

Abstract: English

This thesis investigates the factors controlling two-photon absorption (2PA) in retinal protonated Schiff bases and bovine Rhodopsin using quantum-chemical and quantum mechanics/molecular mechanics (QM/MM) methods.

First, calculations using the third-order approximate coupled-cluster method (CC3) were performed to obtain reference excitation energies, two-photon transition strengths, and 2PA cross-sections for reduced retinal models. Lower-level coupled-cluster methods and time-dependent density functional theory (TD-DFT) were then tested against these reference results. The second-order approximate coupled-cluster method (CC2) reproduced the main trends for the lower excited states at a much lower computational cost, although it became less reliable for closely spaced higher states. Among the tested density functionals, CAM-B3LYP and BHandHLYP gave the best overall description of the low-energy electronic and optical properties. The higher excited states were more difficult to describe because their 2PA values were strongly affected by state ordering and near-resonant enhancement.

The influence of retinal structure was then studied using seven 11-cis retinal protonated Schiff-base models with different methylation patterns along the polyene chain. Small changes in the number and position of methyl groups produced clear changes in the S_1 two-photon response. These changes were linked mainly to excitation energies, transition dipole moments, and excitation-induced charge redistribution. The two-state model reproduced the relative trends obtained from full quadratic-response calculations, although it overestimated the absolute 2PA values.

Finally, bovine Rhodopsin was investigated using QM/MM calculations with polarizable embedding. Ten molecular-dynamics snapshots and four QM-region sizes were examined. The S_1 excitation and its one-photon properties were relatively stable with respect to configurational sampling and QM-region size. In contrast, the higher excited states and their 2PA properties were more sensitive to the protein environment, molecular configuration, energetic compression, and near-resonant effects.

Overall, the work provides CC3 reference data for retinal models, validates lower-cost electronic-structure methods, shows how methylation along the polyene chain can tune 2PA, and examines the effect of the protein environment using QM/MM with polarizable embedding. The results also provide practical guidance for future calculations by showing which lower-cost methods can reproduce the main qualitative trends and where more accurate treatment is required.

