Supporting Information: Femtosecond anisotropy excitation spectroscopy to disentangle the Q_x and Q_y absorption in Chlorophyll a

Clark Zahn,* Till Stensitzki, and Karsten Heyne*

Department of Physics, Free University Berlin, Arnimallee 14, D-14195 Berlin, Germany

E-mail: clark.zahn@fu-berlin.de; karsten.heyne@physik.fu-berlin.de

Phone: +49 30 838 56107

Transient dynamics of Chlorophyll a

Transient signals of the keto C=O bleaching (BL) at 1688 cm^{-1} (red) and excited state absorption (ESA) at 1660 cm^{-1} (black) are shown in Figure S1 a). Parallel and perpendicular pump-probe polarization orientation are shown in dark and light colors respectively. Pre time-zero signal is associated with perturbed free induction decay. After 0.4 ps no significant change in signal is observed. Dichroic ratio for both the BL as well as for the ESA band are displayed in Figure S1 b). In the observed delay times no decay of dichroic ratio/anisotropy is found. The dichroic ratio obtained from modelling the averaged absorption spectrum with a sum of Lorentzians is shown in blue.

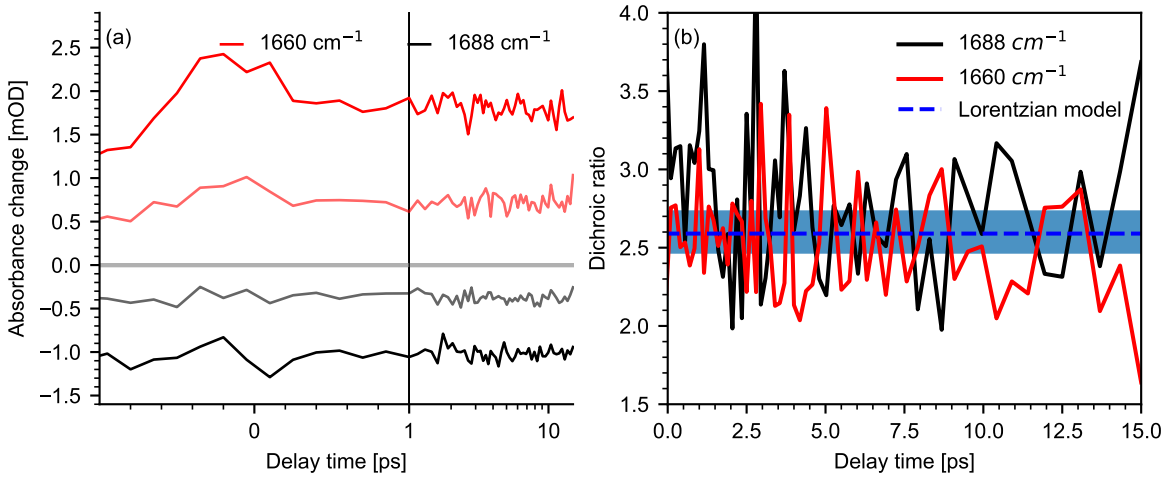

Figure S1: (a)Polarisation resolved transient absorption changes, for parallel (dark colors) and perpendicular (light colors) pump-probe polarisation orientation of the main keto C=O upon excitation at 670 nm. The positive and negative signals at 1660 cm^{-1} and 1688 cm^{-1} are associated with ESA and BL, respectively. After 1 ps no dynamics are observed within the measured delay times.(b) Dichroic ratio of the 1660 cm^{-1} and 1688 cm^{-1} band and dichroic ratio determined from modeling the averaged spectra (dotted blue line). Its corresponding 1σ error range is indicated in light blue

Ensuring photoselection - power titration

Excitation energy has a strong influence for anisotropy measurements leading to possible systematic error, thus this needs to be carefully considered in the experiments. In our experiment, we always only excited less than 20% of the molecules in the sample. However, in order to clearly rule out significant angular bleach at this rate of excited molecules, we performed a power titration, displayed in figure S2. The power titration shows, that within the error margin the angles at low power densities and lower rate of excited molecules are identical. Only at higher power densities a shift towards the magic angle, i.e. smaller anisotropy, occurs. The determined anisotropies are identical within the error margin for an excitation level of up to 20%. The accuracy for calculating the rate of excited molecules mostly depends on the focal diameter. We measured the FWHM of the focal diameter for the x- and y-direction using knife edges and employing the motor controlled sample stage. We detect the intensity change as a function of the position of the knife edge blocking a part

of the beam. Since, the error for measuring the focal diameter does not depend on the focal diameter itself but rather on the minimal resolution using the knife edge method, the relative error increases for smaller spot sizes. In determining the focal pump spot size, we generally estimate the errors towards a smaller spot size in order to prevent too high intensities. Thus, our focal spot sizes are expected to be on the larger side of the error margin of the spot size stated in the manuscript.

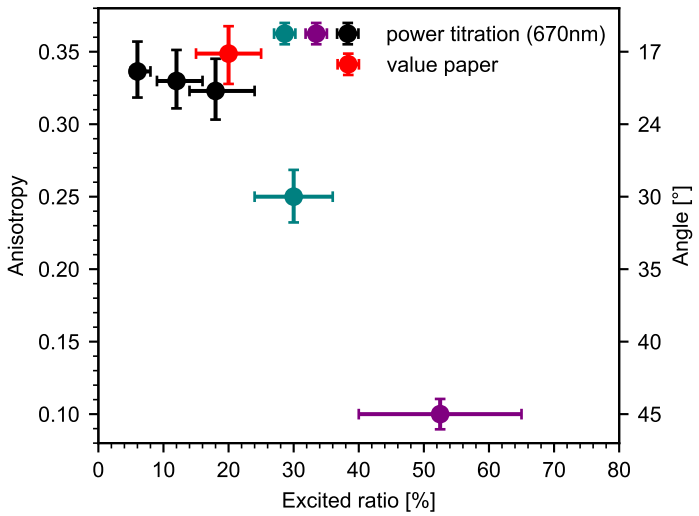

Figure S2: Power titration of the C=O anisotropy upon excitation at 670 nm. The measured anisotropy is plotted as a function of the percentage of excited molecules. The main error for determining the percentage of excited molecules is given by the pump spot size. Measurements with identical pump spot size are plotted in the same color. The pump spot size is decreasing from red, to black, to teal to purple. Pump energy: black: 100, 200, 300 nJ, teal: 350 nJ, purple: 350 nJ, red: 500 nJ.