“Simulating the Hydrated Electron in Aqueous Electrolyte Solutions: Ionic Contact-Pairs Between Cations and Electrons”

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**ABSTRACT:** Aside from being the simplest quantum-mechanical solute, the hydrated electron is a key species in radiation and plasma chemistry due to its potential to efficiently reduce CO2 and participate in aerosol nucleation in the upper atmosphere. Experimental studies have established that when the hydrated electron is introduced into an aqueous electrolyte solution, its absorption spectrum undergoes a concentration-dependent spectral blue-shift that increases roughly linearly at low electrolyte concentration but saturates as the solubility limit is approached. Experiments have also demonstrated that the spectral shift is dependent on the electrolyte identity, with divalent and trivalent cations producing larger blue-shifts than monovalent cations, and perchlorate salts yielding larger shifts than their chloride-based counterparts. To develop a microscopical picture for the experimental trends, we examine the species’ dynamic and structural properties through mixed quantum-classical molecular dynamics simulations of an excess electron in concentrated aqueous NaCl, NaI, CaCl2, and CaI2 solutions. We find that the spectral shift is a consequence of the hydrated electron forming an ionic contact pair with multiple cations simultaneously, with the average number of electron-cation interactions increasing with electrolyte concentration. Furthermore, we find that the dielectric constant of the solution plays a negligible role in the observed spectroscopy, while the strength of the cation/anion ionic contact-pair is of great importance.

Thursday, May 5th, 2022  
12:00 p.m. | Young Hall 2033  
& via Zoom

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