Supplementary Material to

Estimation of Damped Oscillation Associated Spectra from ultrafast transient absorption spectra

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Thirteen figures demonstrating the reproducibility of the data and the quality of the fit, the analysis of the residuals, and the complete DOAS analysis of the data and of the simulations. In addition, the effect of averaging over four consecutive wavelengths is demonstrated.

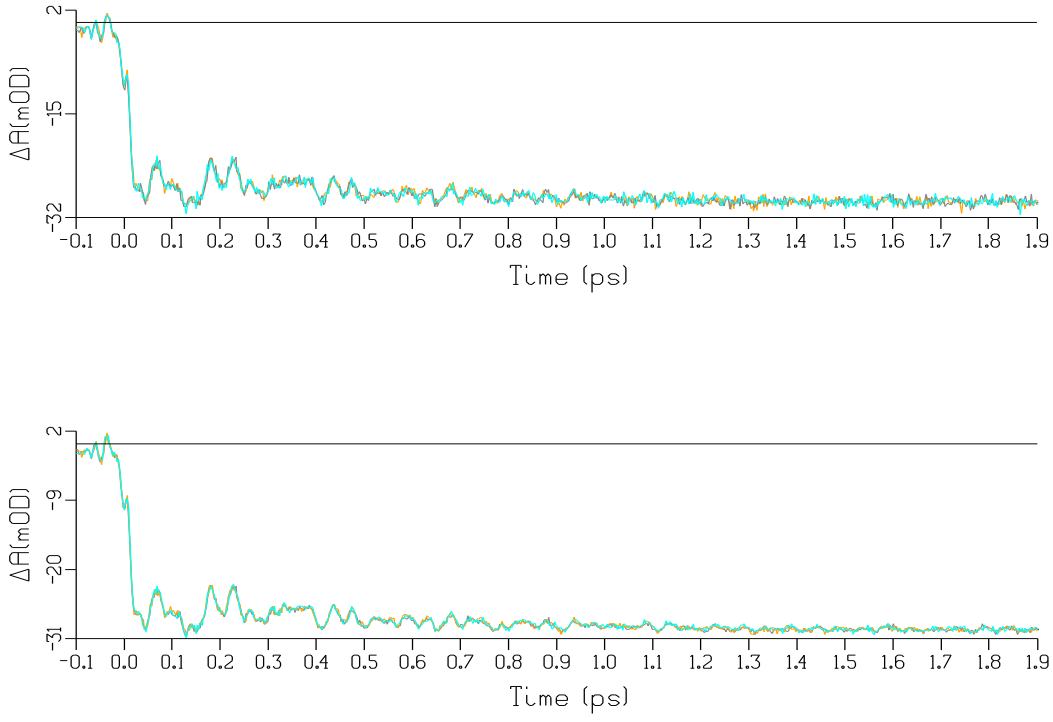

Figure S 1 Reproducibility and signal to noise ratio of transient absorption at 630 nm, wavelength resolution 0.293 nm (top) or 1.172 nm (bottom), three repeats, colored grey, orange and cyan. The maximum of the IRF is at time zero.

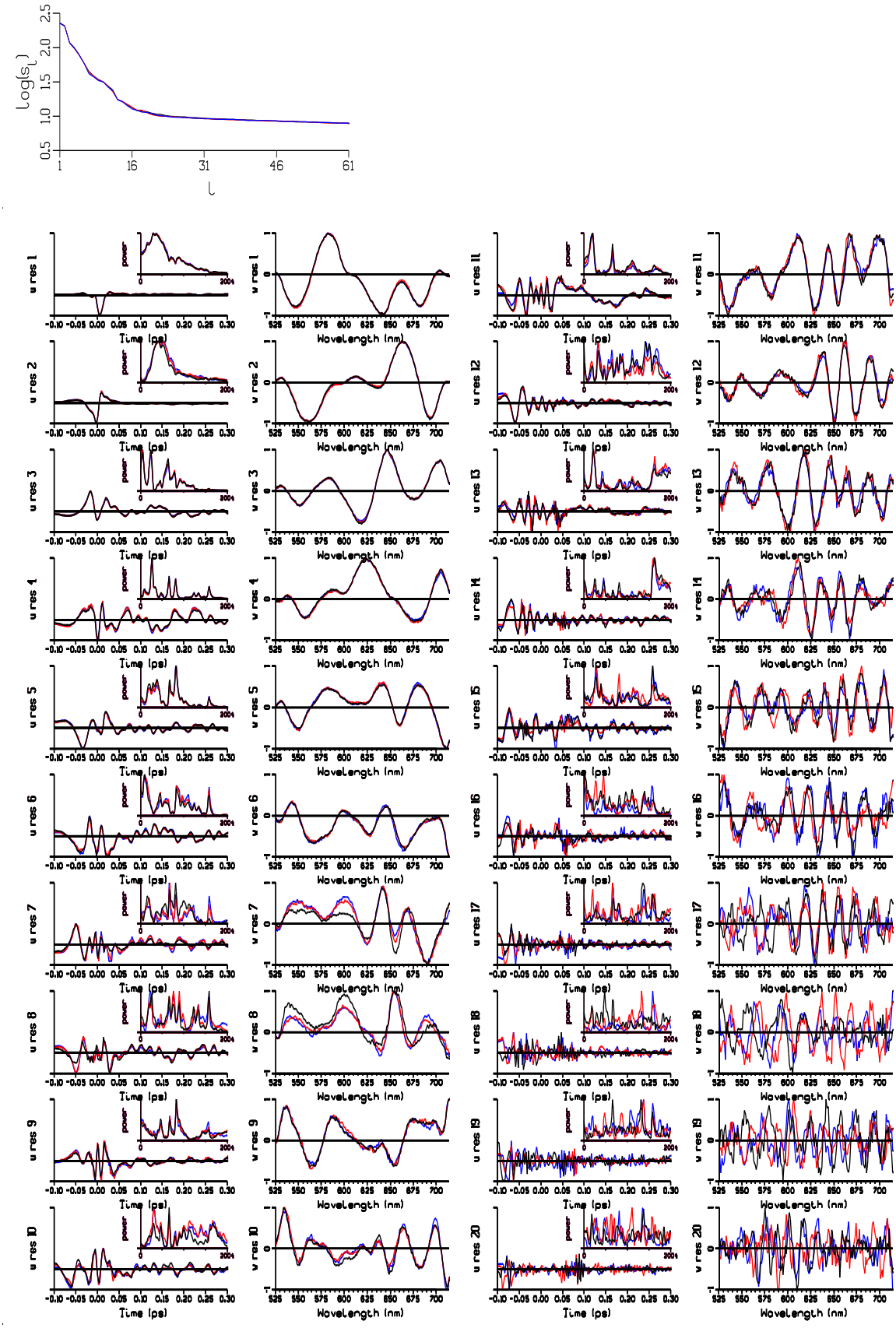

Figure S 2 Residual properties without fitting the damped oscillations. On top the screeplot, depicting the logarithm of the singular values of the matrix of residuals. Below that, the first twenty left (u res, zoom until 0.3 ps after the maximum of the IRF) and right (w res) singular vectors of the residual matrix without fitting the damped oscillations. Insets left: power spectrum from 0 to 2004/cm. Black, red and blue color indicate the three different data sets.

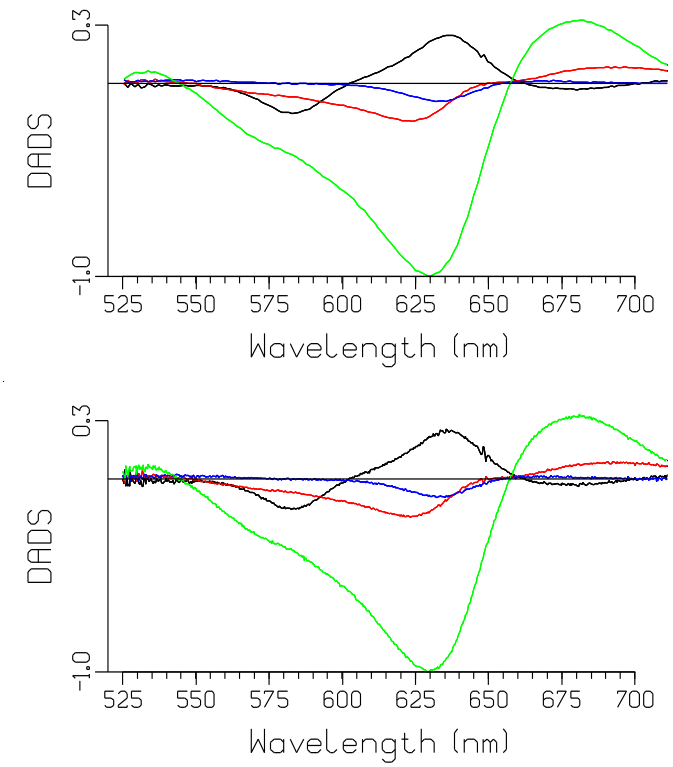

Figure S 3 Comparison of DADS with wavelength resolution 1.172 nm (left) and 0.293 nm (right). Key: 0.84 (black), 7.5 (red), 109 (blue) and 1569 (light green) ps.

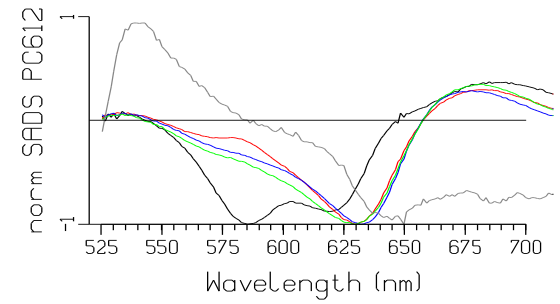

Figure S 4 Normalized SADS from Figure 5 and difference spectrum of the long-lived component (grey).

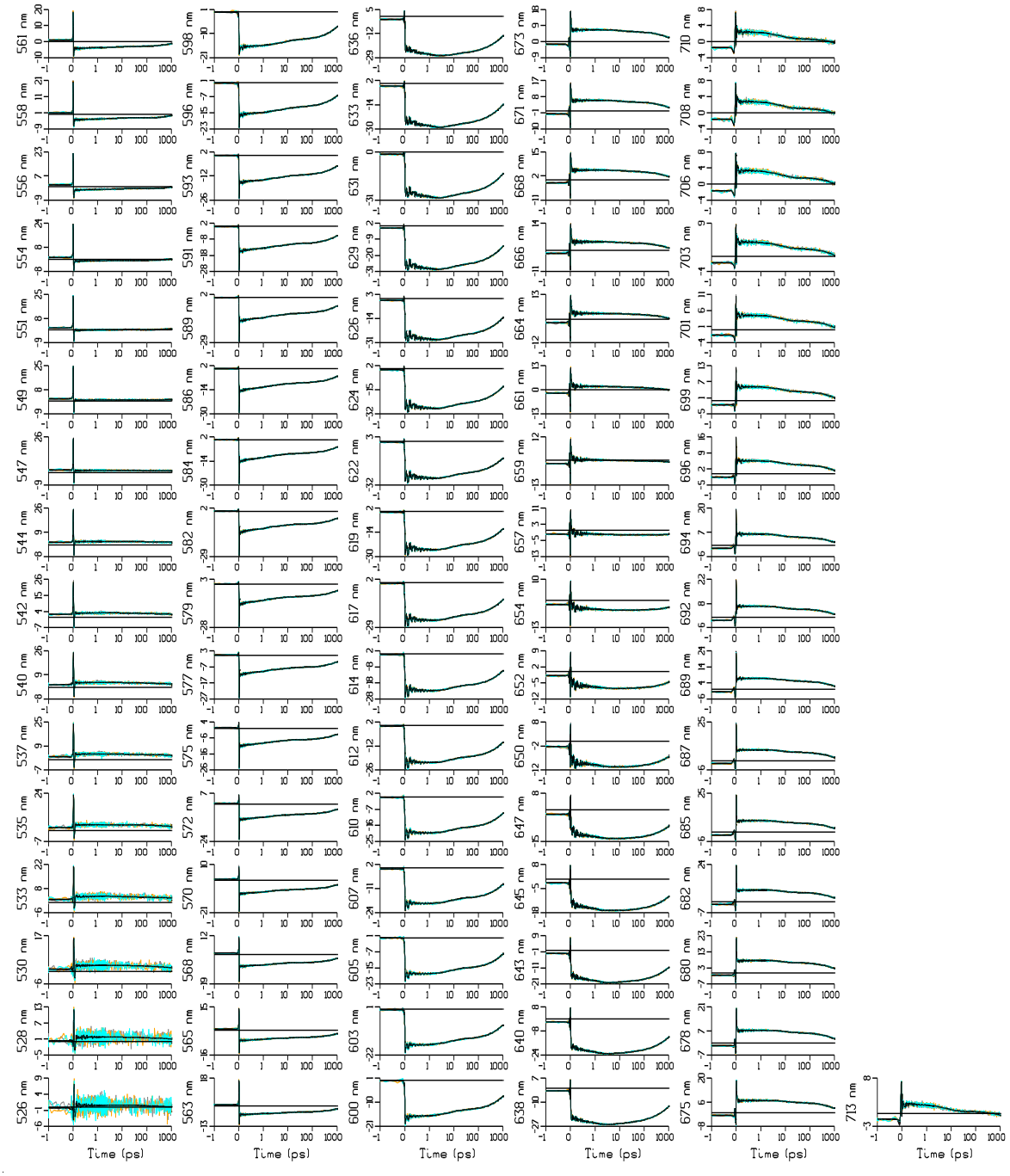

Figure S 5 Selected time traces of PC612 data (in mOD, three experiments indicated in grey, orange, and cyan) and fit (black). Wavelength step 1.172 nm, every second wavelength (indicated in the ordinate label) is depicted. Note that the time axis is linear until 1 ps (after the maximum of the IRF), and logarithmic thereafter.

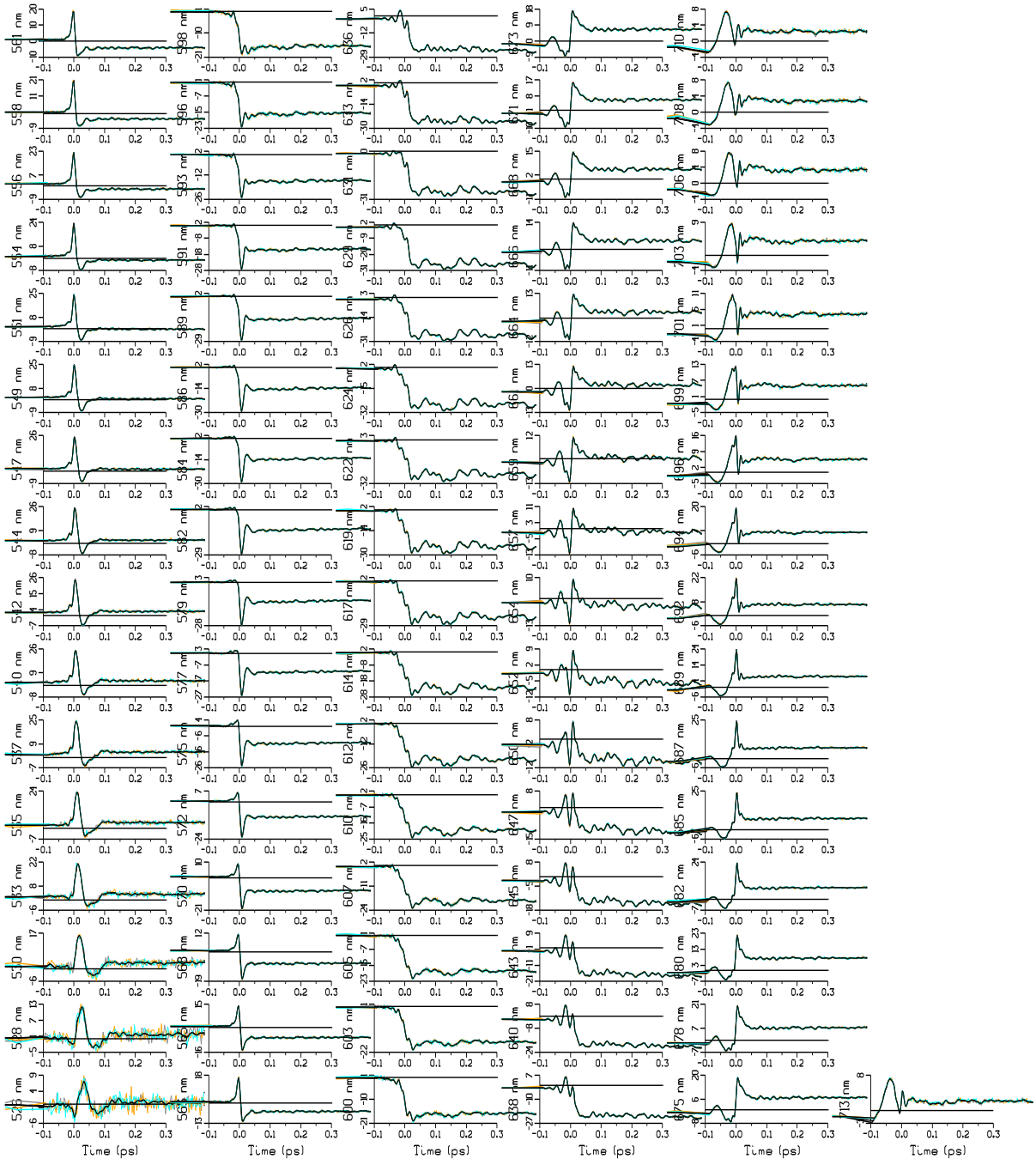

Figure S 6 Selected time traces of PC612 data (in mOD, three experiments indicated in grey, orange, and cyan) and fit (black). Wavelength step 1.172 nm, every second wavelength (indicated in the ordinate label) is depicted. Zoom from -0.1 ps to 0.3 ps (after the maximum of the IRF).

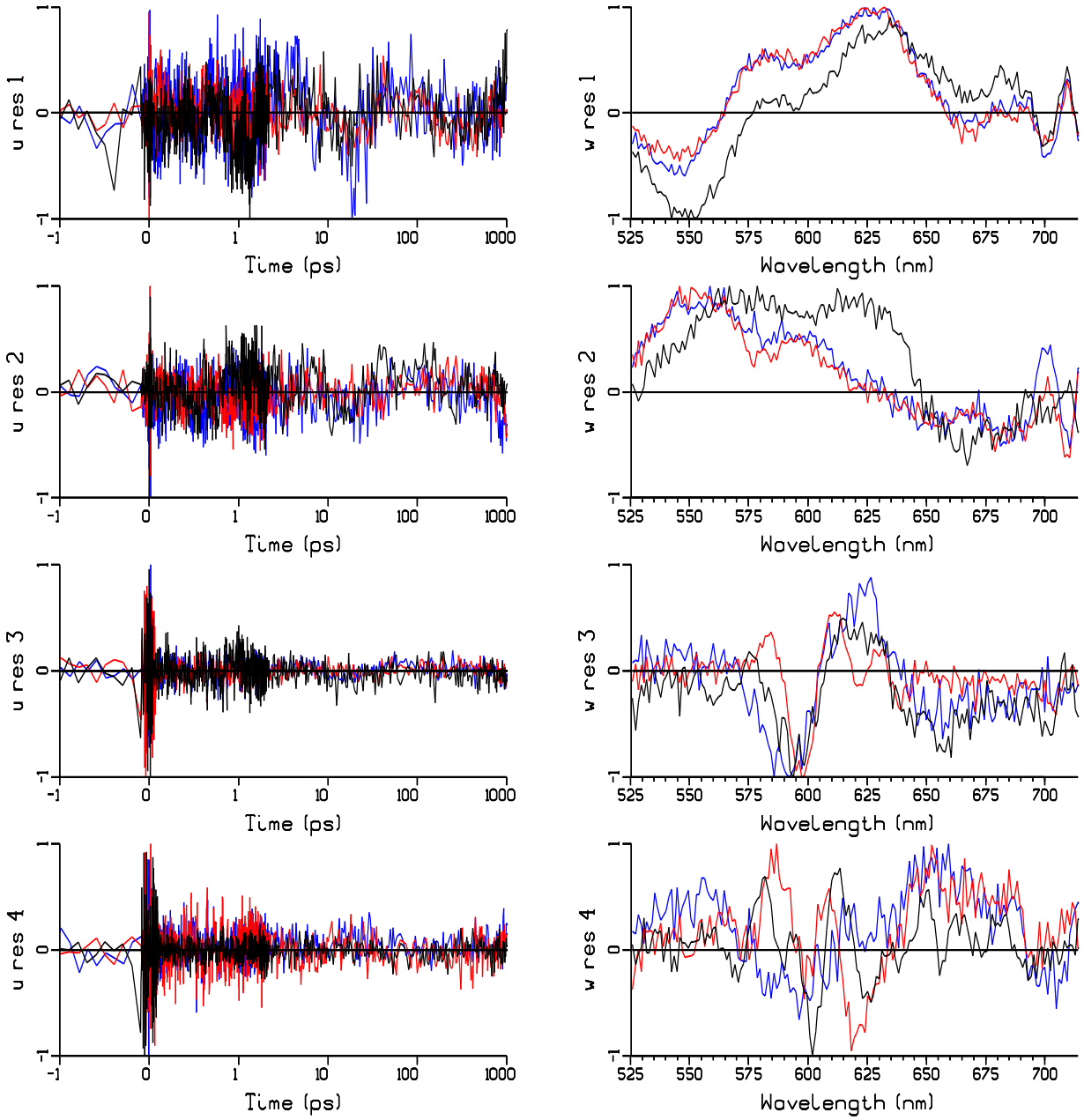

Figure S 7 Residual properties after fitting the damped oscillations. From top to bottom first, second, third and fourth left (u res) and right (w res) singular vectors of the residual matrix. Black, red and blue color indicate the three different data sets. Note that the time axis is linear until 1 ps (after the maximum of the IRF), and logarithmic thereafter.

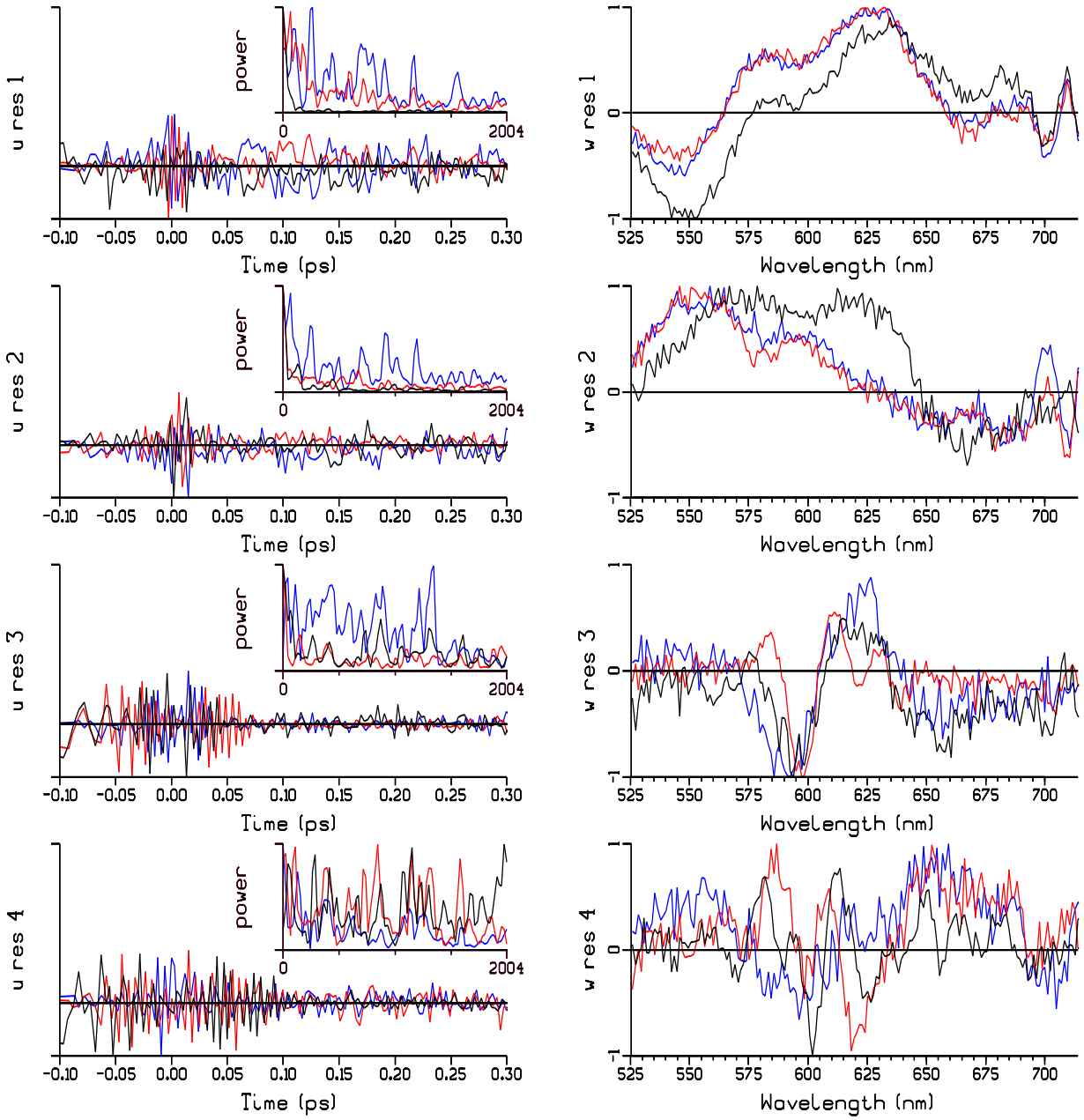

Figure S 8 Residual properties after fitting the damped oscillations. From top to bottom first, second, third and fourth left (u res, zoom until 0.3 ps after the maximum of the IRF) and right (w res) singular vectors of the residual matrix with power spectrum (insets left) from 0 to 2004/cm. Black, red and blue color indicate the three different data sets.

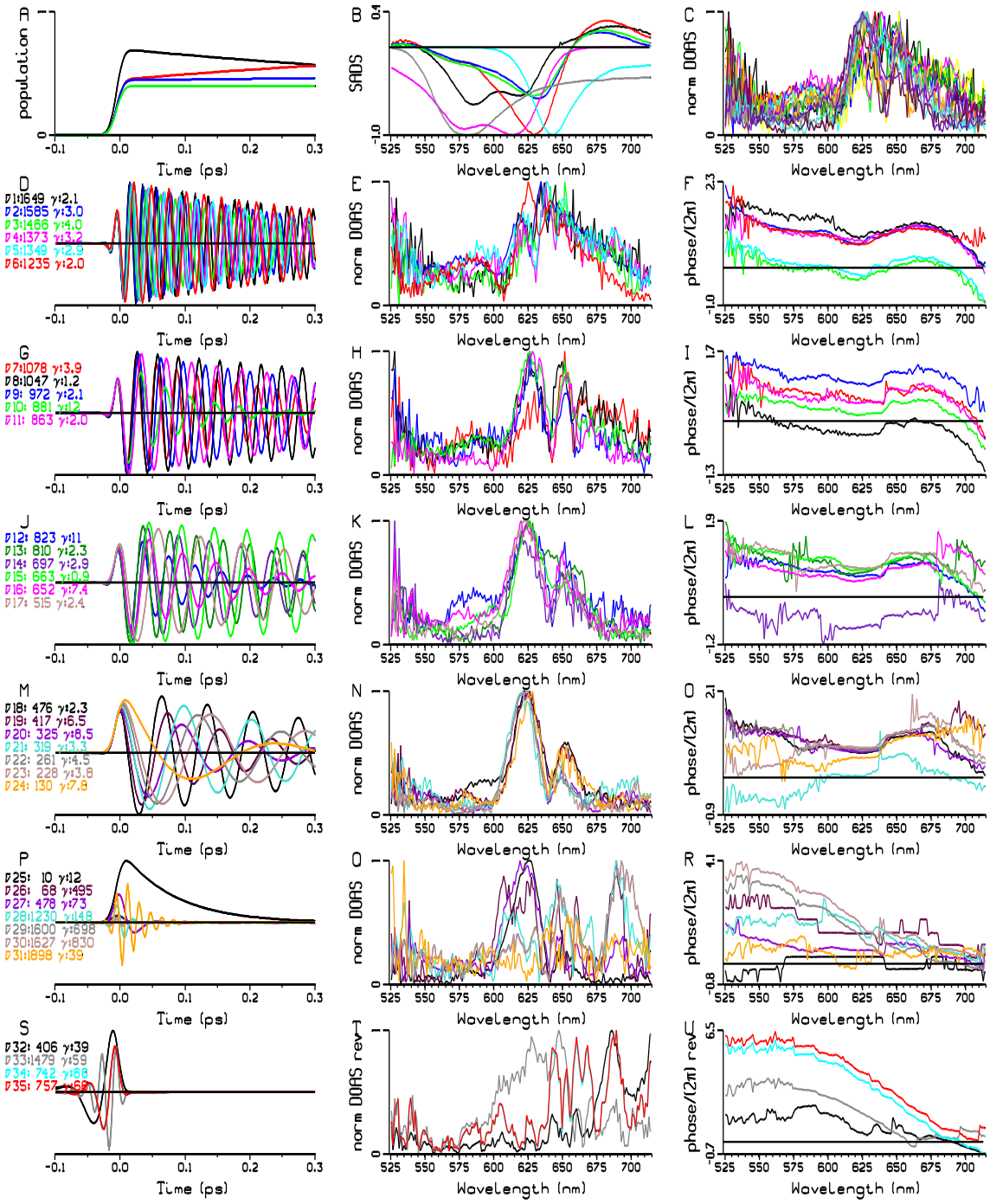

Figure S 9 (A) PC612 species populations from Figure 5B, (B) SADS from Figure 5C. In addition the negative of the steady state absorption (magenta) and emission (cyan) are plotted for reference, (C) superposition of the first 15 DOAS. Row 2-7: Overview of all 35 PC612 DOAS (normalized, to compare shapes). (left column) Cosine oscillations with frequencies $\bar{\nu}n$ (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. The maximum of the IRF is at time zero. (middle column) Estimated DOAS (with number indicated in the legend at the far left), normalized (norm) for comparison, color coded as in the left column. (right column) Accompanying phase profiles.

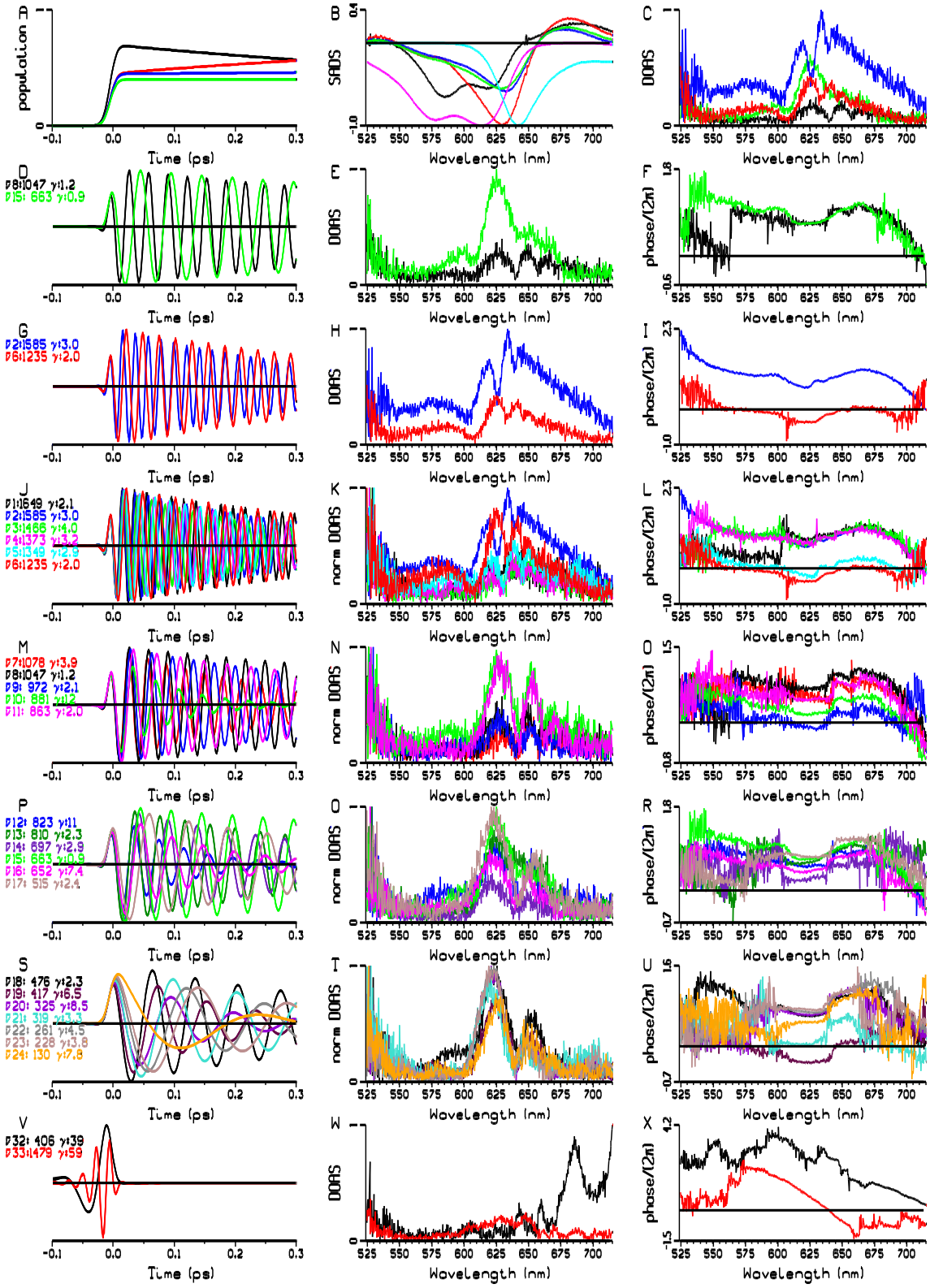

Figure S 10 Overview of the estimated DOAS and phases with wavelength resolution of 0.293 nm, compare to 1.172 nm in Figure 6. (A) species populations from Figure 5B depicted until 0.3ps. The maximum of the IRF is at time zero. (B) SADS. In addition the negative of the steady state absorption (magenta) and emission (cyan) are plotted for reference. (C) superposition of four selected DOAS with frequencies between 663 and 1585/cm, and damping rates between 0.9 and 3.0/ps, which are detailed in panels D-I. Row 2-8: (left column) Cosine oscillations with frequencies $\bar{\nu}n$ (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (middle column) Estimated DOAS (with number indicated in the legend at the far left), normalized (norm) for comparison. (right column) Estimated phase profiles of the DOAS.

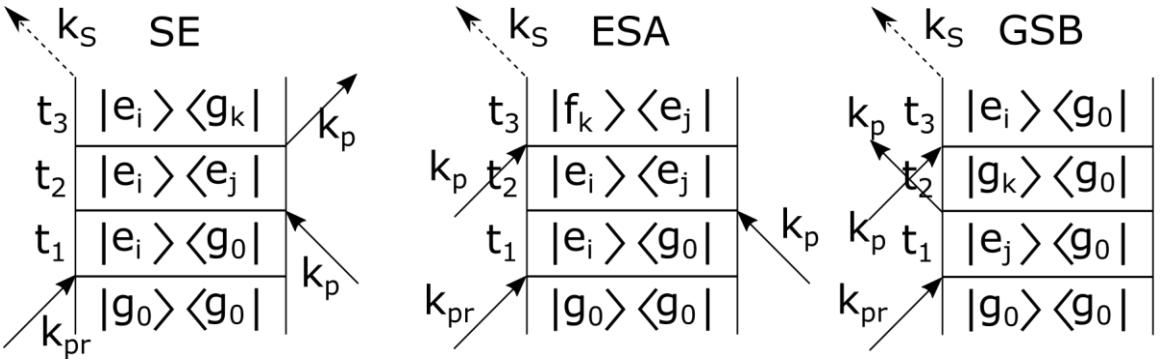

Figure S 11 Double-sided Feynman diagrams for the negative-time oscillatory signals. SE: stimulated emission, ESA: excited state absorption, GSB: ground state bleach. k_p, k_{pr} represent interaction with the pump and probe field, respectively, k_s is the signal emission (always in the $k_s=k_p-k_p+k_{pr}$ direction). The system interacts first with the probe pulse and then twice with the pump. The TA delay time is t_1 and in the snapshot limit $t_2=0$. As in the positive time-ordering, the signal spectrum (Fourier transform in t_3) is detected by a spectrograph, self-heterodyned with the probe field. As the signal field is emitted only after the interaction with the pump, a phase difference between the probe and signal fields depends on t_1. For simplicity we show the dominant contribution which starts from the lowest vibrational state in the ground state.

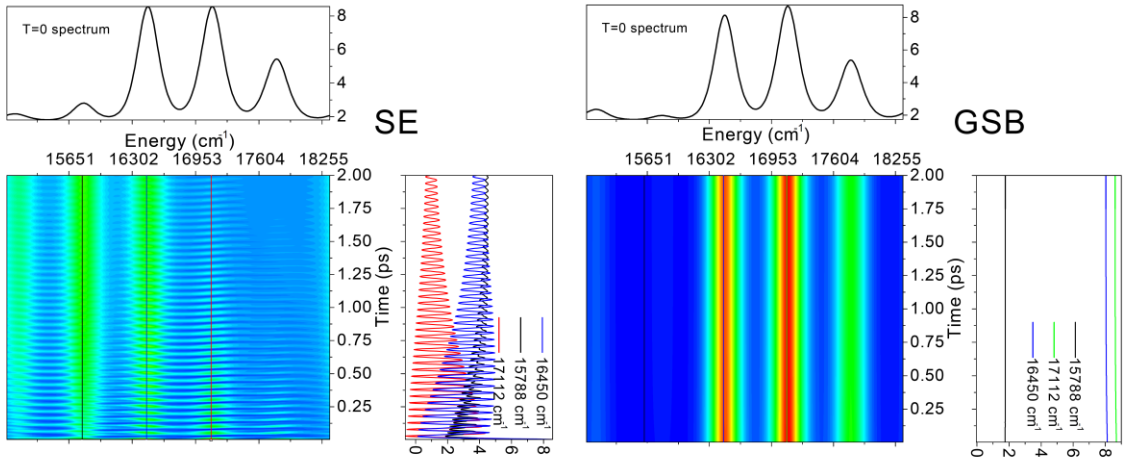

Figure S 12 Simulated transient absorption signals. Left: SE, Right: GSB. Top frames: T=0 spectra, Right frames: time trace at three transition peaks.

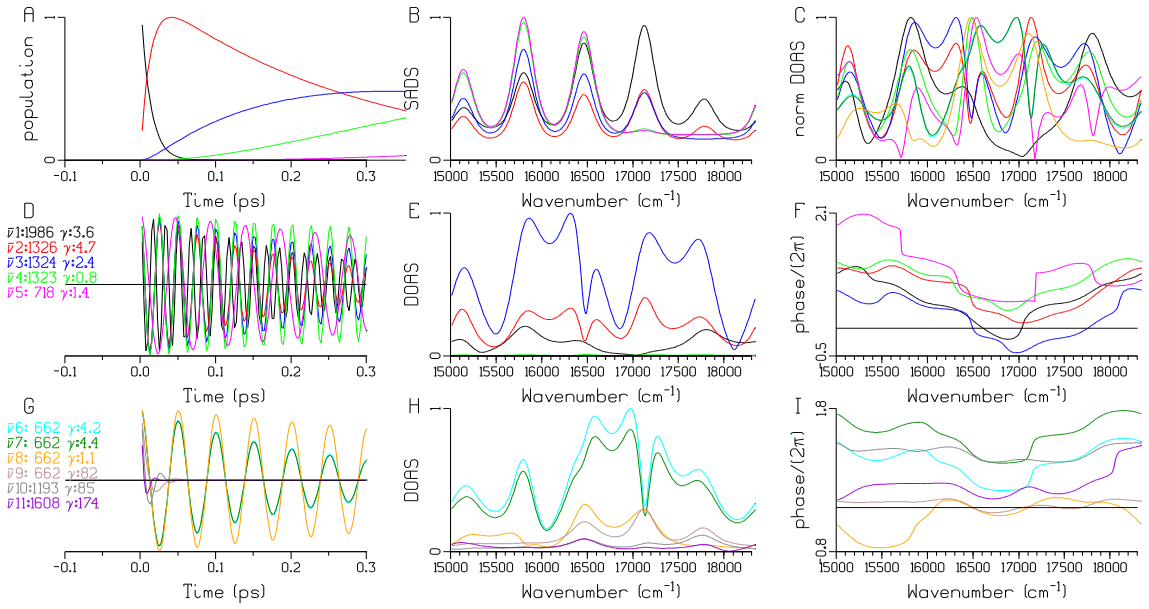

Figure S 13 Global fits of the simulated SE signals. (A) evolution of species populations, (B) associated SADS (C) first eight normalized DOAS. (D and G) Cosine oscillations with frequencies $\bar{\nu}n$ (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (E and H) Estimated DOAS (with number indicated in the legend at the far left), color coded as in (D and G). (F and I) Accompanying phase profiles.