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Photodissociation Spectroscopy of Ruthenium Polypyridyl Complexes in Vacuo SHUANG XU, JAMES SMITH, J. MATHIAS WEBER, JILA/University of Colorado at Boulder — Photoelectrochemical water oxidation is a direct way to produce solar fuels from renewable sources. Since this reaction has a high reaction barrier, a cost-effective catalyst is necessary. Ruthenium polypyridyl complexes are promising catalysts for water oxidation. However, the mechanism of catalytic action is not well understood. One major difficulty of a mechanistic understanding is the complexity of reactive solutions under turnover conditions. To circumvent this problem, we applied electronic photodissociation spectroscopy in the UV and visible spectral range to a series of mass selected ruthenium polypyridyl complex ions in vacuo. The ions in this work are of the form $[\text{Ru}^{II}\text{-L}]^{2+}$, where Ru^{II} represents ruthenium(II)-bipyridine-terpyridine, a prototype catalyst belonging to the ruthenium-polypyridyl family. By varying the ligand L, we were able to study the ligand influence on the photophysical properties of the complex. The cases where $\text{L} = (\text{H}_2\text{O})_{1,2,3}$ are of particular interest because they are directly related to an intermediate in the catalytic cycle for water oxidation. Our experiment in vacuo is an essential complement to experiments in solution and provides unique information for understanding the photophysics and photochemistry of these complexes on a molecular level.

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