

The electronic excitation spectra of both chlorophyllide a (Chl) and pheophorbide a (Pheo) molecules in solvents have been investigated by using the time-dependent density functional theory (TDDFT) along with the polarizable continuum solvation model (PCM). With increasing HF exchange percentage in DFT functionals, the predicted HOMO-LUMO gaps increase linearly while the excitation energies increase gradually and even strongly for excited states with partial intra-molecular charge-transfer (CT) nature. Based on the calculated excitation energies, oscillator strengths and frontier molecular orbital analysis, we provide some new insights into the absorption spectra of Pheo and Chl both in gas-phase and in solutions, especially for the B and higher electronic absorption bands. It is shown that the experimental observed visible Q_y and Q_x, and ultraviolet B_y and B_x bands are all due to singlet 1(π,π^*) valence excitations, with the B bands being more strongly red-shifted by solvent effects. Two 1(π,π^*) dark states are predicted slightly below (or near) the strong B band for both Chl and Pheo, with one related to the excitation of tetra-pyrrole ring and the other related to the excitation of ring I vinyl substituent. The 1(n,π^*) CT state from the conjugated carbonyl substituent is above B bands and further strongly blue-shifted by solvent effects. The higher ϵ and N bands are mainly due to 1(π,π^*) valence excitations with only partial CT character, which are also red-shifted in solvent.