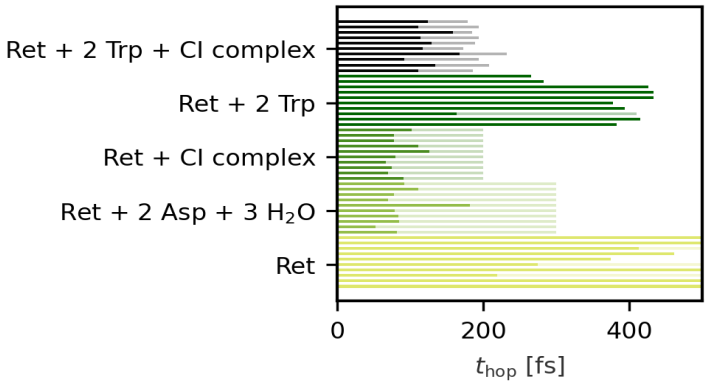
Extended Data Figure 2: QM/MM simulations and IR spectra

Simulations of *Hs*bR dynamics in the excited state were performed for five different QM regions. In the following graph ten trajectories for five different QM regions are presented. Strong colors represent trajectories before hopping, and faded colors trajectories after hopping. The hopping event describes the final transition from the excited state to ground state (parent or product state). The first QM region (black bars) includes retinal, Trp86, Trp182, and the counter-ion (CI) complex consisting of Asp85, Asp212, Arg82, and five water molecules W401, W402, W403, W406, and W407. Hopping occurs in every trajectory before 200 fs. The second QM region (dark green bars) consist of retinal, Trp86, and Trp182. Here, only in one of ten trajectories hopping takes place on a time-scale up to 300 to 400 fs. The third QM region (green bars) includes retinal and the counter-ion complex. In all ten trajectories hopping occurs before 200 fs. The same is observed for the fourth QM region (light green bars) composed of retinal, Asp85, Asp212, W401, W402, and W406. The fifth QM region (yellow bars) includes only retinal and in ten trajectories we find only three hoppings between 200 and 400 fs. Our simulations suggest the counter-ion complex assists fast hoppings or fast photoreaction.



On the basis of our trajectories IR spectra in the ES were generated for the five different QM (same color code as above). The spectral range between 1200 and 1800 cm^{-1} reflects mainly C-C, C=C, and C=N stretching vibrations of the retinal, while the spectral range from 2800 to 4000 cm^{-1} shows mainly OH stretching vibrations of water, HBWN, and N-H stretching vibrations. The spectral range between 2000 and 2600 cm^{-1} is the region where a continuum band (CB) absorbs. A CB is generated upon protonation of a HBWN or due to strengthening and red-shift of a HBWN upon an applied electric field. Our simulations show a significant increase in the CB region in the presence of the CI complex or of Asp85, Asp212, W401, W402, and W406 in addition to retinal. Thus, our simulations point to the CI complex as the origin of a CB during the ES.