P-compounds at Geochemical Interfaces

Ab initio Quantum Chemical Modelling of Phosphorus Compounds at Geochemical Interfaces

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In Short

- The understanding of the fate of P-compounds in soils is vital for the efficient use of natural resources and environmental health.
- First principle quantum chemical modeling has the potential to unravel mechanistic details of the interaction of P-compounds with soil constituents towards a better understanding of P-mobility in the environment.
- The project investigates the binding of exemplary P-compounds to mineral surfaces to shine light at the interactions of P at the water-mineral geochemical interface.

Phosphorus (P) is central to all forms of life and its efficient use in fertilizers is one of the conditions for providing food for a rapidly increasing human population. Facing the projected peak P scenario, world-wide research activities have been triggered to improve our knowledge base such as to enable a more efficient and sustainable use of P resources [1]. On the other hand, the widespread use of the herbicide glyphosate, a synthetic P-compound, has triggered intense discussions related to its potential carcinogenic character.

A central question in this respect relates to the fate of P-compounds in the environment and here in particular in the soil. How do P-compounds react with soil constituents? Are they immobilized due to binding, e.g. to mineral particles or organic colloids or mobile and thus can be transported in the environment? Various P-research platforms such as the European sustainable phosphorus platform, the United States sustainable phosphorus research coordination network, and the Leibniz Science-Campus Rostock “Phosphorus Research” have been established to tackle these questions. To a large extent these efforts are concentrated in the experimental disciplines. Given the success of molecular-level simulations in Chemistry and related cross-disciplinary areas like Chemical Physics and Biochemistry, the minor role played by theory in soil science is surprising at first sight. However, the straightforward implementation of established modeling concepts is hampered by the considerable complexity of the problem, with the soil being an extremely heterogeneous natural entity made up of, e.g., inorganic minerals such as clay and oxide particles, soil organic matter, soil solution and gases, with the details differing from site to site.

The challenge can be met by close cooperation between experiment and theory, focusing on well-characterized soil samples. In a joint effort with the experimental group of Prof. Leinweber, University of Rostock, the group of the PI has been able to make progress in this respect, employing a combination of element-specific analytical methods and quantum chemical modeling. An important aspect has been the preparation of intentionally modified soil samples with controlled composition and the introduction of a test set of representative molecules, which mimics the soils’ compositions. While initial efforts have been directed to the understanding of the interaction of xenobiotics with soil constituents [2], recently we have extended these studies to the cases of phosphates [3] as well as the herbicide glyphosate [4,5].

The success of our approach increased the awareness for theory in the soil science community such that ab initio quantum chemical modeling is now part of two collaborative research projects, i.e. the BMBF InnoSoilPhos and the DFG SPP 1685, which focus on P-related processes in arable and forest soils, respectively. The project “P-compounds at Geochemical Interfaces” supports the work within InnoSoilPhos and the SPP 1685 by broadening the range of investigated systems and physical situations. Further, it is embedded into the activities of the Leibniz ScienceCampus Phosphorus Research Rostock.

The present project considers the exemplary situations of inorganic (orthophosphate, cf. also Fig. 1), organic (inositol hexaphosphate, which is abundant in forest soils), and synthetic (glyphosate) P-compounds, immobilized at the interface between water and different minerals (goethite and diaspore). Periodic density functional theory based molecular dynamics simulations using the CP2K software are performed, making use of quantum mechanics/molecular mechanics hybrid computational schemes. Trajectory-based sampling of the statistical ensemble is supplemented by energy optimization and vibrational frequency calculations. The obtained data are analyzed in terms of binding motifs and energies, putting emphasis on effects of co-adsorption of water and P-compounds and the interaction between P-species at the water-mineral interface. Comparison with results obtained for different coverages allows to connect with experimental adsorption isotherms and measurements of infrared (IR) absorption spectra performed in the respective

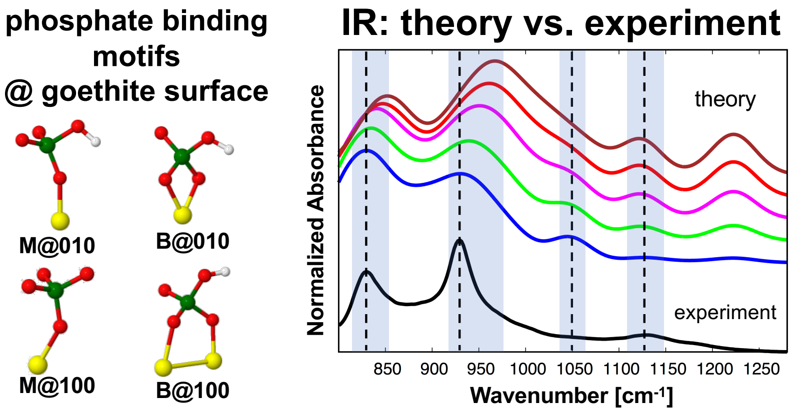

*Figure 1: . Left panel: relevant fragments of the optimized **M** and **B** binding motifs of H_2PO_4 at the 010 and 100 goethite surface planes (atoms are colored in green (P), red (O), white (H), and yellow (Fe)). Left panel: Experimental IR spectrum versus calculated spectra at different mixture of the different binding motifs. The comparison allows to conclude on their relative abundance in the soil sample.*

consortia for well-defined soil samples.

Exemplary results for orthophosphate at the goethite surface are shown in Fig. 1; cf. ref. [3]. In this work, we have obtained evidence that the mono-protonated **B** (bidentate) phosphate complex is favored to be formed at the goethite-water interface, although the **M** (monodentate) motif could exist as a minor fraction. Benchmarking calculated IR-spectra for different binding motifs and surfcae planes with respect to experimental results, we arrived at the conclusion that the common confusion in litearture concerning the correct assignment of phosphate vibrations can only be resolved by taking into account the simultaneous contributions of several motifs to te measured spectra. In the present case this gave a mixing of **M** and **B** motifs with a ratio of 1:8, in good agreement with the interaction energy calculations.

Eventually, this project aims at drawing conclusions on the fate of P-compounds for representative environmental conditions.

WWW

http://web.physik.uni-rostock.de/quantendynamik/

More Information

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