

Supporting Information

Force Field Development for Actinyl Ions via Quantum Mechanical Calculations: An Approach to Account for Many Body Solvation Effects

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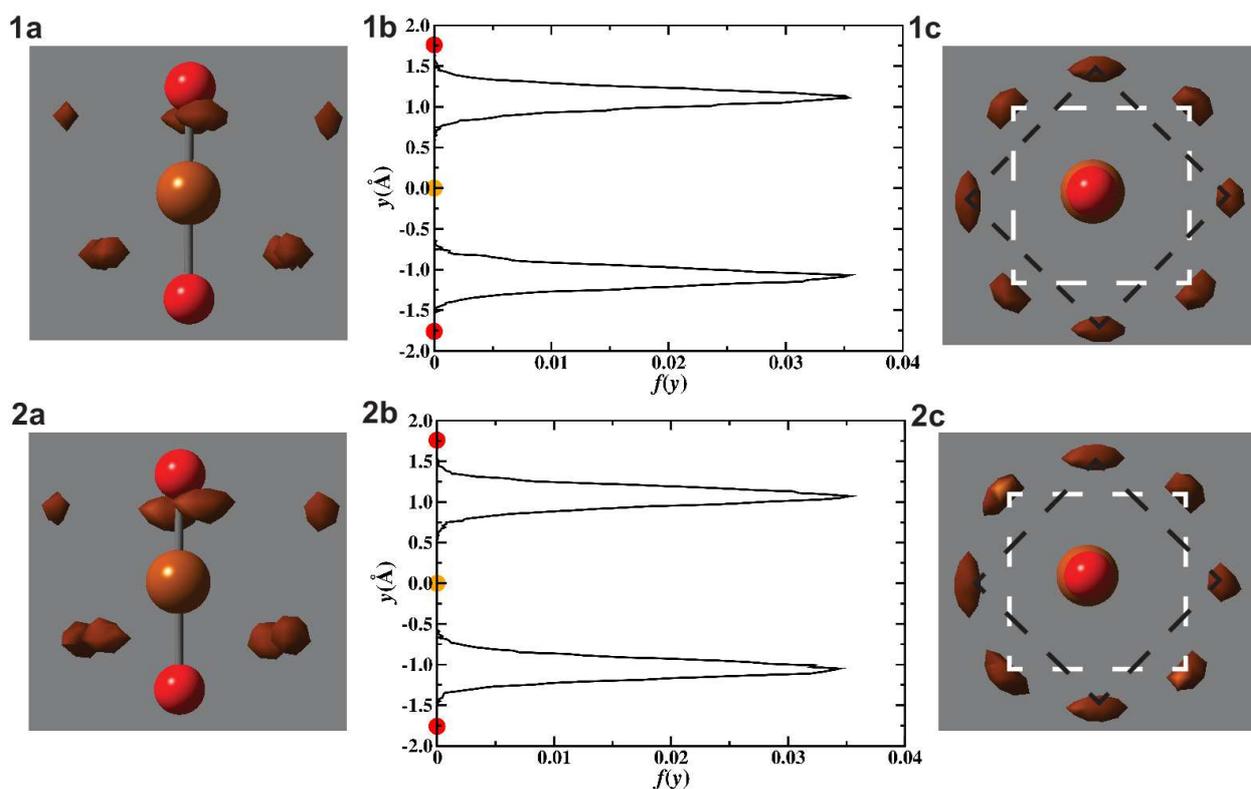


Figure 1: Spatial distribution functions and distributions of y offset from the equatorial plane for water molecules in the first hydration shell of uranyl ion. Subfigures **1a**, **1b**, and **1c** represent the front view of the spatial density plot, distribution of y offset from from the equatorial plane, and the top view of spatial distribution plot in subfigure **1a** for the TIP3P water model, respectively. The subfigures **2a**, **2b**, and **2c** are the corresponding plots for the TIP5P water model. The white and black dashed squares (**1c** and **2c**) connect the most likely positions of water molecules in the plane below and above the equatorial plane, respectively.

Table 1: Surface potential for water models

Water model	$\phi(\text{kJ/mol/e})$
SPC/Fw	-54.255
TIP3P	-50.62
TIP4P	-49.47
TIP5P	-9.106

Soft core potential details

A soft core potential¹⁻³ was used for the LJ transformation to avoid singularities in the potential at short distances for intermediate values of λ

$$V_\lambda = V^A(r_A)(1 - \lambda) + V^B(r_B)\lambda \quad (1)$$

$$r_A = (\alpha\sigma_A^6\lambda^p + r^6)^{1/6} \quad (2)$$

$$r_B = (\alpha\sigma_B^6(1 - \lambda)^p + r^6)^{1/6} \quad (3)$$

where, V^A and V^B are the normal potentials of states A and B respectively, α is the soft-core parameter, p is the soft-core λ power, and σ is the radius of the interaction, which is the normal LJ σ or an input parameter when the LJ σ is zero¹⁻³. We chose $\alpha = 0.5$, $p = 1$, and $\sigma = 0.3$. No soft core potential was used in the Coulombic transformation case because two atoms cannot come too close to give singularities due to LJ repulsion already in effect.

The correction term due to the vacuum/water interface potential^{4,5}

The correction term due the interfacial potential jump, $\Delta G_{\text{corr}}^{\text{surf}}$ is given by

$$\Delta G_{\text{corr}}^{\text{surf}} = z\phi_{\text{surf}} \quad (4)$$

where z and ϕ_{surf} are the ion valency and the liquid/vacuum surface potential, respectively. This term can be calculated using^{4,6}

$$\phi(z) - \phi(z_0) = -\frac{1}{\epsilon_0} \int_{z_0}^z dz_1 \int_{z_0}^{z_1} dz_2 \rho(z_2) \quad (5)$$

where $\rho(z)$ is the z -component of the charge density, and ϵ_0 is the permittivity of vacuum.

To compute surface potential, an explicit vacuum/water interface was created by placing 832 water molecules in a rectangular box with dimensions of 3 x 3 x 9 nm. Simulations were carried out in the NVT ensemble at $T = 298.15$ K. The geometries of water molecules for the rigid TIP3P, TIP4P, and TIP5P water models were constrained using the SETTLE algorithm⁷. A switch function was used for LJ interactions to shift the LJ force starting from 10 Å to make it zero at a cut-off distance of 12 Å. Periodic boundary conditions were applied in all three directions and

particle-mesh Ewald^{8,9} (PME) with tin foil boundary conditions was used to handle long-range electrostatic forces. MD simulations were performed with a time step of 2 fs except in the case of the flexible water (SPC/Fw) system, in which case a time step of 1 fs was used. A Langevin stochastic dynamics (SD) algorithm was used for integrating the equations of motion. The system was equilibrated for 1 ns. The subsequent 4 ns trajectories were used for analysis. Gromacs-4.5.5¹⁻³ was used for simulations and data analysis.

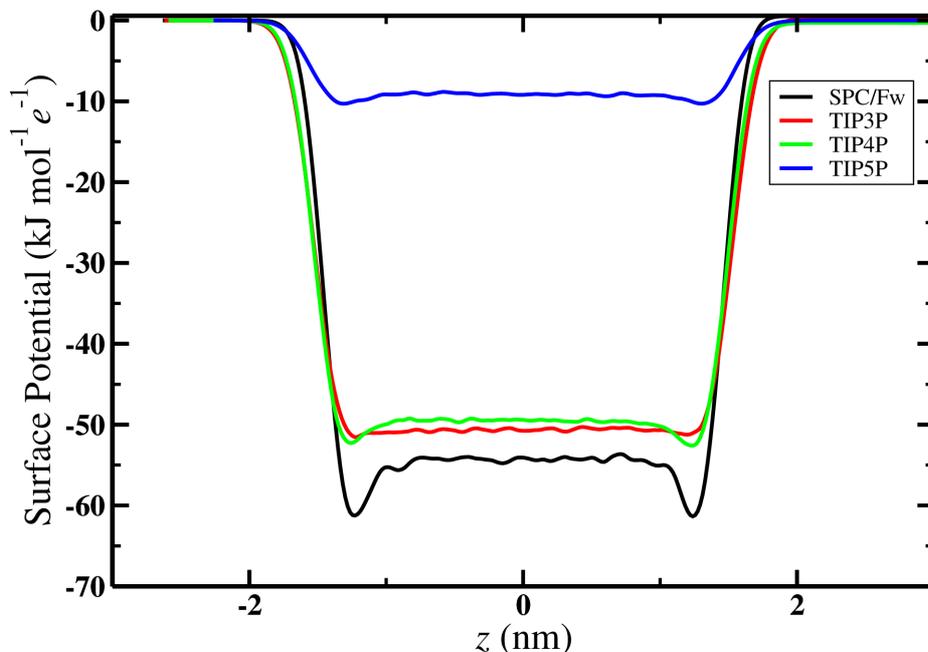


Figure 2: Surface potentials for the vacuum/water interface for different water models.

The surface potentials are presented in Table 1 and Figure 2. The results are in good agreement with reported values for different water models^{4,10} (around -50 kJ/mol) for all but TIP5P model. Since dipole moments of these water models are very similar, the discrepancy is most likely due to difference in the quadrupolar contribution⁴ to the surface potential.

References

- [1] Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. *J. Comput. Theor. Chem.* **2008**, *4*, 435–447.
- [2] Van Der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. C. *J. Comp. Chem.* **2005**, *26*, 1701–1718.
- [3] Beutler, T. *Chem. Phys. Lett.* **1994**, *222*, 529–539.
- [4] Warren, G. L.; Patel, S. *J. Chem. Phys.* **2007**, *127*, 064509.
- [5] Horinek, D.; Mamatkulov, S. I.; Netz, R. R. *J. Chem. Phys.* **2009**, *130*, 124507.
- [6] Wilson, M. A.; Pohorille, A.; Pratt, L. R. *J. Chem. Phys.* **1988**, *88*, 3281.
- [7] Miyamoto, S.; Kollman, P. A. *J. Comp. Chem.* **1992**, *13*, 952–962.
- [8] Darden, T.; York, D.; Pedersen, L. *J. Chem. Phys.* **1993**, *98*, 10089–10092.
- [9] Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. *J. Chem. Phys.* **1995**, *103*, 8577–8593.
- [10] Dang, L. X.; Chang, T.-M. *J. Phys. Chem. B* **2002**, *106*, 235–238.