Calculation of X-Ray Absorption and Photoemission Spectra of Molecules in Complex Environment

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I will present recent results of the calculation of N K-edge absorption spectra and N1s Photoemission spectra of triazine molecules in gas phase and adsorbed on a gold surface.[1] The calculations were performed with the Vasp[2] code and the projector augmented wave approach (PAW)[3]. The main advantage of the periodic scheme in the present context is that the metal surface or the triazine monolayer can easily be included in the calculations. With the same method, we have performed C1s and Ru3d photoemission spectra calculations for Ru complexes in aqueous solution. This work is part of a theory-experiment collaboration to probe the the electrochemical properties of molecular electrocatalysts in aqueous environment by means of in operando spectroscopy employing synchrotron-based X-ray photoelectron spectroscopy (XPS). The photoelectron spectra were measured by means of a liquid jet. We have focused our study on the model system $[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ showing a unique fingerprint of the higher valence *ruthenium oxo* species in the XPS spectra, in relation to the oxidative reaction pathway. In addition to the transition potential approach[5], we have also used *ad hoc* cut water clusters, computed by Monte Carlo simulations to account for the aqueous environment surrounding the complexes.

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