, *Crit. Rev. Environ. Sci. Technol.* 49 (2019) 2359–2396. <https://doi.org/10.1080/10643389.2019.1614848>.
- [2] D.S. Drage, M. Sharkey, H. Berresheim, M. Coggins, S. Harrad, Rapid Determination of Selected PFAS in Textiles Entering the Waste Stream, *Toxics*. 11 (2023) 55. <https://doi.org/10.3390/toxics11010055>.
- [3] H.A. Langberg, H.P.H. Arp, G.D. Breedveld, G.A. Slinde, Å. Høiseter, H.M. Grønning, M. Jartun, T. Rundberget, B.M. Jenssen, S.E. Hale, Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: Source and historic emission tracking, *Environ. Pollut.* 273 (2021) 116259. <https://doi.org/10.1016/j.envpol.2020.116259>.
- [4] J.L. Guelfo, D.T. Adamson, Evaluation of a national data set for insights into sources, composition, and concentrations of per- and polyfluoroalkyl substances (PFASs) in U.S. drinking water, *Environ. Pollut.* 236 (2018) 505–513. <https://doi.org/10.1016/j.envpol.2018.01.066>.
- [5] Å. Høisæter, G.D. Breedveld, Leaching potential of per- and polyfluoroalkyl substances from source zones with historic contamination of aqueous film forming foam - a surfactant mixture problem, *Environ. Adv.* 8 (2022) 100222. <https://doi.org/10.1016/j.envadv.2022.100222>.
- [6] T.A. Bruton, D.L. Sedlak, Treatment of Aqueous Film-Forming Foam by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation, *Environ. Sci. Technol.* 51 (2017) 13878–13885. <https://doi.org/10.1021/acs.est.7b03969>.
- [7] H.D. Whitehead, M. Venier, Y. Wu, E. Eastman, S. Urbanik, M.L. Diamond, A. Shalin, H. Schwartz-Narbonne, T.A. Bruton, A. Blum, Z. Wang, M. Green, M. Tighe, J.T. Wilkinson, S. McGuinness, G.F. Peaslee, Fluorinated Compounds in North American Cosmetics, *Environ. Sci. Technol. Lett.* 8 (2021) 538–544. <https://doi.org/10.1021/acs.estlett.1c00240>.
- [8] M. Sajid, M. Ilyas, PTFE-coated non-stick cookware and toxicity concerns: a perspective, *Environ. Sci. Pollut. Res.* 24 (2017) 23436–23440. <https://doi.org/10.1007/s11356-017-0095-y>.
- [9] E. Panieri, K. Baralic, D. Djukic-Cosic, A. Buha Djordjevic, L. Saso, PFAS Molecules: A Major Concern for the Human Health and the Environment, *Toxics*. 10 (2022) 44. <https://doi.org/10.3390/toxics10020044>.
- [10] S.H. Ho, S.X.H. Soh, M.X. Wang, J. Ong, A. Seah, Y. Wong, Z. Fang, S. Sim, J.T. Lim, Perfluoroalkyl substances and lipid concentrations in the blood: A systematic review of epidemiological studies, *Sci. Total Environ.* 850 (2022) 158036. <https://doi.org/10.1016/j.scitotenv.2022.158036>.
- [11] R.I. Boyd, S. Ahmad, R. Singh, Z. Fazal, G.S. Prins, Z. Madak Erdogan, J. Irudayaraj, M.J. Spinella, Toward a Mechanistic Understanding of Poly- and Perfluoroalkylated Substances and Cancer, *Cancers*. 14 (2022) 2919. <https://doi.org/10.3390/cancers14122919>.



- [12] S.D. Geiger, P. Yao, M.G. Vaughn, Z. Qian, PFAS exposure and overweight/obesity among children in a nationally representative sample, *Chemosphere*. 268 (2021) 128852. <https://doi.org/10.1016/j.chemosphere.2020.128852>.
- [13] M.E. Andersen, B. Hagenbuch, U. Apte, J.C. Corton, T. Fletcher, C. Lau, W.L. Roth, B. Staels, G.L. Vega, H.J. Clewell, M.P. Longnecker, Why is elevation of serum cholesterol associated with exposure to perfluoroalkyl substances (PFAS) in humans? A workshop report on potential mechanisms, *Toxicology*. 459 (2021) 152845. <https://doi.org/10.1016/j.tox.2021.152845>.
- [14] L. Zheng, Z. Wang, R. Yang, W. Chen, J. Zhang, R. Li, W. Lv, B. Lin, J. Luo, The interference between effects of PFAS exposure on thyroid hormone disorders and cholesterol levels: an NHANES analysis, *Environ. Sci. Pollut. Res.* 30 (2023) 90949–90959. <https://doi.org/10.1007/s11356-023-28739-8>.
- [15] T. Schwichtenberg, D. Bogdan, C.C. Carignan, P. Reardon, J. Rewerts, T. Wanzek, J.A. Field, PFAS and Dissolved Organic Carbon Enrichment in Surface Water Foams on a Northern U.S. Freshwater Lake, *Environ. Sci. Technol.* 54 (2020) 14455–14464. <https://doi.org/10.1021/acs.est.0c05697>.
- [16] B. Xu, S. Liu, J.L. Zhou, C. Zheng, J. Weifeng, B. Chen, T. Zhang, W. Qiu, PFAS and their substitutes in groundwater: Occurrence, transformation and remediation, *J. Hazard. Mater.* 412 (2021) 125159. <https://doi.org/10.1016/j.jhazmat.2021.125159>.
- [17] G.B. Post, Recent US State and Federal Drinking Water Guidelines for Per- and Polyfluoroalkyl Substances, *Environ. Toxicol. Chem.* 40 (2021) 550–563. <https://doi.org/10.1002/etc.4863>.
- [18] J.R. Masoner, D.W. Kolpin, I.M. Cozzarelli, K.L. Smalling, S.C. Bolyard, J.A. Field, E.T. Furlong, J.L. Gray, D. Lozinski, D. Reinhart, A. Rodowa, P.M. Bradley, Landfill leachate contributes per-/poly-fluoroalkyl substances (PFAS) and pharmaceuticals to municipal wastewater, *Environ. Sci. Water Res. Technol.* 6 (2020) 1300–1311. <https://doi.org/10.1039/D0EW00045K>.
- [19] Z. Wei, T. Xu, D. Zhao, Treatment of per- and polyfluoroalkyl substances in landfill leachate: status, chemistry and prospects, *Environ. Sci. Water Res. Technol.* 5 (2019) 1814–1835. <https://doi.org/10.1039/C9EW00645A>.
- [20] J. Cui, P. Gao, Y. Deng, Destruction of Per- and Polyfluoroalkyl Substances (PFAS) with Advanced Reduction Processes (ARPs): A Critical Review, *Environ. Sci. Technol.* 54 (2020) 3752–3766. <https://doi.org/10.1021/acs.est.9b05565>.

This study offers a comprehensive assessment of the mechanisms and effectiveness of eliminating PFAS using hydrated electrons. The paper explores the distinctive characteristics of hydrated electrons and their generation in various ARP systems, notably UV/sulfite and UV/iodide. Additionally, it examines and contrasts different degradation mechanisms for PFAS, including PFOA, PFOS, and shorter-chain PFAS compounds.

- [21] Z. Sun, C. Zhang, L. Xing, Q. Zhou, W. Dong, M.R. Hoffmann, UV/Nitritotriacetic Acid Process as a Novel Strategy for Efficient Photoreductive Degradation of Perfluorooctanesulfonate, *Environ. Sci. Technol.* 52 (2018) 2953–2962. <https://doi.org/10.1021/acs.est.7b05912>.
- [22] K. Yu, X. Li, L. Chen, J. Fang, H. Chen, Q. Li, N. Chi, J. Ma, Mechanism and efficiency of contaminant reduction by hydrated electron in the sulfite/iodide/UV process, *Water Res.* 129 (2018) 357–364. <https://doi.org/10.1016/j.watres.2017.11.030>.



- [23] Y. Zhao, C. Zhang, L. Chu, Q. Zhou, B. Huang, R. Ji, X. Zhou, Y. Zhang, Hydrated electron based photochemical processes for water treatment, *Water Res.* 225 (2022) 119212. <https://doi.org/10.1016/j.watres.2022.119212>.
- [24] H.A. Schwarz, Free radicals generated by radiolysis of aqueous solutions, *J. Chem. Educ.* 58 (1981) 101. <https://doi.org/10.1021/ed058p101>.
- [25] E.J. Hart, The Hydrated Electron, *Science.* 146 (1964) 19–25. <https://doi.org/10.1126/science.146.3640.19>.
- [26] M.J. Bentel, Y. Yu, L. Xu, Z. Li, B.M. Wong, Y. Men, J. Liu, Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management, *Environ. Sci. Technol.* 53 (2019) 3718–3728. <https://doi.org/10.1021/acs.est.8b06648>.
- [27] Y. Bao, S. Deng, X. Jiang, Y. Qu, Y. He, L. Liu, Q. Chai, M. Mumtaz, J. Huang, G. Cagnetta, G. Yu, Degradation of PFOA Substitute: GenX (HFPO–DA Ammonium Salt): Oxidation with UV/Persulfate or Reduction with UV/Sulfite?, *Environ. Sci. Technol.* 52 (2018) 11728–11734. <https://doi.org/10.1021/acs.est.8b02172>.
- [28] W.A. Maza, V.M. Breslin, J.C. Owrutsky, B.B. Pate, A. Epshteyn, Nanosecond Transient Absorption of Hydrated Electrons and Reduction of Linear Perfluoroalkyl Acids and Sulfonates, *Environ. Sci. Technol. Lett.* 8 (2021) 525–530. <https://doi.org/10.1021/acs.estlett.1c00383>.

This study provides rate constants and activation energies associated with the initial reduction of linear PFAS by hydrated electrons as measured using temperature-dependent transient absorption spectroscopy. This article highlighted the diffusion-controlled nature of PFAS degradation using hydrated electrons.

- [29] Z. Ren, U. Bergmann, T. Leiviskä, Reductive degradation of perfluorooctanoic acid in complex water matrices by using the UV/sulfite process, *Water Res.* 205 (2021) 117676. <https://doi.org/10.1016/j.watres.2021.117676>.
- [30] H. Tian, J. Gao, H. Li, S.A. Boyd, C. Gu, Complete Defluorination of Perfluorinated Compounds by Hydrated Electrons Generated from 3-Indole-acetic-acid in Organomodified Montmorillonite, *Sci. Rep.* 6 (2016) 32949. <https://doi.org/10.1038/srep32949>.
- [31] C. Guo, C. Zhang, Z. Sun, X. Zhao, Q. Zhou, M.R. Hoffmann, Synergistic impact of humic acid on the photo-reductive decomposition of perfluorooctanoic acid, *Chem. Eng. J.* 360 (2019) 1101–1110. <https://doi.org/10.1016/j.cej.2018.10.204>.
- [32] H. Tian, C. Gu, Effects of different factors on photodefluorination of perfluorinated compounds by hydrated electrons in organo-montmorillonite system, *Chemosphere.* 191 (2018) 280–287. <https://doi.org/10.1016/j.chemosphere.2017.10.074>.
- [33] M. Gar Alalm, D.C. Boffito, Mechanisms and pathways of PFAS degradation by advanced oxidation and reduction processes: A critical review, *Chem. Eng. J.* 450 (2022) 138352. <https://doi.org/10.1016/j.cej.2022.138352>.
- [34] G. Liu, C. Feng, P. Shao, Degradation of Perfluorooctanoic Acid with Hydrated Electron by a Heterogeneous Catalytic System, *Environ. Sci. Technol.* 56 (2022) 6223–6231. <https://doi.org/10.1021/acs.est.1c06793>.

This study introduces a novel approach using a heterogeneous UV/diamond catalytic system to break down PFAS pollutants. The exploration of the capabilities of diamond to release high-energy photoelectrons into a water matrix marks a transformative development in ARPs, paving the way for enhanced utilization of heterogeneous catalytic processes to effectively eliminate PFAS with the assistance of hydrated electrons.

- [35] F. Glaser, C. Kerzig, O.S. Wenger, Multi-Photon Excitation in Photoredox Catalysis: Concepts, Applications, Methods, *Angew. Chem. Int. Ed.* 59 (2020) 10266–10284. <https://doi.org/10.1002/anie.201915762>.
- [36] Y. Gu, T. Liu, H. Wang, H. Han, W. Dong, Hydrated electron based decomposition of perfluorooctane sulfonate (PFOS) in the VUV/sulfite system, *Sci. Total Environ.* 607–608 (2017) 541–548. <https://doi.org/10.1016/j.scitotenv.2017.06.197>.
- [37] L. Yang, L. He, J. Xue, Y. Ma, Y. Shi, L. Wu, Z. Zhang, UV/SO<sub>3</sub><sup>2-</sup> based advanced reduction processes of aqueous contaminants: Current status and prospects, *Chem. Eng. J.* 397 (2020) 125412. <https://doi.org/10.1016/j.cej.2020.125412>.
- [38] L. Zhang, D. Zhu, G.M. Nathanson, R.J. Hamers, Selective Photoelectrochemical Reduction of Aqueous CO<sub>2</sub> to CO by Solvated Electrons, *Angew. Chem. Int. Ed.* 53 (2014) 9746–9750. <https://doi.org/10.1002/anie.201404328>.
- [39] D. Zhu, L. Zhang, R.E. Ruther, R.J. Hamers, Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction, *Nat. Mater.* 12 (2013) 836–841. <https://doi.org/10.1038/nmat3696>.
- [40] W.E. Pickett, Negative Electron Affinity and Low Work Function Surface: Cesium on Oxygenated Diamond (100), *Phys. Rev. Lett.* 73 (1994) 1664–1667. <https://doi.org/10.1103/PhysRevLett.73.1664>.
- [41] G. Liu, H. Zhou, J. Teng, S. You, Electrochemical degradation of perfluorooctanoic acid by macro-porous titanium suboxide anode in the presence of sulfate, *Chem. Eng. J.* 371 (2019) 7–14. <https://doi.org/10.1016/j.cej.2019.03.249>.
- [42] Y.-C. Lee, S.-L. Lo, P.-T. Chiueh, D.-G. Chang, Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate, *Water Res.* 43 (2009) 2811–2816. <https://doi.org/10.1016/j.watres.2009.03.052>.
- [43] W.A. Maza, B.D. Etz, T.C. Schutt, B.L. Chaloux, V.M. Breslin, B.B. Pate, M.K. Shukla, J.C. Owrutsky, A. Epshteyn, Impact of Submicellar Aggregation on Reduction Kinetics of Perfluorooctanoate by the Hydrated Electron, *Environ. Sci. Technol. Lett.* 9 (2022) 226–232. <https://doi.org/10.1021/acs.estlett.1c01020>.
- [44] S.S.R.K.C. Yamijala, R. Shinde, B.M. Wong, Real-time degradation dynamics of hydrated per- and polyfluoroalkyl substances (PFASs) in the presence of excess electrons, *Phys. Chem. Chem. Phys.* 22 (2020) 6804–6808. <https://doi.org/10.1039/C9CP06797C>.

This article provides the first real-time assessment of PFAS degradation in the presence of excess electrons. In particular, this article showed that the initial phase of PFAS degradation involves the transformation of an alkane-type C–C bond into an alkene-type C=C bond, which is initiated by the trans elimination of fluorine atoms bonded to these adjacent carbon atoms.

- [45] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- [46] S. Biswas, S.S.R.K.C. Yamijala, B.M. Wong, Degradation of Per- and Polyfluoroalkyl Substances with Hydrated Electrons: A New Mechanism from First-Principles Calculations, *Environ. Sci. Technol.* 56 (2022) 8167–8175. <https://doi.org/10.1021/acs.est.2c01469>.

This research provides the first ab initio molecular dynamics study of PFAS degradation via hydrated electrons, a configuration that has been previously overlooked in prior computational studies. This study emphasizes that PFAS degradation is primarily diffusion-

controlled and any C–F bond is susceptible to electron attachment and subsequent defluorination.

- [47] S. Biswas, B.M. Wong, Beyond Conventional Density Functional Theory: Advanced Quantum Dynamical Methods for Understanding Degradation of Per- and Polyfluoroalkyl Substances, *ACS EST Eng.* (2023). <https://doi.org/10.1021/acsestengg.3c00216>.
- [48] M.B. Oviedo, B.M. Wong, Real-Time Quantum Dynamics Reveals Complex, Many-Body Interactions in Solvated Nanodroplets, *J. Chem. Theory Comput.* 12 (2016) 1862–1871. <https://doi.org/10.1021/acs.jctc.5b01019>.
- [49] S.S.R.K.C. Yamijala, Ma.B. Oviedo, B.M. Wong, Density Functional Tight Binding Calculations for Probing Electronic-Excited States of Large Systems, in: *Rev. Comput. Chem.* Vol. 32, John Wiley & Sons, Ltd, 2022: pp. 45–79. <https://doi.org/10.1002/9781119625933.ch2>.
- [50] N.V. Ilawe, M.B. Oviedo, B.M. Wong, Real-Time Quantum Dynamics of Long-Range Electronic Excitation Transfer in Plasmonic Nanoantennas, *J. Chem. Theory Comput.* 13 (2017) 3442–3454. <https://doi.org/10.1021/acs.jctc.7b00423>.

### Graphical Abstract

