Time-Dependent 5th Order Bands in Nominally 3rd Order 2D IR Vibrational Echo Spectra

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Supporting Information: Intensity Dependence of Fifth Order Bands

Shown in Figure S1 are 2D IR spectra of the CO stretching mode of horse heart myoglobin with CO bound at the active site (MbCO) encompassing a wider frequency range than shown for cyt P450-CO in Figures 1 and 6 of the main paper. Panel A shows the spectrum obtained with full laser energy, while panel B shows the spectrum obtained with 90% reduction in the energy of only the first pulse. In A, fifth order bands are observed along ω_τ of the 1-2 transition frequency (1920 cm^{-1}), as discussed in the main paper. Because of the wider frequency range, fifth order

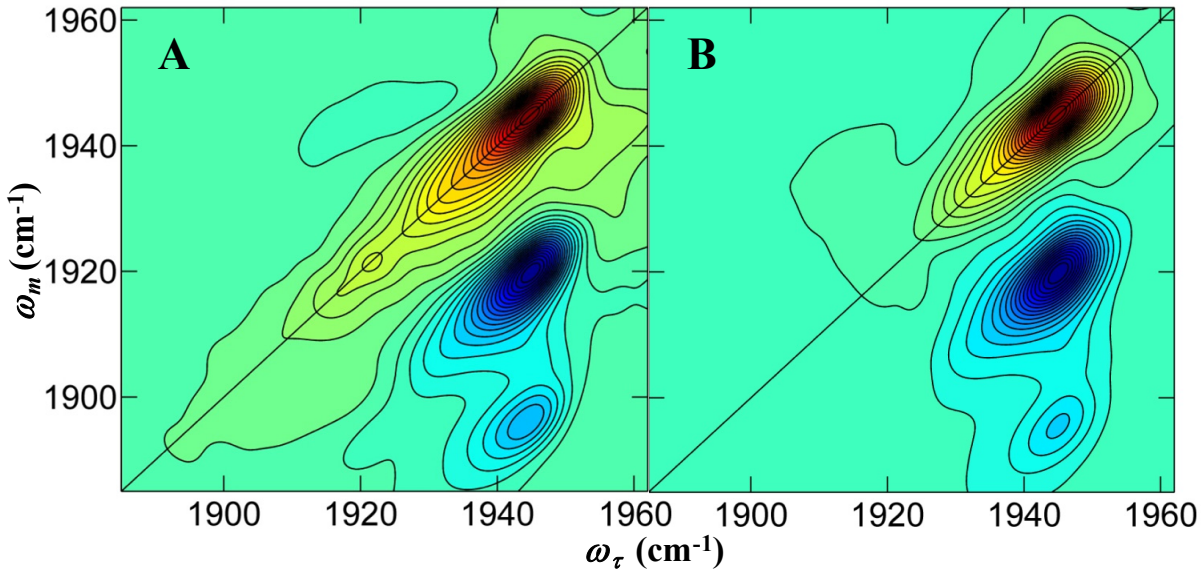

Figure S1: 2D IR spectrum of MbCO at 0.5 ps with full laser energy (A) and with 90% reduction in energy of the first pulse (B). Both spectra show a total of 40 contour lines.

bands along ω_m of the 2-3 transition frequency are also observed. The small negative band at ω_τ/ω_m of the 1-2/2-3 transition frequencies is associated with diagram J of Figure 2 (the band is more apparent from slice taken along ω_τ of 1920 cm^{-1} shown in Figure S2) and the larger

negative band at ω_τ/ω_m of the 0-1/2-3 transition frequencies is associated with diagrams R and S of Figure 7 of the main paper. In B, the fifth order bands along 1920 cm^{-1}, which involve multiple interactions with the first pulse, selectively disappear upon reduction in the first pulse energy. Note that the negative going band at (ω_τ, ω_m) = (1945 cm^{-1}, 1890 cm^{-1}) does not vanish as predicted by the theory presented in the main paper. This negative going band arises from three interactions in the second or third pulses, so turning down the energy of the first pulse does not change its amplitude relative to the diagonal 0-1 band.

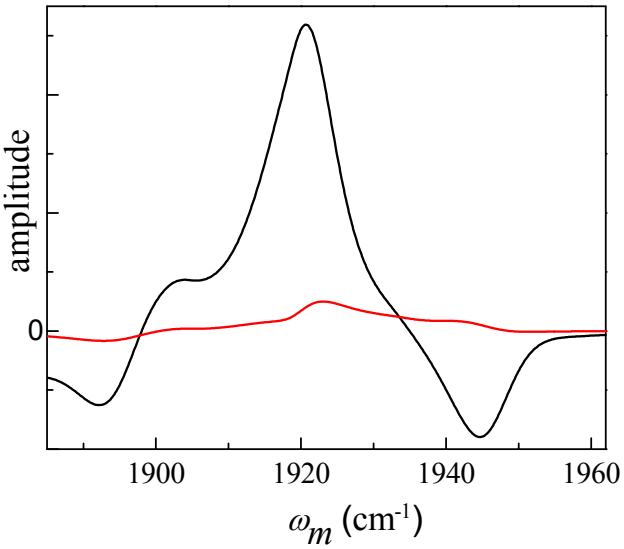

Figure S2: Slices thought the 2D IR spectrum along ω_τ = 1920 cm^{-1} at full laser energy (black) and with 90% reduction in the first pulse energy (red).

Figure S2 shows a vertical cut along ω_τ = 1920 cm^{-1} for the full power spectrum (black curve) and with the first pulse energy reduced by 90% (red curve). In the full power spectrum, the positive going peak and the two negative going peaks are clearly visible. At reduced first pulse energy, they are absent.