CALCULATION OF GAS-PHASE ELECTRONIC SPECTRA OF TRANSITION-METAL COMPLEXES[a]

JAMES T. MUCKERMAN, *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000*.

Despite widespread interest in the electronic structure and spectra of transition-metal complexes such as the starting and intermediate species of redox catalysts for water oxidation or hydrogen production, theoretical predictions of their electronic spectra generally come only from time-dependent density functional theory (TD-DFT) and are limited to one-electron excitations. Here we compare the results of TD-DFT to those of multi-reference configuration-interaction calculations for predicting the electronic spectra of some model and actual transition-metal-containing catalysts. Of particular interest are complexes with redox-active ligands that complicate the assignment of formal oxidation states, and complexes containing second- and third-transition-series metals.

[a]This work was performed at Brookhaven National Laboratory and funded under contract DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences. The U.S Department of Energy is also gratefully acknowledged for funding under the BES Hydrogen Fuel Initiative.