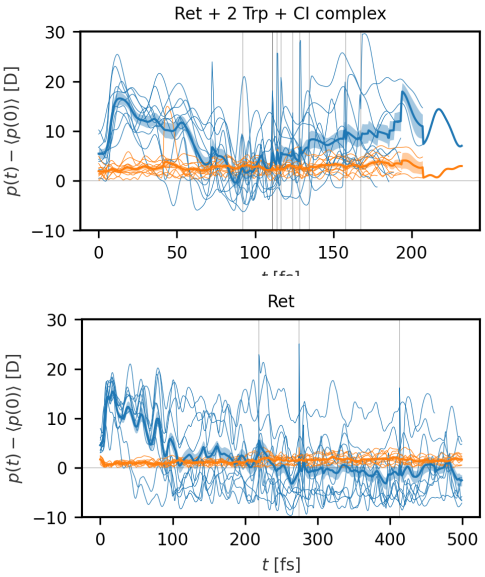
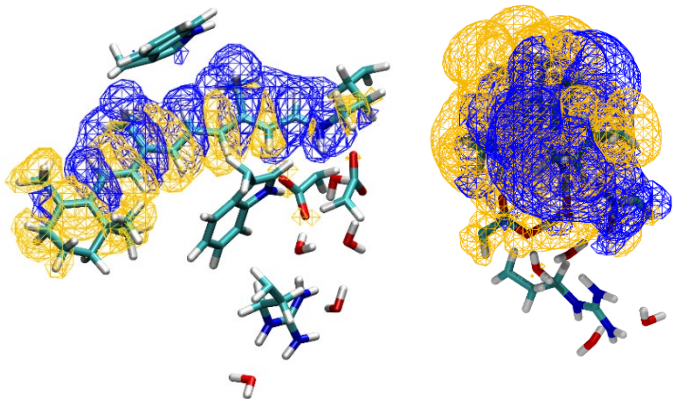
Extended Data Figure 1: QM/MM simulations of ultrafast dynamics

Trajectories were simulated in the S_1 electronic excited state and the dipole moment changes p(t) are compared to the average dipole moment in the S_0 ground state <p(0)> in the Figure below. Upper panel: the QM region includes retinal (Ret), the two tryptophans Trp86 and Tpr182, and the counter-ion complex (CI) consisting of Arg82, Asp212, Asp85, and five water molecules W401, W402, W403, W406, and W407. Blue curves indicate dipole moment change along the retinal backbone, while orange lines indicate dipole moment change perpendicular to retinals's backbone. Thick lines represent the average of all trajectories. Vertical grey lines indicate surface hopping events between the electronic states. Lower panel: Same for retinal only (Ret) on a longer time scale. It is evident that only a few surface hopping events occur and much later compared to simulations with 2 Trp and CI complex.



Simulated ED show strong fluctuations in the ES, due to relaxation of retinal's backbone, slightly different for various trajectories. In our pictures blue mesh represent increased ED and yellow mesh reduced ED. Here, we depict snapshots of ED change at 0 fs for retinal, Trps, and counter-ion complex (left side, lateral view on retinal) prior structural changes. Right side: ED changes at the counter-ion complex at 10 fs (top view on SB) (without Trps) at higher ED contour level. It is clearly visible that ED is mainly reduced at the counter-ion complex, and in this trajectory a proton seems to be shared between Asp85 and W402.

The adjacent tryptophans Trp86 and Trp182 experience a dipole moment change upon photoexcitation of retinal. In the graph below dipole moment changes of Trp86 and



Trp182 computed from the Mulliken partial charges are plotted for parallel (blue lines) and perpendicular (orange lines) orientations to retinal's backbone for individual trajectories and their average (thick lines). Both Trps experience a dipole moment change for individual (thin lines) and averaged (thick line) trajectories at Trp86 (left side) and Trp182 (right side) induced by retinal photoexcitation. Both Trps have a similar dipole moment change magnitude perpendicular to retinal backbone, but Trp86 exhibits a dipole moment change of about -2 D parallel to retinal's backbone. Note, that in contrast to retinal discussed above, dipole moment change at both Trps stays rather constant even upon reaching conical intersection around 130 fs and afterwards.