

A First Principles Insight into an Environmental Problem

Ab-Initio Molecular Dynamics Simulation for the Treatment of Water with Organic UV filters as Pollutants

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In Short

- Simulate the electrochemical treatment of water polluted with the seven most common UV filters.
- Model the oxidizing anodic environment using the **CPMD** code.
- Introduce the products from the previously obtained oxidative reactions into new systems iteratively.
- Implement AI to analyze the data quickly, thus scaling the amount of dynamics runs.

The global demand of sunscreens had raised due to awareness of the risk that solar overexposure represents. In the case of the southern hemisphere, every year the ozone hole affects the territories of “Tierra del Fuego” and “Patagonia” (Argentina and Chile) and their population of about 500 000 people for several days between the months of August to December [1]. Currently, approximately 40 active ingredients have been registered in different countries, but only nine are widely employed. These include the inorganic compounds titanium dioxide (TiO₂) and zinc oxide (ZnO), and seven organic UV filters: BMD, BP3, BP4, HS, ODP, OMS and OS [2]. The increasing use of organic UV filters implies contamination of large amounts of water. It was found that the current environmental concentrations of these UV filters are reaching levels that can produce adverse effects, particularly on corals and microalgae [3]. For these reasons, UV filters are considered as emerging contaminants and there has been a growing interest in the development of wastewater treatment methods (**WWTMs**) that remove these compounds.

The most common WWTM is chlorination, which has been linked to the formation of toxic by-products. Consequently, alternative and supplementary methods are being investigated [4]. An additional alternative is electrochemical water treatment, since it provides a versatile, efficient, cost-effective, easily automatable, and clean process. However, it is important to know what kind of products can be obtained when treating contaminated water with electrochemical methods, so it is necessary to study the possible oxidation mechanisms of these UV filters [5].

Car-Parrinello Molecular Dynamics (**CPMD**) [CPMD] simulations is used to determine reaction mechanisms at the ab-initio level of theory, *i.e.*, without experimental information. The electronic cloud of any molecular system is computed using the density-functional theory (**DFT**) approximation to the electronic Schrödinger equation. Nuclear motion is treated classically using Newton dynamics. Thus, this study aims to compose an arbitrary chemical system atom by atom and let it develop with time using the Car-Parrinello equations.

UV filter	Phase 1	Phase 2
 BMD		?
 BP3		?
 BP4		?
 HS		?
 ODP		?
 OMC		?
 OS		?

Figure 1: UV filters to be studied and their products from the first phase of oxidative reactions.

The objective of this project is to implement a theoretical model of the electrochemical treatment of water containing organic UV filters as pollutants using CPMD. This model had been used for different systems [6, 7] and adapted to this specific problem [8]. In this model, the organic frame is introduced in a water box and then 8 OH radicals are produced

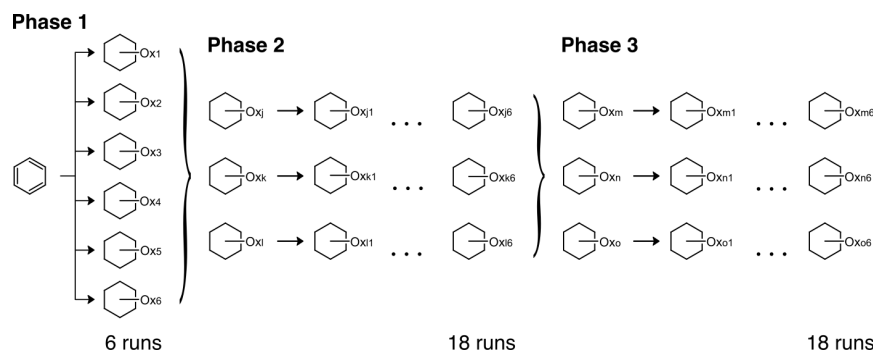


Figure 2: Scheme of the proposed workflow, where the organic UV filter is the input for phase 1. Then, three products are chosen as an input for the next phase iteratively.

by removing H atoms from the solvent, simulating the anodic environment after the electric discharge. Three products of the first row of radical reactions will be chosen to be introduced in a new phase of dynamics and again, leading to highly oxidized products. The time scale of the dynamics runs will then be lengthened in order to observe more complex mechanisms and further products.

Within each phase, the geometry of the UV filters is optimized by DFT calculations employing the BLYP level of theory, a cutoff of 70 Ry and the Troullier-Martins pseudo-potentials. Then, the optimized structure is introduced in a suitable cubic box of water and the system is let to evolve by itself at a temperature of 300 ± 100 K over 10 000 steps (time step of 4 a.u., almost 1 ps), reaching the state of equilibrium. The BLYP functional was chosen as it represents an excellent compromise between cost and accuracy for simulations using large plane-wave basis sets. Finally, eight hydroxyl radicals are generated in the simulation cell. The number of eight radicals results from our experience from previous studies: It guarantees high reactivity on the picosecond timescale, but is not too high as to produce side reactions and too strongly oxidative conditions [7, 8]. The molecular dynamics runs are restarted until every OH radical had reacted, or the system reached equilibrium. These simulations show feasible oxidative processes that every molecule would follow. For comparison, the previously described dynamics runs are repeated using the NVE and NVE ensembles with 3 different sets of radicals, for a total of 6 dynamics runs per system and 294 calculations for the complete project. Since the first phase is already done, this project contemplates the 252 dynamics runs corresponding to the phases 2 and 3. This large amounts of simulations will be analyzed with an AI trained to extract the chemical reactions from the trajectory files, quickly obtaining the reactions involving the organic compounds and side-reactions.

WWW

<https://www.pci.uni-hannover.de/de/forschung/arbeitsgruppen/simulation-chemischer-dynamik>

More Information

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DFG Subject Area

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