Abstract Submitted
for the MAR15 Meeting of
The American Physical Society

Solvation of a Ruthenium Water Oxidation Catalyst, [Ru(tpy)(bpy)(H_2O)]$^{2+}$ ERIN DUFFY, BRETT MARSH, JONATHAN VOSS, ETIENNE GARAND, University of Wisconsin-Madison — The splitting of H_2O into H_2 and O_2 is an important reaction for alternative energy sources, but it is hindered by the water oxidation step due to its unfavorable thermodynamics. Production of a suitable water oxidation catalyst (WOC) has posed a challenge to researchers for decades, and the reaction mechanism is not well understood. One of the most well-known and extensively studied WOCs is [Ru(tpy)(bpy)(H_2O)]$^{2+}$ (tpy = 2,2':6,2"-terpyridine, bpy = 2,2'-bipyridine) and its derivatives. In this talk, infrared vibrational spectra (2400-3800 cm^{-1}) obtained by Cryogenic Ion Vibrational Spectroscopy (CIVS) of [Ru(tpy)(bpy)(H_2O)]$^{2+}$ and its water clusters, [Ru(tpy)(bpy)(H_2O)]$^{2+}$•$n$$H_2$O, are presented. In particular, the OH stretches are used as a probe of solvation strength, and trends in their spectral shifts are examined as a function of cluster size. Determination of water binding geometries are facilitated by comparison with density functional theory (DFT) calculations. Additionally, IR and mass spectral data of electrochemically-produced intermediates of the water oxidation cycle are shown, which provide evidence of proton-coupled electron transfer (PCET) events, in agreement with proposed mechanisms.

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Date submitted: 14 Nov 2014

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