

Ab initio study of the excited state properties of azobenzene-functionalized photoresponsive MOFs

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Abstract: Carbon capture and sequestration is emerging as an important technology for mitigation of climate change. Novel porous materials acting as solid state adsorbents for CO₂ gas have shown promise of energy efficient carbon capture when used with temperature and pressure swing operation. Metal-organic frameworks (MOFs) which are crystalline and hybrid porous materials made of organic linkers and metal nodes constitute an important family of candidates for carbon capture. Metal-organic frameworks functionalized with azobenzene, a widely studied photoswitch capable of changing its geometry from trans to cis configurations and vice-versa, are capable of capturing carbon with light stimulated photoswitching process. The use of light as a stimulus, in this case, can reduce greatly the energy costs of the carbon capture. Modeling atomistically the azobenzene functionalized PCN-123 MOF within the density functional theory (DFT), the microscopic mechanism of the carbon capture is determined to be the blocking and unblocking of the metal-node, a prominent adsorption site of CO₂, by the cis and trans configurations of azobenzene. To achieve high efficiency of gas capture using such MOFs, the photoswitching of the azobenzene must be controlled by using light stimuli of appropriate wavelengths yielding higher fractions of either isomers. A detailed understanding of the optical absorption of the azobenzene photoswitches is indispensable for achieving the same. Many-body perturbation theory (MBPT) methods, namely GW and Bethe-Salpeter equation, are used to accurately compute the optical spectra of solvated azobenzene derivatives and azobenzene functionalized MOF. In case of solvated azobenzene molecules, the GW/BSE approach is combined with a non-equilibrium embedding scheme to account for the dielectric screening by the solvents. The problem of the dependence of the BSE spectra on DFT exchange-correlation functional is addressed by tuning the PBE global hybrid functional such that the DFT and GW ionization potentials (IP) are matched to the fulfillment