CPP 34: Focus Session: Water – from Atmosphere to Space V (joint session CPP/DY)

Time: Wednesday 11:00–12:00 Location: ZEU/0260

CPP 34.1 Wed 11:00 ZEU/0260

Scalable Machine Learning Model for Energy Decomposition Analysis in Aqueous Systems — •Thomas Kühne — CASUS/HZDR, Görlitz, Germany

Energy decomposition analysis (EDA) based on absolutely localized molecular orbitals provides detailed insights into intermolecular bonding by decomposing the total molecular binding energy into physically meaningful components. Here, we develop a neural network EDA model capable of predicting the electron delocalization energy component of water molecules, which captures the stabilization arising from charge transfer between occupied absolutely localized molecular orbitals of one molecule and the virtual orbitals of another. Exploiting the locality assumption of the electronic structure, our model enables accurate prediction of electron delocalization energies for molecular systems far beyond the size accessible to conventional density functional theory calculations, while maintaining its accuracy. We demonstrate the applicability of our approach by modeling hydration effects in large molecular complexes, specifically in metal-organic frameworks.

CPP 34.2 Wed 11:15 ZEU/0260

Advances in absolute-scale electronic structure measurements of liquid water and aqueous solutions — •Florian Trinter — Fritz-Haber-Institut, Berlin, Germany

Recent advances in liquid-jet photoelectron spectroscopy (LJ-PES) have enabled the precise determination of absolute electronic energetics of liquid water and aqueous solutions, both in the bulk and at interfaces. By implementing refined vacuum and Fermi-level referencing procedures, rooted in condensed-matter concepts, vertical ionization energies (VIEs) and solution work functions can now be measured with high accuracy. We show that binding energy determinations near the ionization threshold are strongly influenced by quasi elastic electron scattering and indirect ionization processes. Vibrational excitation and autoionization via super-excited states lead to spectral distortions at electron kinetic energies below ∼14 eV, necessitating careful data interpretation to extract intrinsic properties. Applying these methods to neat water and aqueous solutions of sodium iodide (NaI) and tetrabutylammonium iodide (TBAI), we reveal solute-specific effects: NaI primarily alters water's bulk structure, increasing the $1b_1$ binding energy with concentration, while TBAI affects surface potentials through interfacial dipole formation, leading to an apparent binding energy decrease. Additionally, we determine the work function of neat water as 4.73 ± 0.09 eV and quantify its reduction in TBAI solutions. These findings establish a framework for quantitative studies of molecular interactions and electronic-structure modifications in aqueous systems, with implications for electrochemical and interfacial science.

CPP 34.3 Wed 11:30 ZEU/0260

Liquid-vapor critical behavior of the TIP4P/2005 water model: Effects of NaCl solutes and hydrophobic confinement — •Mayank Sharma and Peter Virnau — Institute of Physics, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

The liquid-vapor critical behavior of water is strongly influenced by both ionic solutes and confinement. Molecular dynamics simulations of aqueous NaCl solutions using the TIP4P/2005 water model and the Madrid-2019 ion parameters reveal a systematic increase in the liquid-vapor critical temperature and pressure with salt concentration, consistent with experimental trends. In contrast, confinement between parallel hydrophobic plates leads to a depression of the critical point. The critical temperature was determined using the Binder cumulant crossing in the NVT ensemble, based on a recently developed method originally applied to an active Brownian particle system [1]. The reliability of this approach was verified through complementary NPT simulations using histogram reweighting. We further demonstrate the pronounced sensitivity of the estimated critical point to the van der Waals cutoff distance, underscoring the importance of properly accounting for long-range interactions. The present results capture qualitative shifts in the critical point of water arising from ionic interactions and confinement, and the Binder-cumulant framework used here is readily extendable to other critical phenomena, including the putative liquid-liquid critical point of water.

[1] J.T Siebert et al., Phys. Rev. E 98, 030601 (2018).

CPP 34.4 Wed 11:45 ZEU/0260

Cooperative molecular dynamics and nuclear quantum effects in bulk water — •Margarita Russina — Helmholtz-Zentrum Berlin for Materials and Energy, Berlin, Germany

The cooperative dynamics in water remain difficult to access due to the lack of long-range order and the short lifetimes of molecular correlations. Neutron scattering is well suited to probe such phenomena on the nanoscale but has been hindered by the weak coherent signal of H2O. Using a novel neutron polarization-analysis approach, we directly measure the coherent scattering in H2O and D2O with high accuracy [1]. Beyond self-diffusion and molecular rotation, we identify a picosecond cooperative process in liquid water, likely associated with rearrangements of several neighboring molecules and the reorganization of hydrogen bonds. This process may act as a precursor to large-scale molecular transport. In the intermediate wave-vector range $Q < 1$ 1/Å, the coherent signal in H2O is enhanced compared to the expectation for rigid, noninteracting, randomly oriented molecules. Since this Q-range corresponds to distances of several molecular spacings, our results provide evidence that intermolecular correlations in water extend beyond short-range correlations and involve more distant neighbors, giving rise to cooperative dynamical fluctuations. Such an enhancement can be rationalized by correlated preferential molecular orientations, hydrogen-bond rearrangements, and nuclear quantum effects. In contrast, D2O follows a more hydrodynamic behavior consistent with reported differences in the molecular bonding and symmetry of H2O and D2O. [1] M. Russina et al., J. Phys. Chem. Lett. (2025).