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How dispersion interactions at the excited state can tune photochromism of embedded chromophores?

The importance of dispersion forces for structural stability, molecular recognition, reactivity, and catalytic properties in molecular systems, from materials to biology, is well recognized. For instance, the relaxation dynamics of the initial excited state involved in the photoisomerization process of chromophores are highly influenced by their surrounding environment. [1] Since computational schemes exclusively accounting for the effect of the protein atomic charges can lead to a qualitatively wrong picture, [2] modeling a responsive protein environment is fundamental to successfully capture its tuning effects on the chromophore. However, our current knowledge of how dispersion affects excited chromophores interacting with the surrounding environment remains limited. [3] Current multiscale quantum/classical models that employ an atomistic description of the environment are generally based on electrostatic or polarizable embedding protocols and dispersion is described using Lennard-Jones or other empirical models. In this talk, we introduce a customized state-specific model designed specifically to investigate excited systems using a quantum/classical hybrid multiscale protocol [4]: the atomistic polarizable environment that includes dispersive interactions responds to the excited state electron density of the chromophore, and we call this model QM/MMpol-cLR3 [7]. Here we show that QM/MMpol-cLR3 is able to accurately capture solvatochromic shifts in two paradigmatic systems where dispersive interactions with the environment prevail, azulene and bacteriochlorophyll a (BChl a) in low polarity solution. Our analysis, surprising, indicates a different origin for dispersion shifts in these two cases. Finally, we apply the model to the BChl a pigments of LH2 of purple bacteria, showing that heterogeneities in the atomistic environment led to significantly different dispersion shifts in the BChl pigment.

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