Charge Separation and Energy Transfer in a Caroteno-C_{60} Dyad: Photoinduced Electron Transfer from the Carotenoid Excited States

Figure 1 depicts the kinetic traces fitted with a 5-component sequential model rather than 6 components. Estimated lifetimes were 100 fs, 1.0 ps, 7.9 ps, 2 ns and a nondecaying component. As can be seen in at 512 nm, the rise of the triplet is not well described in this way. With the 6 component analysis, the sequential occurrence of spectrally silent species with a ~1 ns lifetime induces a delay in the onset of the carotenoid triplet rise, as observed experimentally. Figure 2 shows four selected traces at 464, 512, 580 and 621 nm fitted with a 6-component model obtained from the global analysis. The trace recorded at 464 nm is representative of the rise and decay of the carotenoid ground state bleach. The ultrafast rise of the bleach corresponding to the excitation of the S_2 state is followed by a multiphasic decay; at longer delays it shows a rise due to the population of the carotenoid triplet. The trace at 512 nm shows the rise of the carotenoid triplet; the trace recorded at 580 nm is taken as representative of the rise and decay of the carotenoid S_1 state while the trace at 621 nm shows the relaxation of the vibrationally hot S_1 state and the decay of the S_1 state.

A few selected traces at single wavelengths, 474, 530, 596, 632, 689 and 990 nm along with the corresponding fit from the target analysis of the transient absorption data obtained with the C–C_{60} dyad in toluene are shown in Figure 3.

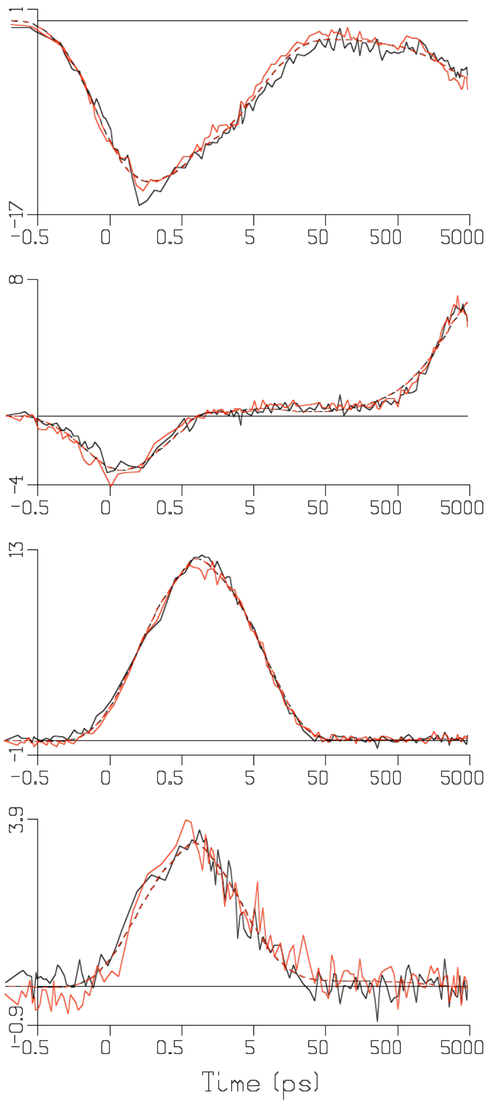

Figure 1. Kinetic traces at selected wavelengths (red and black lines correspond to two different data sets) along with the corresponding fit (dash line) that follows from the global analysis (with 5 kinetic components) of the time-resolved experiments on the C–C_{60} dyad in hexane.

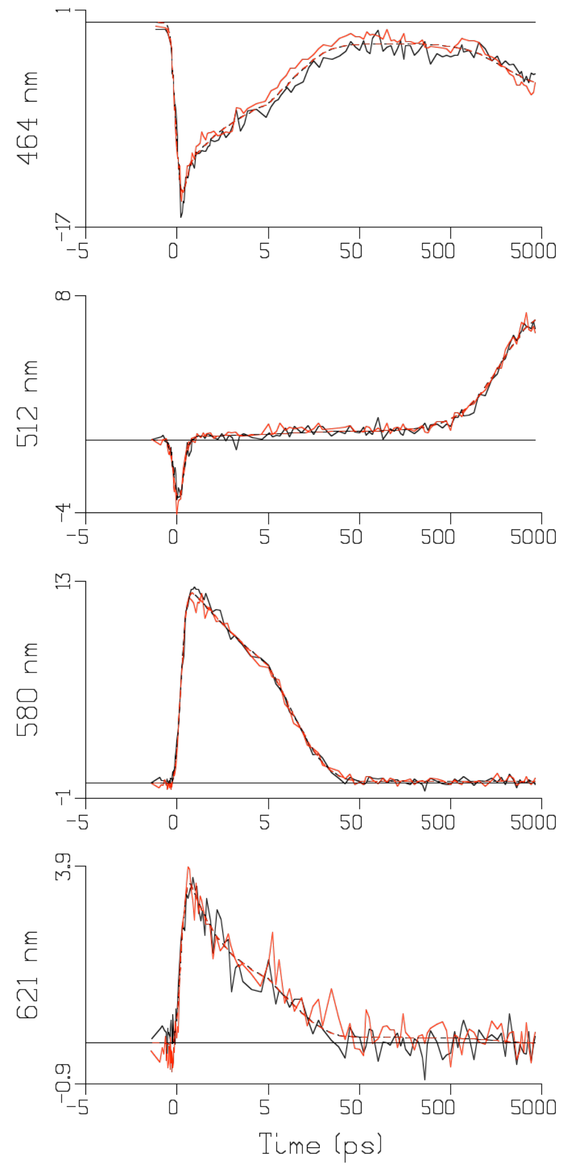

Figure 2. Kinetic traces at selected wavelengths (red and black lines correspond to two different data sets) along with the corresponding fit (dash line) that follows from the global analysis (with 6 kinetic components) of the time-resolved experiments on the C–C_{60} dyad in hexane.

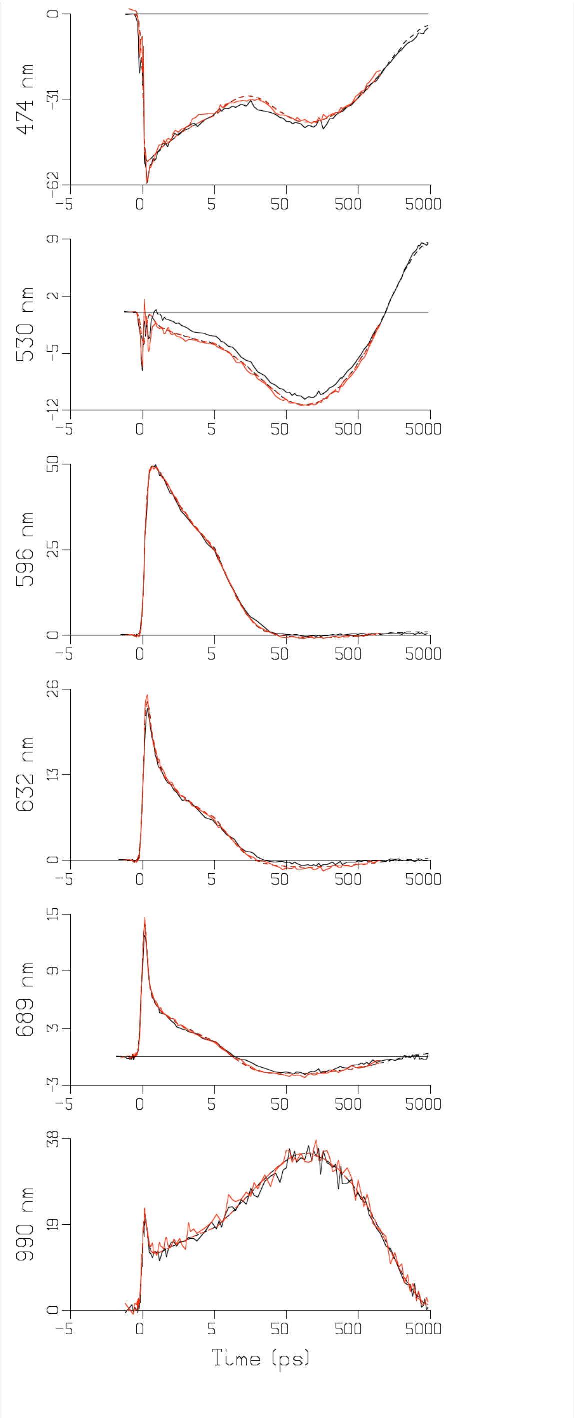

Figure 3. Kinetic traces at selected wavelengths (red and black lines correspond to two different data sets) along with the corresponding fit from a target analysis (dash line) of the time-resolved experiments on the C–C_{60} dyad in toluene with excitation at 475 nm.

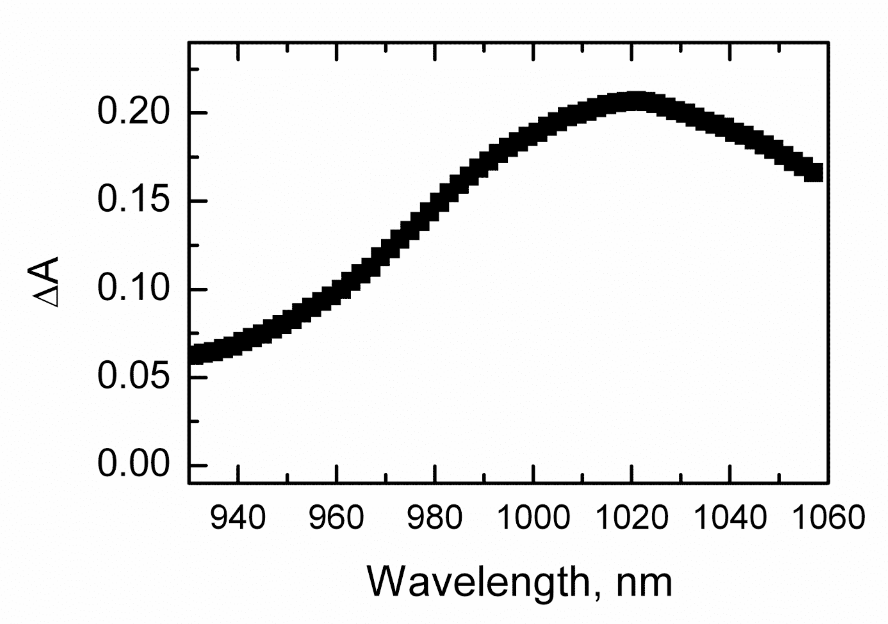

Figure 4. Transient absorption spectrum at 50 ps delay time of the C–C_{60} dyad in toluene with excitation at 480 nm.

The quantum yield of charge separation is calculated as follows based on 93% of the incident light being absorbed by the carotenoid and 7% by the C_{60}. The yield of charge separation from excited C_{60} is 100%. Of the light absorbed by the carotenoid, 16% gives direct photoinduced electron transfer from S_2, 21% gives energy transfer from S_2 to populate the excited singlet state of C_{60}, and 13% gives direct electron transfer from S_1

Therefore, the overall quantum yield of charge separation is given by

$(0.93)(0.16 + 0.13 + 0.21) + (0.07)(1) = 0.54$