First-principles interpretation of ultrafast time-resolved core-level spectroscopies investigating photo-induced charge transfer

C. D. Pemmaraju[1] and David Prendergast [2]

[1]*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

[2]*The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

Ultrafast time-resolved core-level spectroscopies provide valuable real-time element-specific probes of chemical dynamics and play an ever more prominent role in the characterization of photoelectrochemical (PEC) systems for energy harvesting applications [1]. However an unambiguous interpretation of the observed transient spectroscopic signatures requires theoretical methods capable of connecting these to structural and dynamical models of materials. We present two case studies of first-principles theoretical methods applied in conjunction with experimental time-resolved x-ray photoemission spectroscopy (TRXPS) and time-resolved x-ray absorption spectroscopy (TRXAS) to investigate charge transfer dynamics at organic-inorganic interfaces relevant to PEC technologies. We use a combination of constrained density functional theory (CDFT) and time-dependent density functional theory (TDDFT) to interpret measured transient core-level shifts in femtosecond to picosecond time-resolved XPS/XAS measurements. In the first study, the dynamics of electron injection from a N3 dye molecule chemisorbed onto a ZnO substrate, within the first picosecond after photo-excitation, is investigated. We argue that the core-level shifts observed a few hundred femtoseconds after photo-excitation of the dye are consistent with a charge-separated exciplex state [2]. In the second study, we theoretically interpret spectroscopic signatures of laser-excited Zn-porphyrin based donor-pi-acceptor dyes [3] as observed in TRXAS measurements with 80ps time resolution. These studies illustrate the utility of combined experimental and theoretical studies in achieving an in-depth understanding of dynamical processes in PEC materials.

References:

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