Supplementary Information (SI)

Infrared Spectroscopic Characterization of Phosphate Binding at the Goethite-Water Interface

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S1. Details about the interaction energy calculations

In general, the effect of water on the phosphate-goethite interaction has been considered during the geometry optimization due to the water-phosphate-goethite interactions based on the electronic and Van der Waals interactions. However, this effect has not been considered explicitly for computing the interaction energy in Eq. 1. In practice, each phosphate-goethite-water model could be considered as three sub-systems (fragments). These fragments are phosphate (fragment1), goethite (fragment2), and water (fragment3). Within CP2K it is possible to calculate the pair interaction energy between two fragments. According to Eq. 1 ($E_{int} = E_{phosphate-goethite-complex} - (E_{phosphate} + E_{goethite surface})$), we have defined phosphate as the first fragment and goethite as the second fragment. Water enters only insofar as it determines the actual geometry of the interacting fragments. The interaction energy is calculated within the BSSE counterpoise correction philosophy, i.e. by performing five energy calculations as follows: total electronic energy of phosphate including only the phosphate basis functions ($E_{phosphate}^{Phosphate}$, goethite including only the goethite basis functions (

 $E_{goethite}^{goethite}$), phosphate including the basis functions of phosphate and goethite ($E^{phosphate + goethite}_{phosphate}$), goethite including the basis functions of phosphate and goethite ($E^{phosphate + goethite}_{goethite}$), and finally phosphate-goethite complex including the basis functions of phosphate and goethite ($E_{phosphate-goethite-complex}$). From these numbers one gets the interaction energy phosphate and goethite as between $E_{int} = E_{phosphate - goethite - complex} - (E^{phosphate + goethite}_{phosphate} + E^{phosphate + goethite}_{goethite})$. Similarly, the interaction water energies between phosphate and ($E_{int} = E_{phosphate - water - complex} - (E^{phosphate + water}_{phosphate} + E^{phosphate + water}_{water})$)) and between goethite and water $(E_{int} = E_{goethite - water - complex} - (E_{goethite}^{goethite + water} + E_{water}^{goethite + water}))$ could be calculated.

S2. X-ray diffraction data



Fig. S1. X-ray diffraction pattern of the synthetic goethite sample used in this study (lattice parameters: a = 4.61 Å, b = 9.96 Å, and c = 3.02 Å).



S3. Comparison between calculated and experimental difference spectra over the full range

Fig. S2. Experimental difference IR spectrum relevant to the P-goethite complex (in blue, compare Fig. 2) versus the phosphate-related spectra calculated for **M@010** a), **B@010** b), **M@100** c), and **B@100** d) in the range of 800-1300 cm⁻¹. The original scale for the experimental spectrum was added to the right axis in blue.

Figure S2 shows that the IR spectrum for the **B@010** complex (Fig. S2b) is closest to the experimental IR spectrum compared to the other calculated spectra. This holds specifically for the first two IR spectral features, i.e. in the spectral range of 800–1000 cm⁻¹. Here, it is important to mention that the first feature observed around 850 cm⁻¹ for the **B@010** complex involves $2O_{b}$ –P– $2O_{nb}$ symmetric stretching and P–O–H bending vibrations. The second observed feature around 945 cm⁻¹ for the same complex corresponds mainly to $2O_{b}$ –P– O_{nb2} symmetric stretching and O_{b2} –P– O_{nb1} asymmetric stretching vibrations. Moreover, the IR spectrum for the **M@100** complex is also close to the experimental IR spectrum (see Fig. S2c). Here, the first feature seems as a bimodal peak with a local maximum, around 840 cm⁻¹, closer to the experimental feature that corresponds to P– $2O_{nb}$ stretching and bending vibrations. Furthermore, the second feature observed around 930 cm⁻¹ is due to P– O_{b} stretching, P– O_{nb1} stretching, O_{b} –P– $2O_{nb1,2}$ symmetric stretching, P– $3O_{nb}$ asymmetric stretching vibrations. For the **M@010** complex (see Fig. S2b), and the **B@100** complex, (see Fig. S2d), one observes a larger deviation in the position for the first two features compared to the experimental ones especially for the first

feature. The first two features in the spectrum of the **M@010** complex are at 800 and 965 cm⁻¹ and are due to P–3O_{nb} complex vibration and O_{b} –P–2O_{nb1,3} symmetric stretching vibration, respectively, in addition to P–O–H bending vibration. For the **B@100** complex, the first two features existed around 830 and 960 cm⁻¹. The first feature involved an O_{b2} –P–2O_{nb} symmetric stretching vibration while the second one involved P–O_{nb1} stretching, O_{b2} –P–O_{nb1} antisymmetric stretching, and P–O–H bending vibrations. For the latter two complexes, the shape of the calculated spectra in the range of 800–1000 cm⁻¹ is somehow different than the experimental one. This also confirms that spectra of both **B@010** and **M@100** complexes are closer to the experimental spectrum than the other two complexes.