Supplementary Material (ESI) for *PCCP*

Elucidation of oxyanion coordination geometries at solid surfaces of varied electric field strengths

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SUPPLEMENTARY INFORMATION

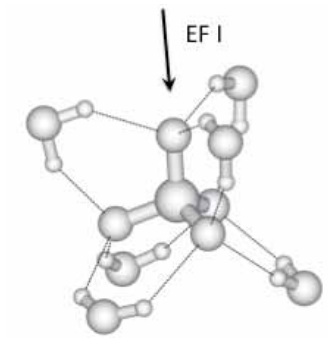

Fig S1. Optimised geometry of $[SO_4(H_2O)_6]^{2-}$ under EF I (0.26 V/Å) (B3LYP/6-311+G(3df,pd)).

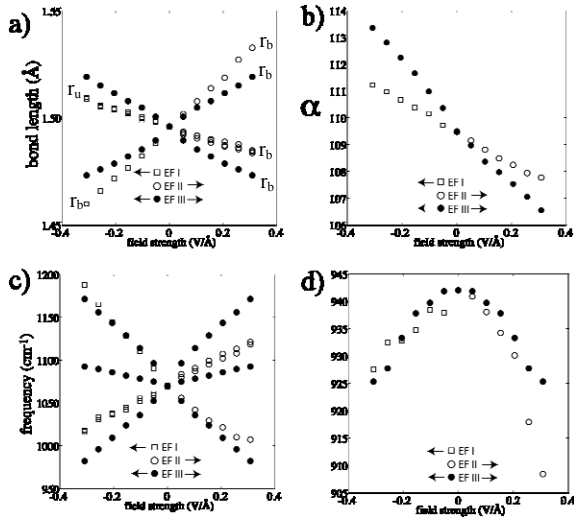

Fig. S2. Field strength effects on (a) bond lengths, (b) angle, (c) ν_3 S-O and (d) ν_1 S-O (raw B3LYP/6-311+G(3df,pd) frequencies) of $[SO_4(H_2O)_6]^{2-}$.

Table S1. Field strength-dependence (δ) of geometry and stretching frequencies

	SO_4^{2-}	$[SO_4(H_2O)_6]^{2-}$
EF I & EF II		
$\delta(r_u)$, $\delta(r_b)$ [a]	0.0193, 0.0578	0.0356, 0.120
$\delta(\alpha)$ [b]	2.73	5.70
$\delta(\nu_1)$, $\delta(\nu_3)$ [b]	80, 154	160, 207
EFIII		
$\delta(r_{S-O})$ [a]	0.0326	0.0782
$\delta(\alpha)$ [b]	4.64	11.36
$\delta(\nu_1)$, $\delta(\nu_3)$ [b]	15, 133	73, 319

[a] Å per V/Å. [b] cm^{-1} per V/Å

Methods

Geometries and frequencies were calculated with the program Gaussian03[1] at an integration grid of 99 radial shells and 590 angular points per shell. Vibrational frequencies were determined analytically from the Hessian matrix on the fully-optimized structure at the same level of theory. All molecular geometries presented in this study correspond to potential energy surface minima, as confirmed by the lack of negative frequencies. No frequency shift factors[2] were however applied to these theoretical frequencies given the focus of this paper on spectral shifts, rather than absolute values. Electron Localization Function calculations were carried out with the program TopMod[3] using Gaussia03-formatted wave function files generated from single point calculations of fully-optimized geometries.

The synthetic spectra of Fig. 3 were generated from the theoretical frequencies by applying a Lorentzian function with a half maximum band with of 30 cm^{-1}. This band width was chosen as an approximate value for the triply degenerate ν_3 band of sulfate in aqueous solution at room temperature.

References

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