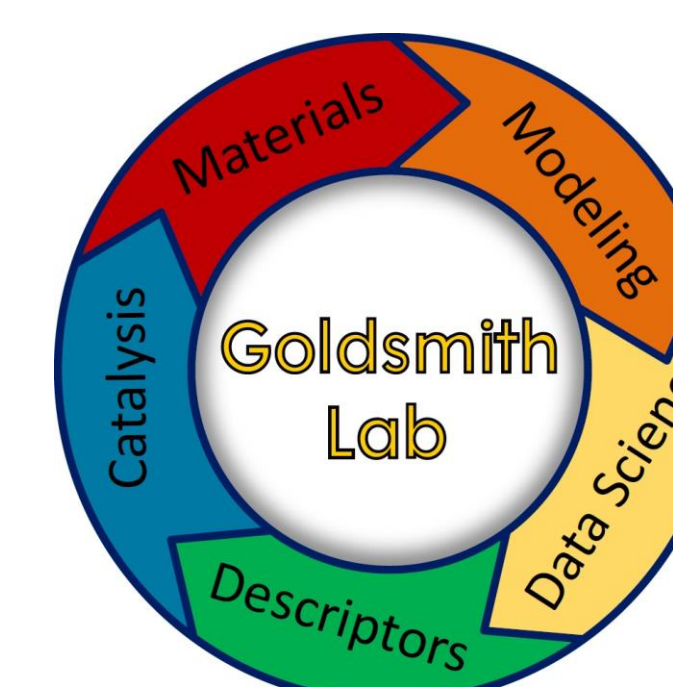# Predicting Structure and Redox Kinetics of $Ce^{3+/4+}$ Complexes in Acidic Electrolytes

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Background and Objective

The Ce^{3+}/Ce^{4+} redox couple is applicable to many fields such as energy storage, organic synthesis, and wastewater remediation, however, little is known about the structures of Ce species in solution and the mechanism of the charge transfer reaction. In specific, the dependence on electrolyte and extreme asymmetry of the charge transfer reaction is not well understood.
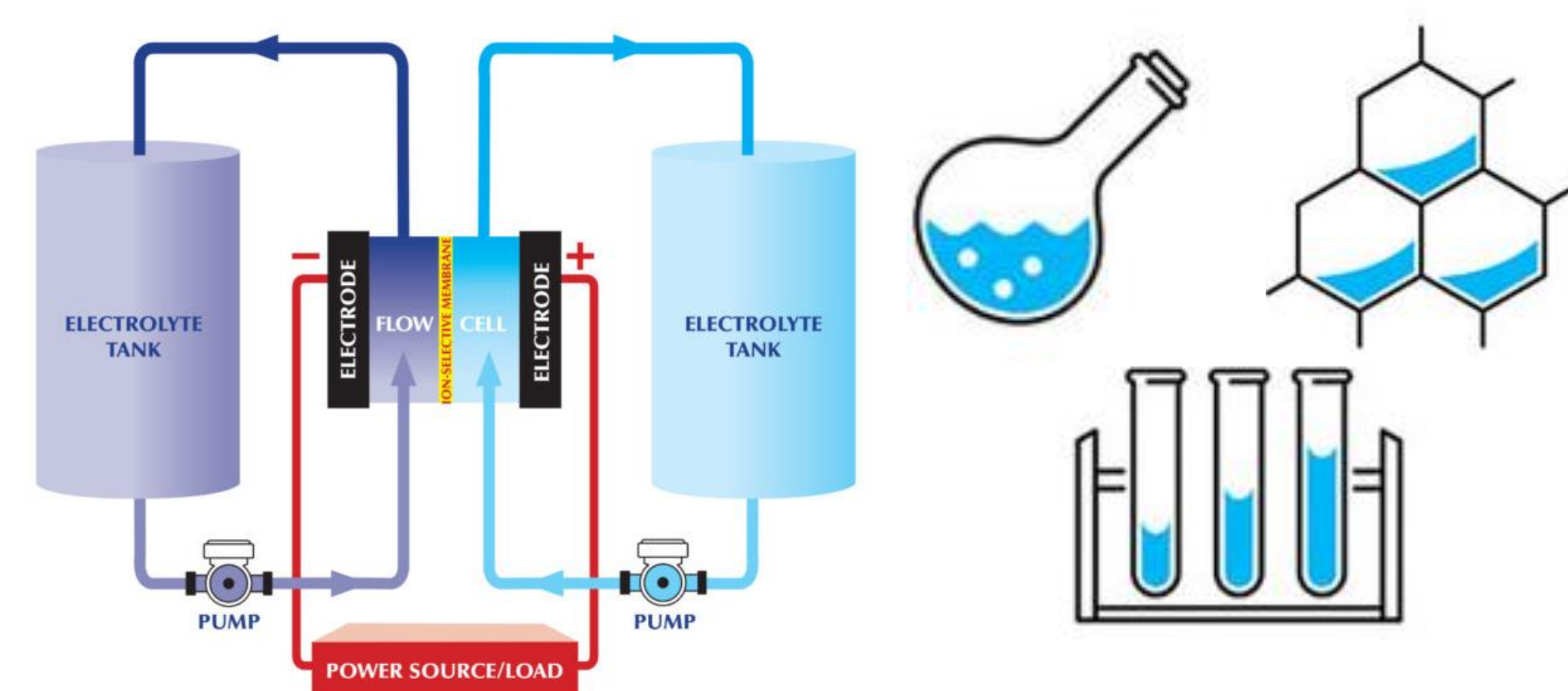
It is the objective of this study to elucidate structures of complexes in electrolytes via comparison of experimental EXAFS with MD-EXAFS to use these structures to predict electron-transfer (ET) kinetics.
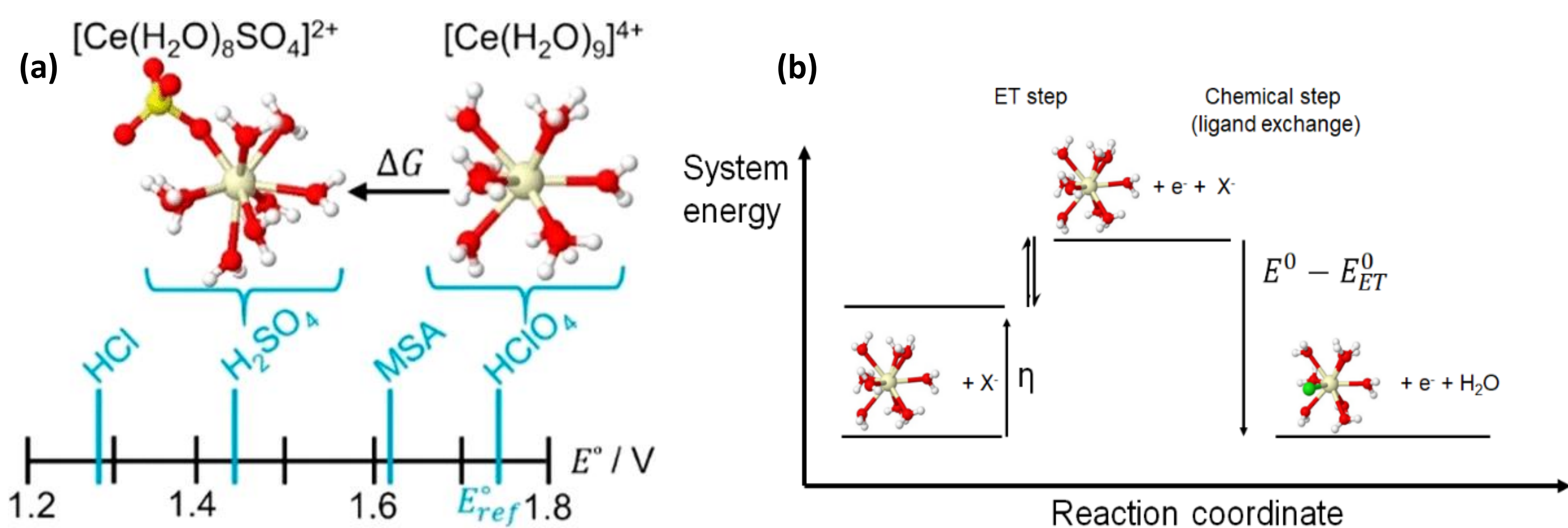

Figure 1: (a) Dependence of standard reduction potential of Ce^{3+}/Ce^{4+} on electrolyte and **(b)** hypothesized reaction mechanism

Free Energy Calculations

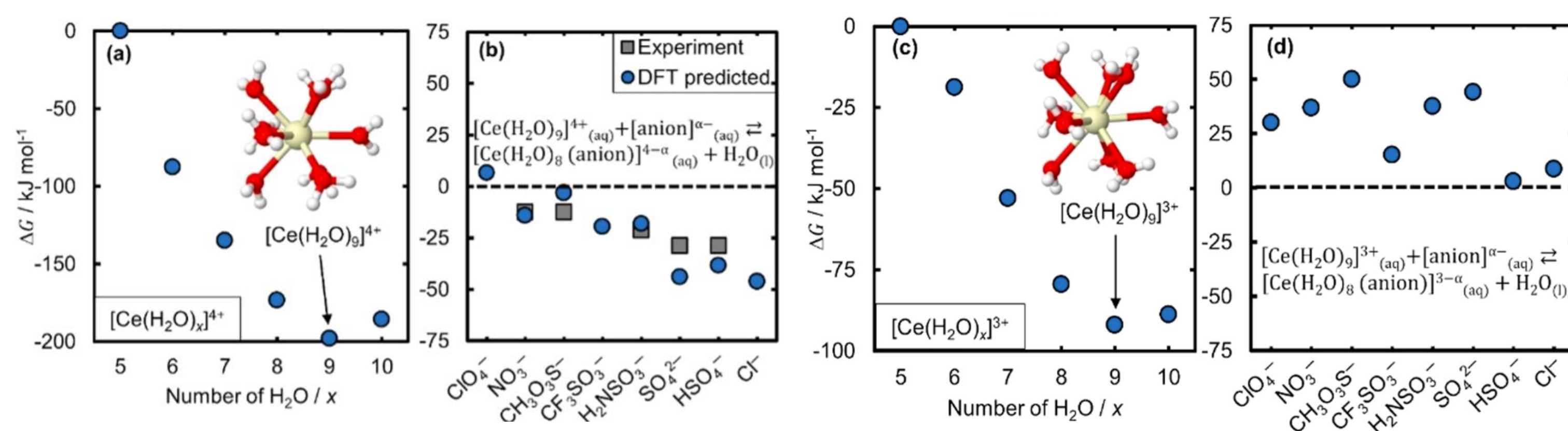Free energies of water/anion exchange give clues to the dominant structure of Ce^{3+}/Ce^{4+} in the acidic electrolyte[1].

Figure 2: Free energy of Ce^{4+} with varying **(a)** number of water molecules complexed and **(b)** anion. Free energy of Ce^{3+} with varying **(c)** number of water molecules complexed and **(d)** anion.

Both Ce^{3+}/Ce^{4+} favorably form a complex with 9 water molecules in the inner coordination sphere. Ce^{4+} favorably exchanges a single water molecule with an anion from the electrolyte while Ce^{3+} does not **(Fig. 2)**.

MD-EXAFS Methods

Molecular dynamics EXAFS (MD-EXAFS) are generated by averaging the EXAFS signals generated by the FEFF9 code of geometries over a MD trajectory **(Fig. 3)**.
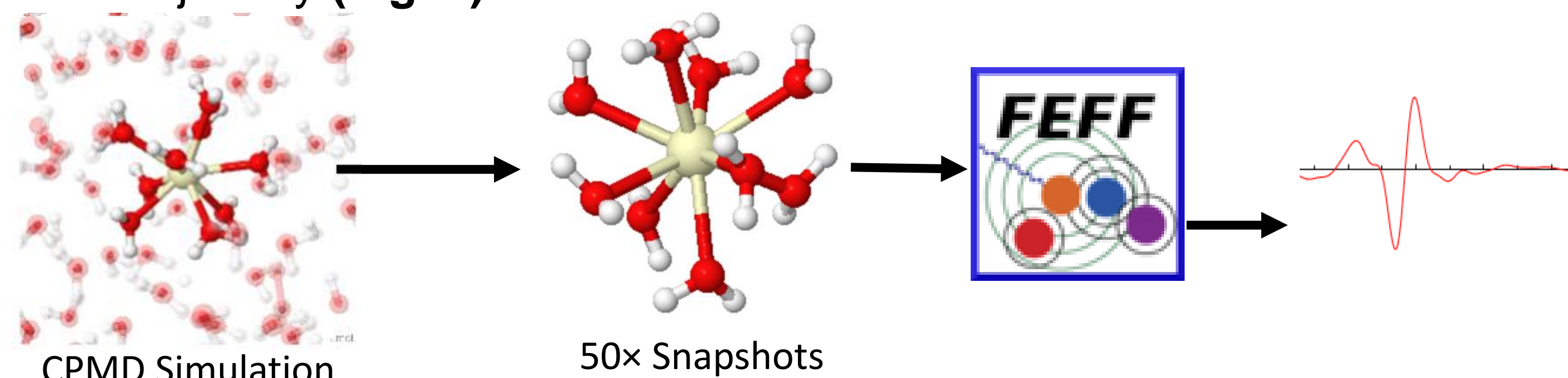

Figure 3: Workflow for calculating MD-EXAFS spectra

Calculated MD-EXAFS are compared with experimentally measured EXAFS to determine the Ce^{3+} and Ce^{4+} species present in sulfuric acid.
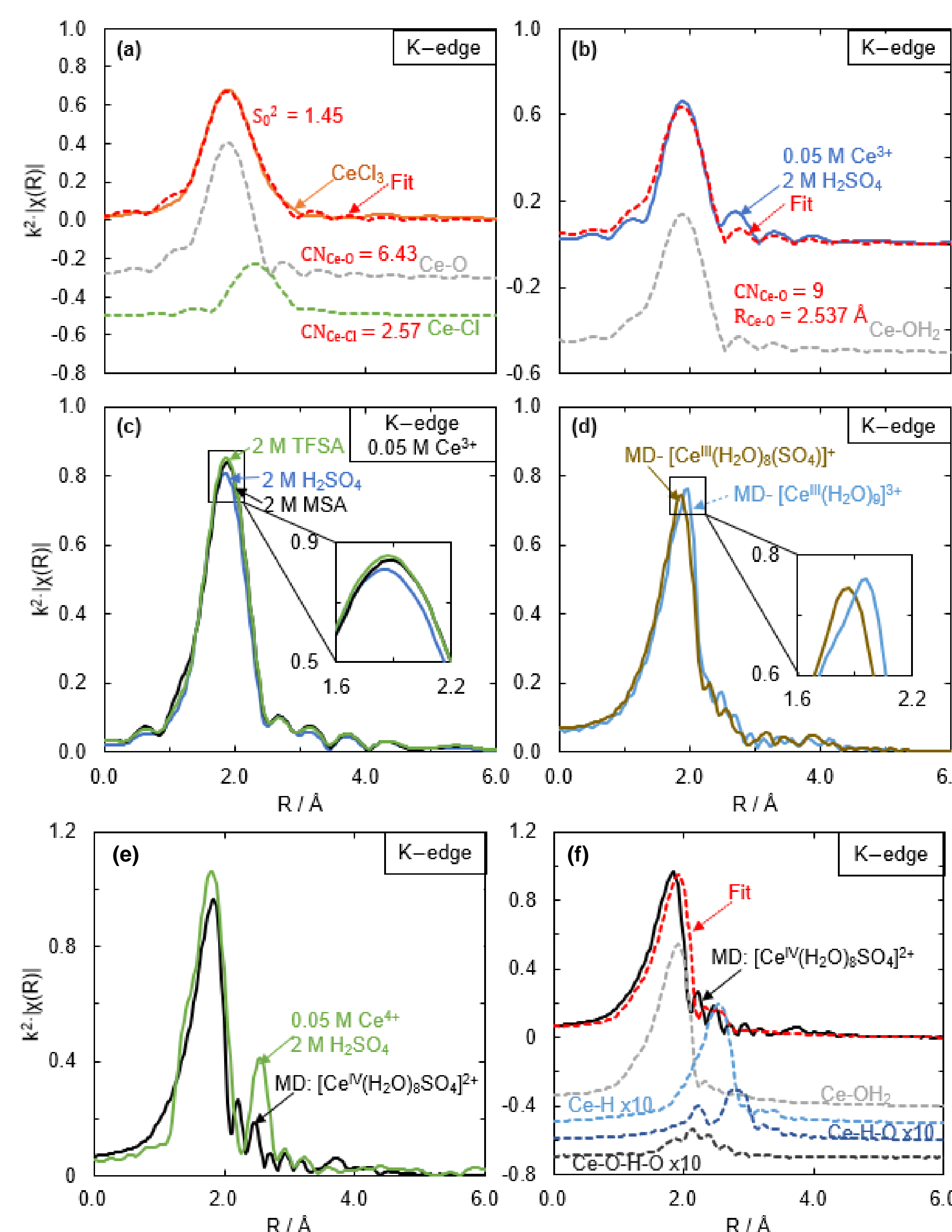
MD-EXAFS Results

Figure 4: $\chi(R)$ magnitude plots for Ce complexes including **(a)** experimental EXAFS of a $CeCl_3$ standard, **(b)** experimental EXAFS of Ce^{3+} in H_2SO_4, **(c)** experimental EXAFS of Ce^{3+} in H_2SO_4, MSA , and TFSA and **(d)** two MD-EXAFS of $[Ce^{III}(H_2O)_9]^{3+}$ and $[Ce^{III}(H_2O)_8(SO_4)]^+$ **(e)** MD-EXAFS of $[Ce^{IV}(H_2O)_8(SO_4)]^2$ and experimental EXAFS of 0.05 M Ce^{4+} in H_2SO_4 **(f)** MD-EXAFS of $[Ce^{IV}(H_2O)_8(SO_4)]^2$ with individual scattering paths
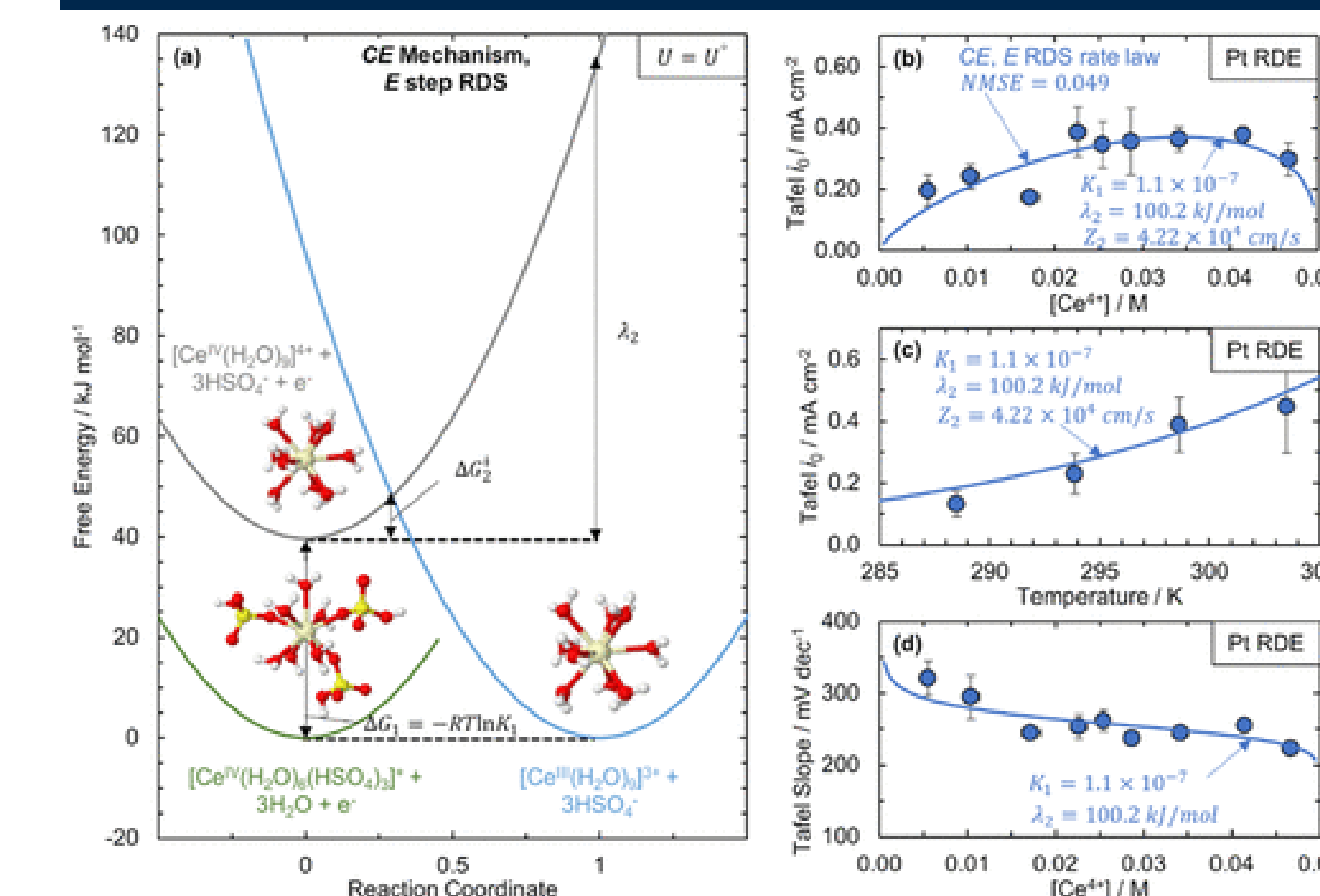
Kinetics Results

Figure 5: (a) Free energy profiles at the equilibrium Ce3+/Ce4+ potential ($U = U^o$) in H2SO4. Parabolas represent the free energies of the species as a function of reaction coordinate. The Ce3+/Ce4+ electron transfer is described by the reorganization energy λ_2 and the transition-state free energy, $\Delta G_2^{\ddagger}$, and the ligand exchange is described by the equilibrium constant K_1. **(b) (c) (d)** Tafel slope method used to determine kinetic parameters[4]

Discussion

- Fitting the experimental and simulated EXAFS gave CN = 9, consistent with free energy calculations **(Fig. 4b)**.
- Including a Ce-S scattering path worsened the EXAFS fit for Ce^{3+}, indicating S is likely not present in the inner coordination sphere.
- All the Ce^{3+} complexes EXAFS look near identical in all electrolytes tested, further evidence Ce^{3+} does not complex with anions **(Fig. 4c)**.
- Including Ce-S-O scattering paths improved the fit for Ce^{4+}, which indicates that the anion complexed form of Ce^{4+} is the dominant species in solution.
- Experimentally determined reorganization energies (71.8-100.2 kJ/mol) are consistent with DFT calculated values (87.2 kJ/mol)

Conclusions and Future Work

- **Ce^{3+} does not undergo ion exchange with sulfuric acid**
- **Ce^{4+} does undergo ion exchange in sulfuric acid**
- **Two-step mechanism with ligand exchange and outer sphere electron transfer as rate-determining step accurately describes system**
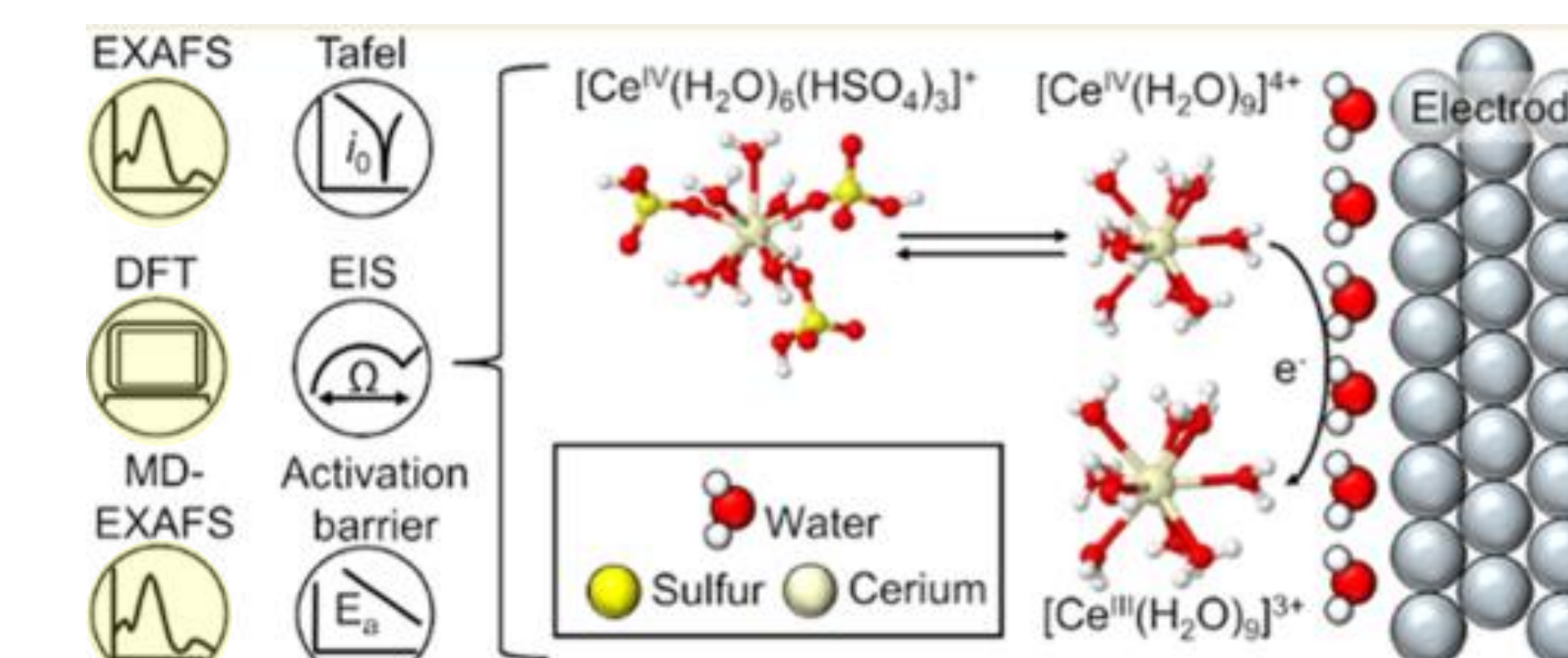

Figure 6: Summary of methods used to understand Ce charge transfer mechanism.

Acknowledgements

References

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2. Ikeda-Ohno, Atsushi and Tsushima, Satoru and Hennig, Christoph and Yaita, Tsuyoshi and Bernhard, Gert. *Royal Society of Chemistry* 7190-7192 (2012)
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