Abstract:
In a computational study we addressed the adsorption of uranyl UO\(_2^+\) on solvated (110) and (010) edge surfaces of pyrophyllite, applying a density functional approach to periodic slab models. We explored bidentate adsorption complexes on various partially deprotonated adsorption sites: octahedral Al(O,OH), tetrahedral Si(O, OH), and mixed AlO-SiO. Aluminol sites were determined to be most favorable on the (110) surface of pyrophyllite, while on the (010) surface mixed AlO-SiO sites are preferred. The structural parameters of all low-energy complexes on both surfaces agree rather well with EXAFS results for the structurally similar mineral montmorillonite. We calculate the average U-O distance to surface and aqua ligand oxygen atoms to increase with the increasing coordination number of uranyl whereas EXAFS results indicate the opposite trend. According to our results, several adsorption species, with different coordination numbers on different edge faces, may coexist on clay minerals. This computational finding rationalizes why earlier spectroscopic studies indicated the existence of more than one adsorption species, whereas a single type of adsorption complex was suggested from most EXAFS results.
Notker Kremleva, Alena/K-7309-2012 Bundesministerium fur Wirtschaft und Technologie [02E10186]; Fonds der Chemischen Industrie (Germany) This work was supported by the Bundesministerium fur Wirtschaft und Technologie (grant No. 02E10186) and Fonds der Chemischen Industrie (Germany). Leibniz-Rechenzentrum Munchen provided a generous allotment of computational resources. 1 Royal soc chemistry Cambridge