

SUPPLEMENTARY MATERIAL

Crystallographic controls on uranyl binding at the quartz/water interface.

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Description of force field model and parameters

Potential energy was calculated in Gromacs¹ (v.3.3.3) as the sum of non-bonded (Coulombic and van der Waals) and bonded (bond stretch and bend) interactions. Coulombic energy is expressed as:

$$V_C(\mathbf{r}_{ij}) = \frac{q_i \cdot q_j}{f \cdot r_{ij}} \quad [1]$$

where $f = 4\pi\epsilon_0\epsilon_p e^{-2}$, ϵ_0 is the permittivity of vacuum, ϵ_p the relative dielectric constant and e elementary charge. van der Waals energy is represented by the Lennard-Jones (12-6) function:

$$V_{LJ}(\mathbf{r}_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad [2]$$

using Lorentz-Berthelot mixing rules:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad [3]$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad [4]$$

Finally the bonded potential energies were described by harmonic stretches

$$V_b(\mathbf{r}_{ij}) = \frac{1}{2}k_{ij}^b (r_{ij} - b_{ij})^2 \quad [5]$$

for all hydroxyl (O-H) and uranyl (U=O) bonds, and harmonic bends

$$V_a(\theta_{ijk}) = \frac{1}{2} k^\theta (\theta_{ijk} - \theta_{ijk}^0)^2 \quad [6]$$

in water (H-O-H), surface sites (Si-O_s-H_s) and uranyl (O_u-U-O_u). More details on computational procedures (*e.g.* cut-off etc...) for the quartz-water system are detailed in the Methods section of this paper.

Force field parameters of CLAYFF² for α-SiO₂, flexible SPC³ for water and CHARMM⁴ parameters for uranyl were converted for equations and units used in Gromacs (Table S1).

Table S1. Potential parameters^a

atom ^a	description	q	σ	ε	source
H	H ₂ O, OH ⁻	0.410	0	0	[2-3]
H _s	OH surface	0.425	0	0	[2]
O	H ₂ O, OH ⁻	-0.820	0.31655	0.65019	[2-3]
O _q	SiO ₂	-1.050	0.31655	0.65019	[2]
O _s	O(H) surface	-0.950	0.31655	0.65019	[2]
O _u	UO ₂	-0.250	0.31655	0.65019	[4]
Si	SiO ₂	2.100	0.33020	7.7007×10 ⁻⁶	[2]
U	UO ₂	2.500	0.28152	1.6736	[4]

bond ^b		k ^b	b	
O-H	H ₂ O, OH ⁻	463700	0.100	[2-3]
O _q -H _s	OH surface	463700	0.100	[2]
U-O _u	UO ₂	8368	0.177	[4]

bend ^c		k ^θ	θ ⁰	
H-O-H	H ₂ O	383	109.47	[2-3]
Si-O _s -H _s	OH surface	251	109.47	[2]
O _u -U-O _u	UO ₂	1255	180.00	[4]

a. q is charge (e), σ(nm) is the finite distance at which the inter-particle Lennard-Jones potential is zero and ε (kJ/mol) is the Lennard-Jones potential well. Values of σ (nm) from R_o (Å) in CLAYFF ($V_{LJ} = \epsilon((R_{o,ij}/r_{ij})^{1/12} - 2(R_{o,ij}/r_{ij})^{1/6})$) were obtained as $\sigma = R_o/10/2^{1/6}$. Those from CHARMM-compatible R* of Guilbaud and Wipff ($V_{LJ} = \epsilon((R^*_{ij}/r_{ij})^{1/12} - 2(R^*_{ij}/r_{ij})^{1/6})$ where $R^* = R^*_i + R^*_j$) were obtained as $\sigma = (R^* + R^*)/10/2^{1/6}$. These latter values are consistent with those of the OPLS database already present in Gromacs¹.

b. k^b (kJ mol⁻¹ nm⁻²) is the harmonic potential constant and b (nm) the equilibrium bond length.

c. k^θ (kJ mol⁻¹ rad⁻²) is the harmonic angle potential and θ⁰ (deg) is the equilibrium angle.

References

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