Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information to

Spectral Watermarking in Femtosecond Stimulated Raman spectroscopy: resolving the nature of the carotenoid S* state.

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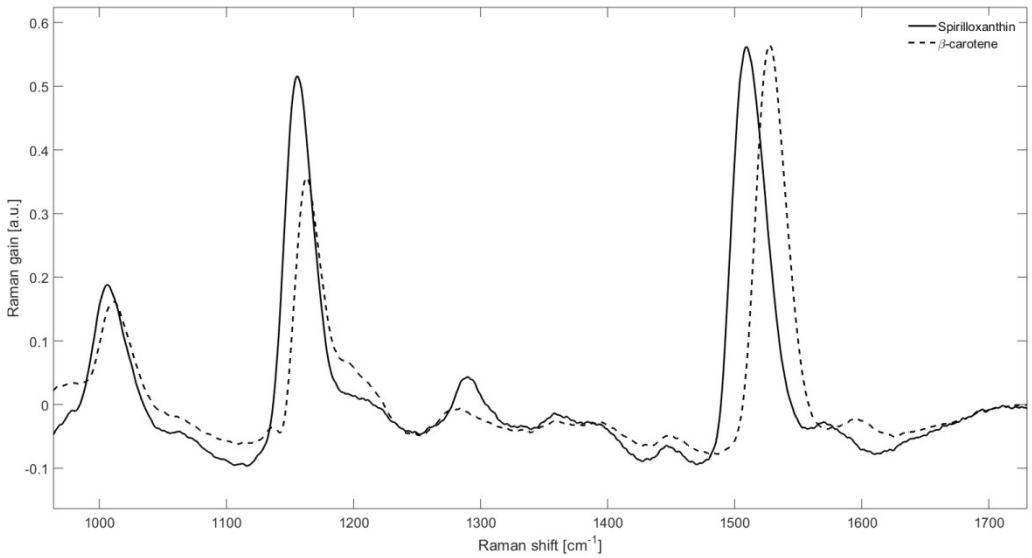

Figure S1. Ground state stimulated Raman spectra of β-carotene (dashed line) and spirilloxanthin (solid line) in CS_2. Solvent peaks were not removed. The C=C stretch vibrational mode is upshifted to higher wavenumbers for the shorter β-carotene (11 conjugated double bonds) compared to the longer spirilloxanthin (13 conjugated double bonds).

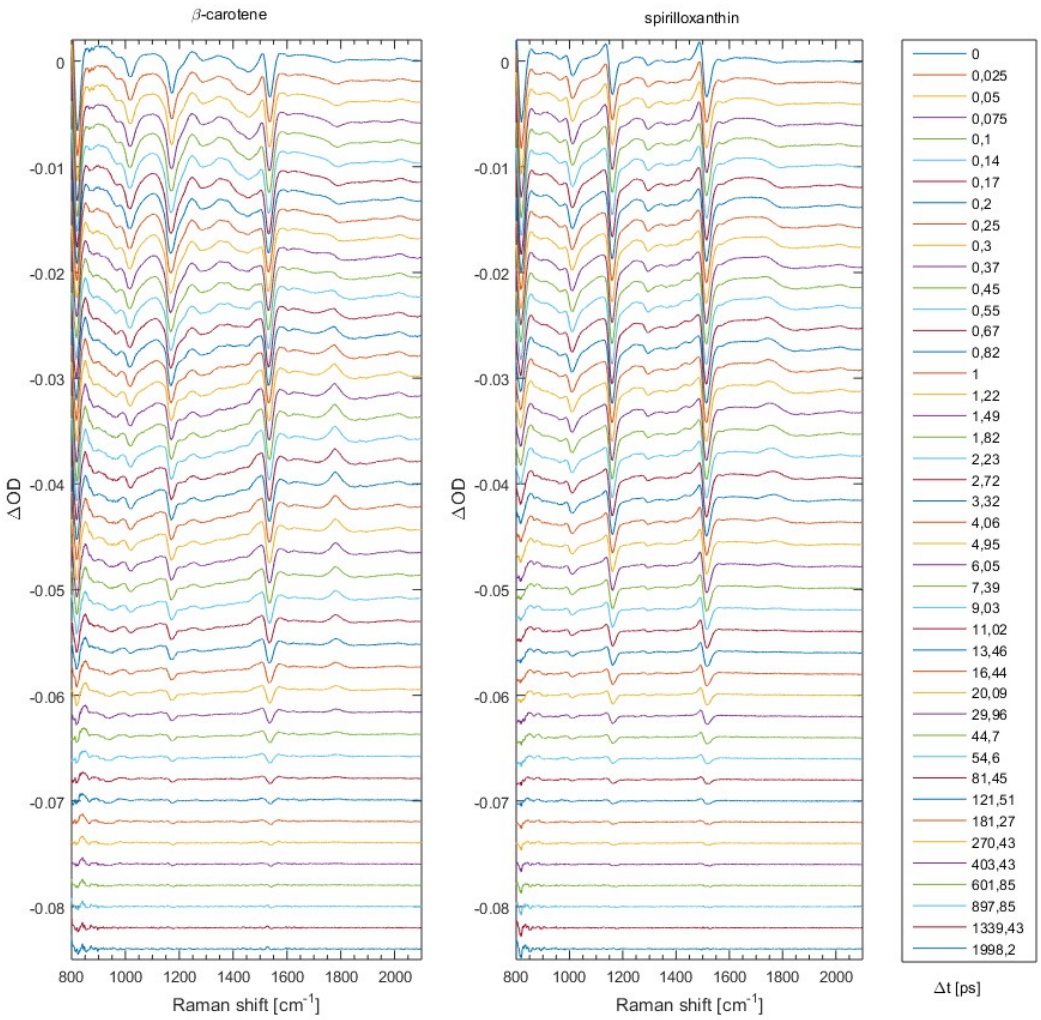

Figure S2. Full transient watermarked FSRS spectra of β-carotene (left panel) and spirilloxanthin (right panel) in CS_2.

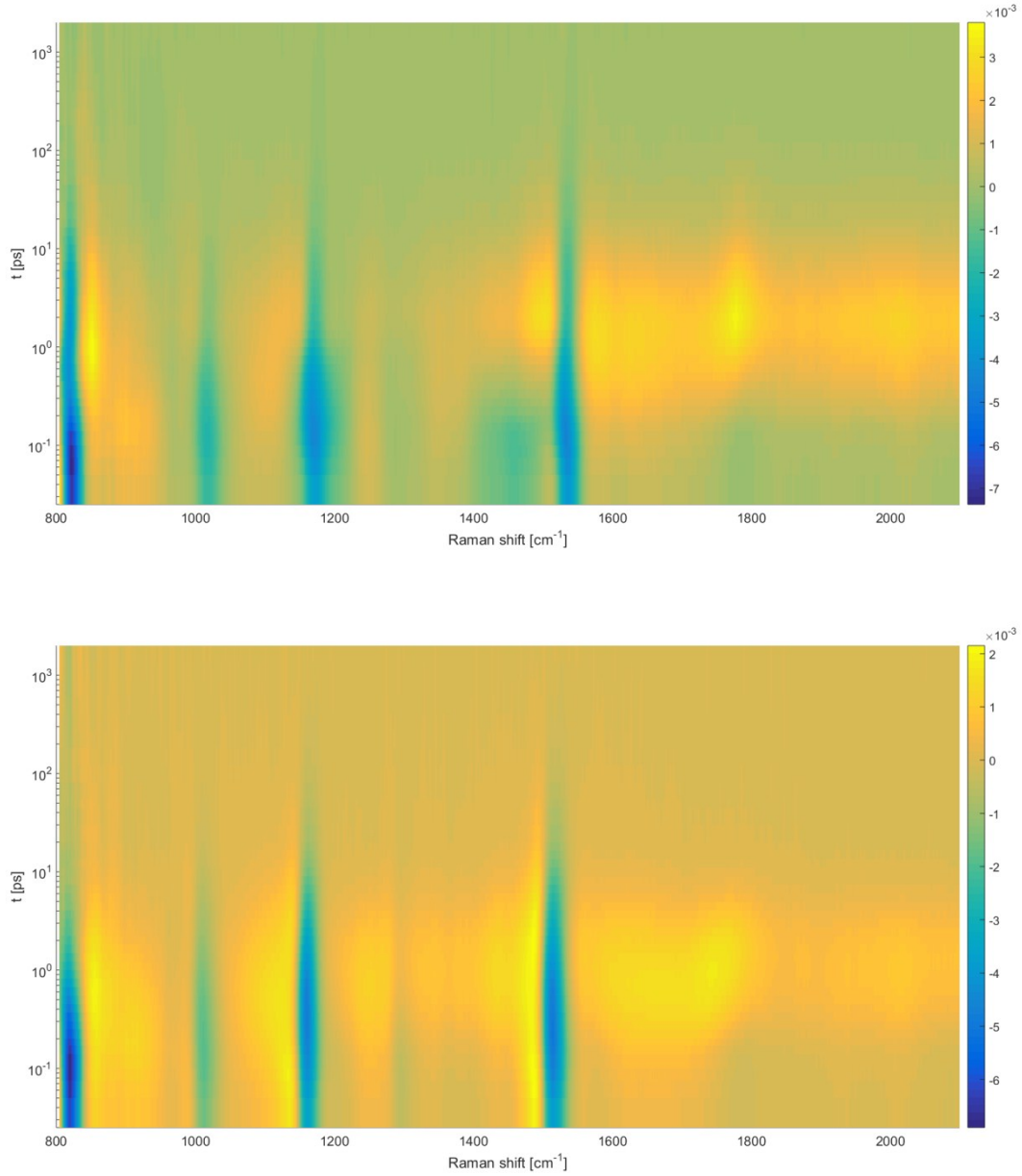

Figure S3. False color time evolution maps of the watermarked FSRS data on b-carotene (upper panel) and spirilloxanthin (lower panel).

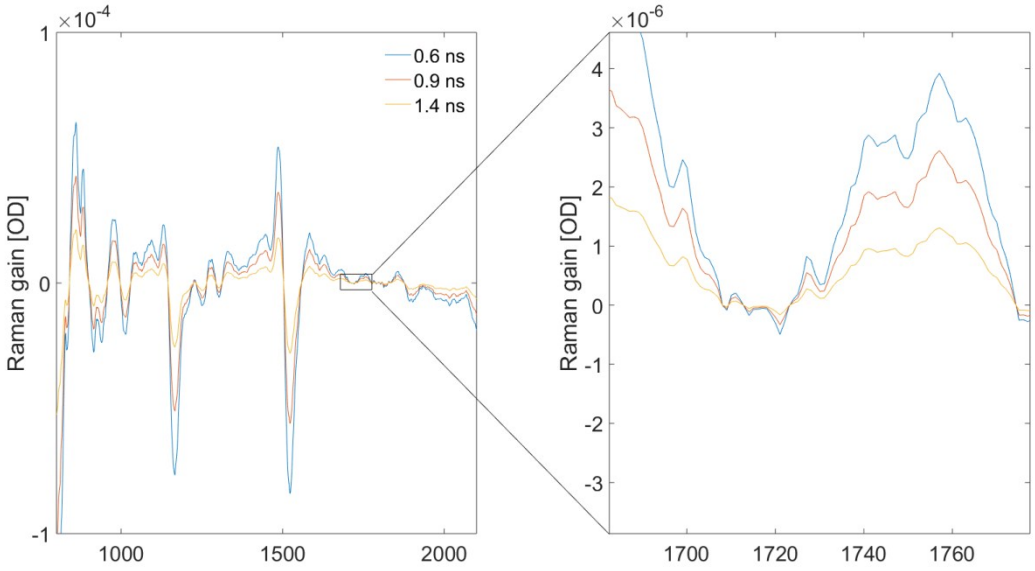

Figure S4. Transient watermarked FSRS of spirilloxanthin in CS_2 at long delays (2 ns). One can see recording of still on-going relaxation of solvent bleach and baseline around 1 µOD based on averaging only 1.5 seconds (1500 laser shots).

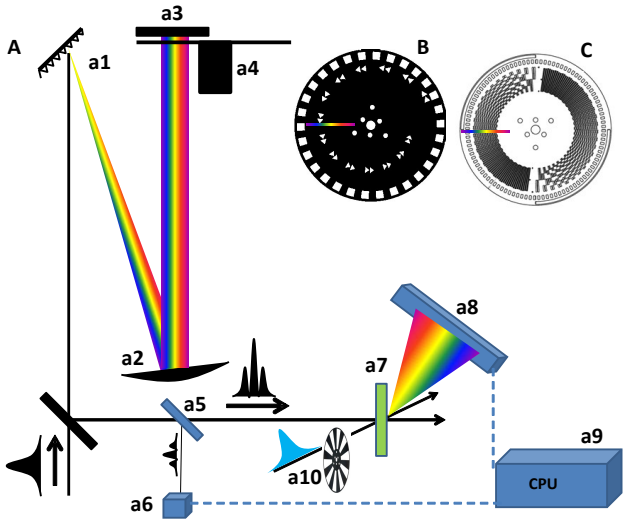

Figure S5A. Simplified scheme of the experimental set-up

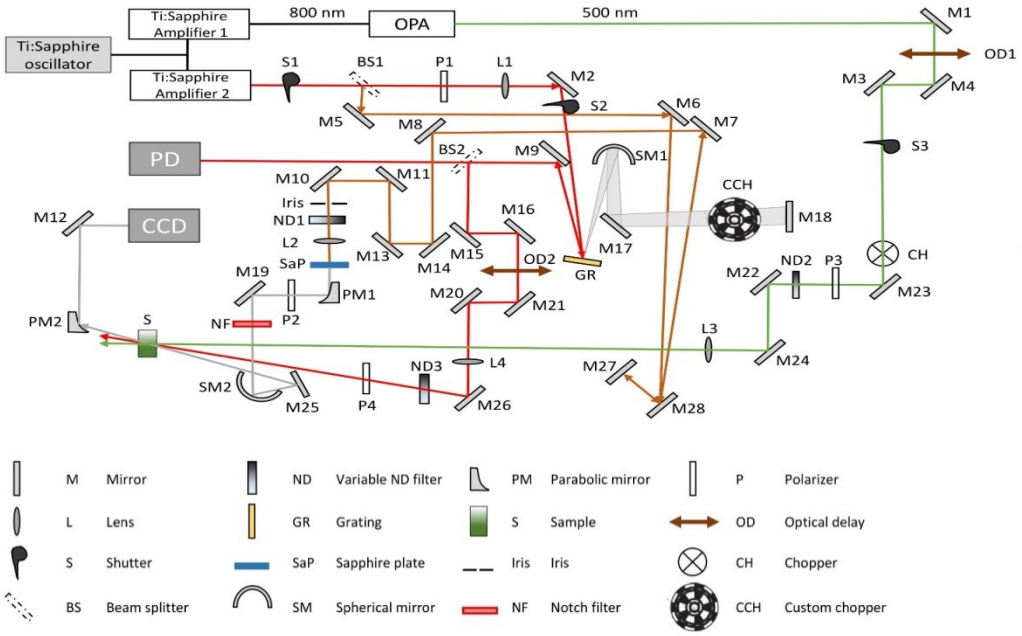

Figure S5B. Detailed scheme of the experimental set-up

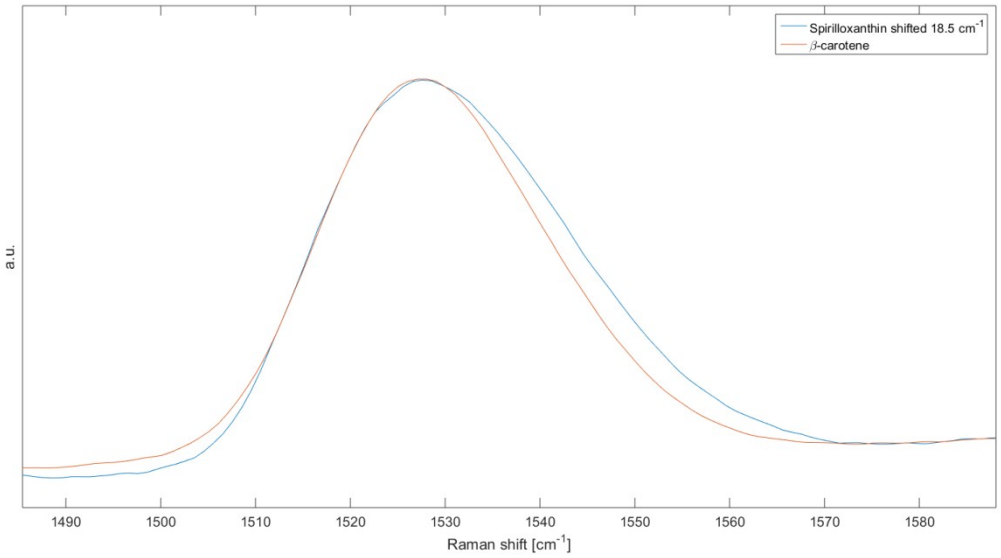

Figure S6 Comparison of shapes of spirilloxanthin and β-carotene C=C ground state modes. When the spirilloxanthin mode is shifted to fit with the β-carotene maximum, one can recognize a clear high-energy shoulder that is not present on the more symmetric β-carotene C=C mode. Note that the data presented in this picture were not subjected to smoothing.

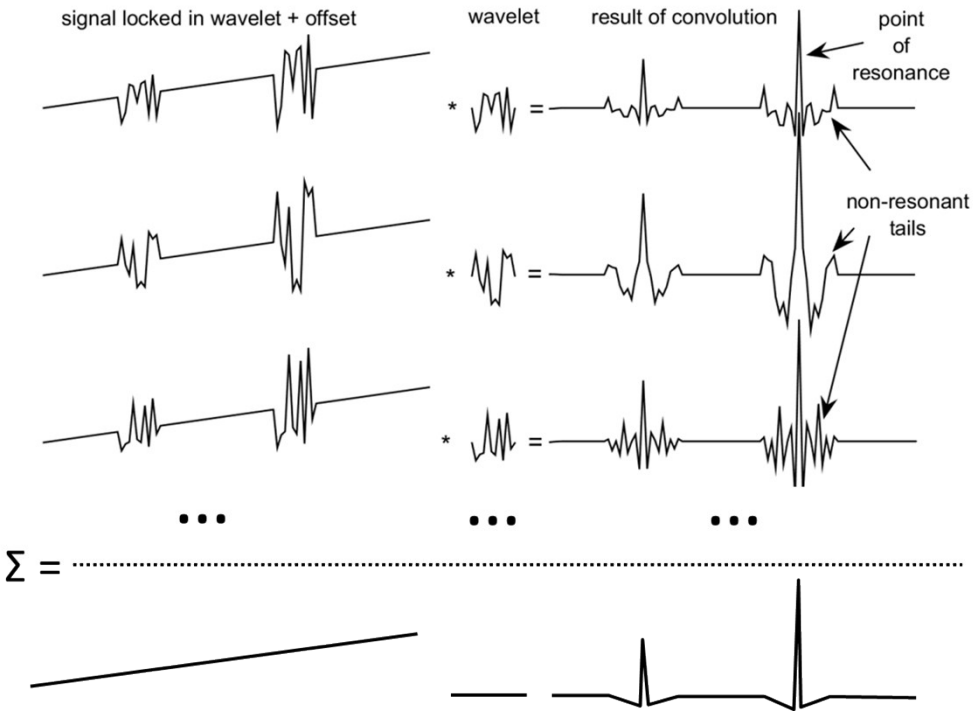

Figure S7. Demonstration of the interference of a watermark with itself: For clarity, the carrier signal is reduced to a simple linear offset (this because a complex carrier signal generates pseudorandom effects of its own). When the watermarked signal is convoluted with the model watermark, it is converted into a sharp spike, but accompanied with symmetric pseudorandom tails. The ratio between the amplitude of these tails and the resonant spike depends on the width of the watermark. For demonstration purposes the watermark in this figure has only 8 pixels so the tails are still substantial. The important property of the tails is that they are different for each specific watermark realization while the resonant spike is not. This means that when various watermarks are used and the results averaged, only the resonant spike remains. The “sombrero” shape of the peak after averaging is a consequence of using watermarks artificially adjusted to have a mean value exactly equal to zero.