

Coherent High-Frequency Vibrational Dynamics in the Excited Electronic State of All-*Trans* Retinal Derivatives

Jan Philip Kraack, Tiago Buckup, and Marcus Motzkus

Physikalisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, D-69210 Heidelberg, Germany.

E-mail: marcus.motzkus@pci.uni-heidelberg.de

Supporting Information

Comparison of Pump-DFWM FFT-spectra of ATR and RSB in different solvents

The following results show, that the newly reported bands in the FFT-spectra stems from the excited electronic state of ATR and RSB. This is accomplished by recording pump-DFWM dynamics of both samples in different solvents that do not exhibit vibrational modes at the frequencies in question ($> 1500\text{ cm}^{-1}$). To this end, Fig. S1 shows pump-DFWM spectra of ATR in ethanol (Fig. S1 a)) and acetonitrile (Fig. S1 c)). For both measurements, the newly reported bands at 1510 cm^{-1} and 1580 cm^{-1} are clearly observed.

Fig S1 b) and d) report on pump-DFWM experiments on RSB in ethanol (b)) and hexane (d). Again, measurements in both solvents show very similar peaks in the FFT-spectra above 1500 cm^{-1} . Note, that in hexane the two bands below 1600 cm^{-1} are down-shifted to 1550 cm^{-1} and 1500 cm^{-1} , respectively, compared to measurements in ethanol (b)). The different structures of the $\sim 1700\text{ cm}^{-1}$ modes for pump-DFWM spectra of RSB in ethanol and hexane point to different solute-solvent interactions in the excited state. Partial hydrogen-bonding of the imine-moiety in polar-protic solvents may for instance result in a distribution of C=N-frequencies therefore explaining the broad band and multiple frequencies in ethanol compared to apolar-aprotic hexane.

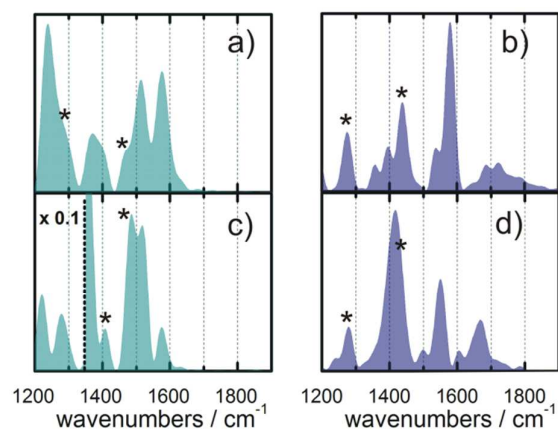


Figure S1. FFT-spectra of pump DFWM dynamics for ATR (a) and c)) and RSB (b) and d)) in different solvents. FFTs of pump-DFWM experiments were acquired at $T = 1$ ps for b) ATR in ethanol (cyan DFWM-spectrum, Fig 1 a) in the manuscript), c) ATR in acetonitrile (cyan DFWM-spectrum, Fig 1 a) in the manuscript). FFTs of pump-DFWM experiments were acquired at $T = 2$ ps for b) RSB in ethanol (blue DFWM-spectrum, Fig 1 b) in the manuscript), d) RSB in hexane (blue DFWM-spectrum, Fig 1 b) in the manuscript). For clarity, the energetic regions separated by the vertical dashed lines are multiplied with the indicated factors. Vibrational bands assigned to solvent dynamics are indicated with asterisks.

Demonstration of excited state vibrational coherences in a reference-sample – β -carotene

As discussed in the manuscript, polyenes such as carotenoids exhibit a well documented vibrational band around 1800 cm^{-1} in the lowest-lying excited singlet state (S_1). Such a band is, however, not observed for ATR and RSB in the excited state in the reported pump-DFWM experiments. In order to exclude possible effects of insufficient temporal resolution in the experiment, test-scans on β -carotene samples were conducted which clearly showed the existence of the vibrational band around 1780 cm^{-1} in the S_1 -state (Fig. S2). This implies a molecular effect regarding the absence of a frequency-upshift of the C=C-stretching mode in the excited state of ATR and RSB.

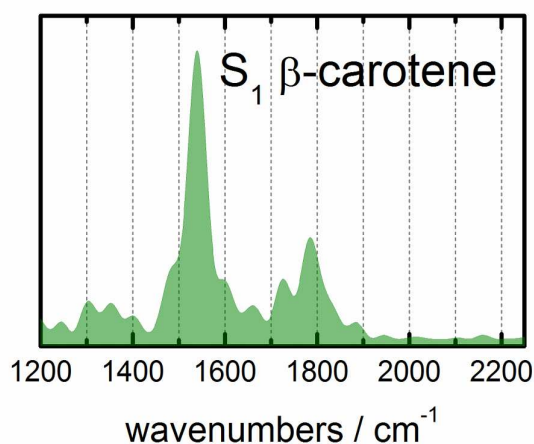


Figure S2. Demonstration of temporal resolution in the experiment by means of pump-DFWM test scans on β -carotene samples in cyclohexane (detected around 16200 cm^{-1}) with the green DFWM-spectrum (Fig. 1 in the manuscript). A vibrational mode around 1780 cm^{-1} is clearly resolved.

Examples of the full high-frequency range in the FFT-spectra

The dominant period of the oscillations presented in Fig. 2 in the manuscript is around 30 fs. This is reasoned by a very intense response of the solvent, i.e. ethanol (885 cm^{-1}) as shown in the following. Fig. S3 presents an expanded spectral region of the same FFT-spectra as already presented in Fig. 3 b) in the manuscript. The upper panel in Fig. 2 below presents the original FFT-spectrum calculated from the residuals in Fig. 2 in the manuscript of ATR in ethanol with the cyan DFWM-spectrum (Fig. 1 in the manuscript). The most dominant band is observed as the well-documented Raman-active band of ethanol around 885 cm^{-1} . The lower panel in Fig. S3 shows an expansion of the spectral region above 1050 cm^{-1} by a factor of 10. This provides a clear view of the high-frequency region around 1500 cm^{-1} . These results demonstrate the powerful advantages of homodyne-detected pump-DFWM signals which provide background-free dynamics with very high signal-to-noise ratio. Very similar results are also observed for the other DFWM-spectra as well as for RSB results.

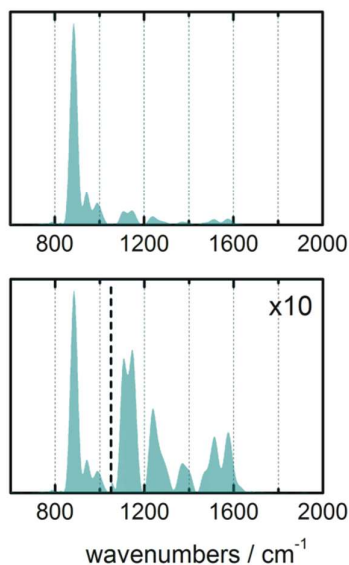


Figure S 3. Expansion of FFT-spectral regions of pump-DFWM FFT-spectra of ATR in ethanol acquired with the cyan DFWM-spectrum (Fig. 1 in the manuscript). The upper panel depicts the originally calculated FFT-spectrum from the oscillatory residuals presented in Fig. 2 in the manuscript. The lower-panel depicts an expanded view (factor 10) of the high-frequency region ($> 1050\text{ cm}^{-1}$).

Examples for invariance of population dynamics with IP-intensity

As discussed in the manuscript, pump-probe experiments have been conducted for both RSB as well as ATR in addition to the presented pump-DFWM experiments (Fig. 1 in the manuscript). The pump-probe experiments were performed on a series of excitation energies between 50 – 300 nJ. The pump-probe experiments of different excitation energies up to 300 nJ resulted in nearly identical population dynamics, thus demonstrating that excitation of higher lying electronic states does not play a role in the presented pump-DFWM experiments (Fig. S 4). The similarity of the dynamics at different detection wavelengths conducted at different excitation energies indicate that no alteration of population dynamics is observable for the excitation energies used in the pump-DFWM experiments.

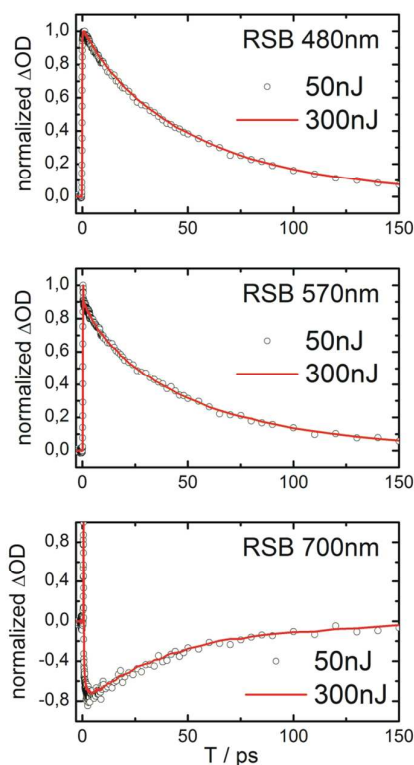


Figure S4. Comparison of examples of normalized pump-probe dynamics at different detection wavelengths (480 nm, 570 nm, 700 nm) for RSB for 50 nJ excitation (open circles) and 300 nJ (red lines).