SPECTROSCOPIC INVESTIGATION OF PROTON-COUPLED ELECTRON TRANSFER IN WATER OXIDATION CATALYZED BY A RUTHENIUM COMPLEX, [Ru(tpy)(bpy)(H₂O)]²⁺

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The splitting of H₂O into H₂ and O₂ is an attractive option for alternative energy, but the oxygen evolution step poses a significant challenge. A decades-long effort to produce a suitable water oxidation catalyst (WOC) has made progress on this front, but the precise reaction mechanism of these catalysts is still not well understood. One of the most extensively studied WOCs is [Ru(tpy)(bpy)(H₂O)]²⁺ (tpy = 2,2':6,2″-terpyridine, bpy = 2,2′-bipyridine). Presented here are gas-phase infrared spectra of water clusters of [Ru(tpy)(bpy)(OH₂)]²⁺ and the first intermediate of the catalytic cycle, [Ru(tpy)(bpy)(OH)]²⁺. In particular, the O-H stretches are used as a probe of solvation strength, and trends in their spectral shifts are examined as a function of cluster size. With the aid of density functional theory (DFT) calculations, these spectra reveal structural changes induced by solvation that provide clear evidence for proton-coupled electron transfer (PCET), in support of proposed mechanisms.