

9 LEURQLF &RXSOLQJ LQ ([FLWHG (OHFWU  
ZLWK 5HVRQDQW ' 5DPDQ 6SHFWURVFRS\

7 %XF-NXS.UDDFNODUHNORWGNV

3K\VLNDOLVFK &KHSPLSUFHKFKW, QVWQW XWLYHUVLWLVHCHLGHUJ  
\*HUPDQ\

\$EVWUDFW FRXSOLQJ EHWZHHQ PROHFODU YLEUDWLRQDQ  
LQYHVWLJDWHG E\ UHLPHODQW QSDOPDLWHZ BSHARQYDHWVSHFW  
' 5DPDQ H[SORLWV HOHFWURQLFUGHVURQDQDSSOAWRKHQKDKQ  
DSSURDFK WRFKHURPDSORLJHRV LQ VROXWLRQ

## , QWURGXFWLRQ

The coupling between structural degrees-of-freedom plays a major role in the evolution of photo-activated chemical reactions. In general, Franck-Condon active modes are not necessarily reactive modes, but can excite reactive modes via intramolecular vibrational coupling. Such a coupling originates from strong anharmonicity terms, which are normally hidden from lower order techniques.[1] Nevertheless, this issue can be addressed by using higher order time domain experiments, like fifth- and seventh-order spectroscopic methods.[2] Higher order-methods require demanding experimental setups with specific phase matching conditions or polarization configurations in order to suppress cascaded  $\mathbb{R}^3$  artifacts.[3] In this work, we present a resonant fifth-order time resolved approach to probe the coupling between Raman active modes in electronic excited states. It is based on two consecutive pairs of resonant excitations ( $k_1/k_2$ ,  $k_3/k_4$ ) followed by a resonant probe interaction  $k_5$  (Figure 1). Such an approach has been already used to detect electronic dark states in carotenoid[4,5].

The first two pairs of excitations  $k_1/k_2$  and  $k_3/k_4$  are electronically resonant with different electronic transitions, inducing, for example, Raman transitions in the excited state. Since the resonant signal is orders of magnitude stronger than non-resonant contributions, cascaded  $\mathbb{R}^3$ -contributions are strongly suppressed.

## ( [SHULPHQWDO ,PSOHPHQWDWLRQ

All excitation pulses are generated in non-collinear optical parametric amplifiers (nc-OPA) with pulse durations shorter than 16 fs and a repetition rate of 1 kHz. The first two pulses,  $k_1$  and  $k_2$  are generated in one nc-OPA, while  $k_3$ ,  $k_4$  and  $k_5$  pulses are generated in a second nc-OPA. This way, it is possible to select independent spectra for  $k_1$ ,  $k_2$  compared to  $k_3$ ,  $k_4$  excitation beams, and to suppress cascaded  $\mathbb{R}^3$ -artifacts. Polarization of the incident beams can be independently varied and different  $\mathbb{R}^5$ -terms can be selected or specifically suppressed.

Resonant 2D spectra were obtained by either spectrally integrated signals or at specific detection wavelengths.

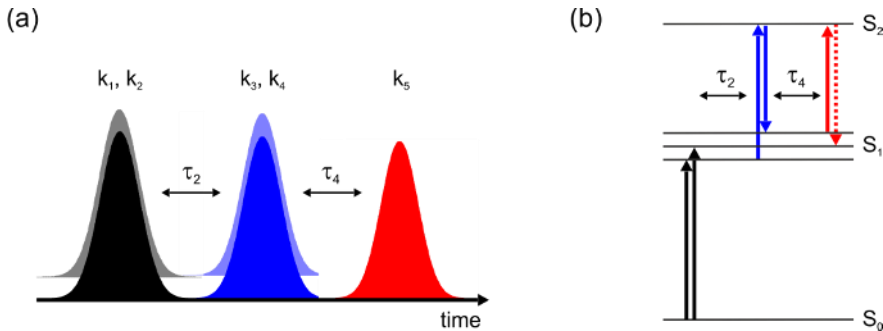


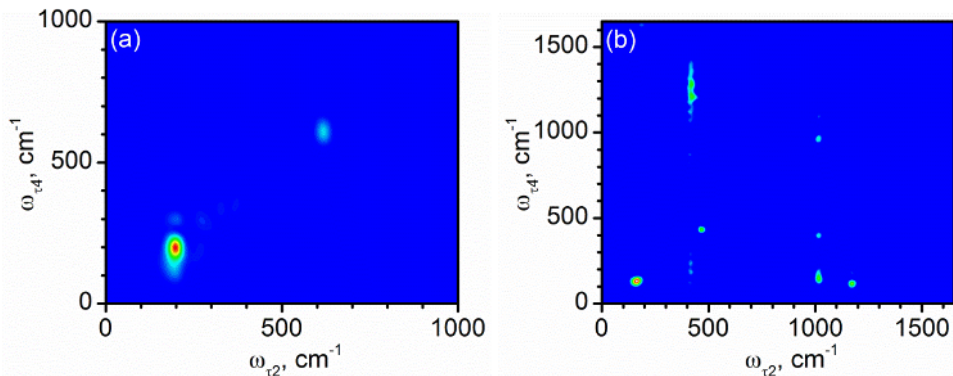
Fig. 1. 6FKHPH RI UHVRQDQW ' 5DPDQ PHWKR G D 7LPH RUGH  
DQG EOXH DQG SUREH SXOVH UHG E (IFLWDWL'ROW WIFHP  
UH G DUURZ UHSUHVHQWV WKH VLJQDO

### 5HVRQDQW ' 5DPDQ 6SHFWUD

The resonant 2D CARS spectra are obtained by scanning the probe delay  $\Delta$  while varying the delay  $\Delta$  (Figure 1). After removing the slowly-varying contributions from population terms, the 2D time-resolved signal is Fourier transformed along the  $\Delta$  and  $\Delta$  coordinates. The calculated Fourier spectra are shown along the respective frequency axes  $\omega_{\Delta}$  and  $\omega_{\Delta}$ . Peaks in the diagonal are expected if the respective vibrational coherence is induced in both delay times  $\Delta$  and  $\Delta$ . The symmetry of the peak contains information about the relaxation mechanisms during these delay times. For example, double quantum Raman transitions in highly anharmonic potentials are expected to have an asymmetric peak form. Cross-peaks are generated if, for instance, the amplitude of the respective vibrational coherence is modulated by another molecular mode. The distribution of cross-peaks is not necessarily symmetric with respect to the diagonal line. This can be easily understood since different Raman transitions can be induced after each excitation pair. For example, in Figure 1(b) the first excitation pair induces vibrational coherence  $|0\rangle\langle 1|$  between the  $v=0$  and  $v=1$  in the  $S_1$  manifold. The second excitation pair re-induce the vibrational coherence to  $|2\rangle\langle 1|$  between the  $v=2$  and  $v=1$  in the same  $S_1$  manifold. If the second excitation pair had induced another Raman transition in another electronic potential, the respective modes generated during the delay  $\Delta$  would not be observable during delay  $\Delta$ . Besides, due to the applied homodyne signal detection, cross-peaks between solvent and solute Raman active modes can also be detected.

### 5HVXOWV DQG 'LVFXVVL RQ

A typical 2D spectrum for rhodamine B in solution is shown in Figure 2(a). The spectrally integrated  $R^{(5)}$  signal was obtained by tuning  $k_1, k_2$  resonant to the  $S_0-S_1$  transition and  $k_3-k_5$  resonant to the stimulated emission band at about 600 nm. The 2D spectrum shows two dominating diagonal structures centred at about 200 and 600  $\text{cm}^{-1}$ , which are two well known Raman active modes of rhodamine-dyes. The asymmetric peak form for both Raman modes suggests that during  $\Delta$  delay time the dephasing of such modes is much faster than in the  $\Delta$  delay time. Moreover, the lack of any cross-peak in Figure 2(a) shows that molecular coupling between these low frequency modes plays negligible role in the dynamics. It is interesting to note, that for spectrally resolved detection, weak cross-peaks indicate that coupling of modes can occur but is dependent on the probed potential surface position (not shown).



**Fig. 2.** 2D Raman spectra of (a) rhodamine B in methanol and (b) Ecarotene in benzonitrile. The integrated resonant 2D Raman signal of rhodamine B shows two main diagonal peaks. The signal of Ecarotene in benzonitrile at 610 nm shows a more complex 2D Raman spectrum with several off-diagonal contributions.

A more complex resonant 2D Raman spectrum can be observed for Ecarotene in benzonitrile (Figure 2(b)). In this case, the spectrally resolved R signal was obtained by tuning  $k_1/k_2$  resonant to the  $S_1 \rightarrow S_2$  transition and  $k_3-k_5$  resonant to the excited state absorption band at about 560 nm. The spectrally resolved 2D spectrum at 610 nm shows several contributions. Diagonal peaks at about 170  $cm^{-1}$  and 480  $cm^{-1}$  are possibly due to low-frequency modes in the excited state of Ecarotene, while the contribution at about 1000  $cm^{-1}$  ( $CH_3$ -rocking mode) contains both solute and solvent information. The low-frequency modes of Ecarotene are strongly coupled to  $CH_3$  rocking mode as well as to the fingerprint mode at about 1170  $cm^{-1}$  (C-C stretching). It is interesting to note, that the distribution of cross-peaks is not symmetric for Ecarotene in benzonitrile, which suggests strong coupling between modes from the low-frequency and fingerprint region in the excited-state of Ecarotene.

### & R Q F O X V L R Q

The coupling between Raman modes in the excited state of molecules can be addressed by resonant fifth-order spectroscopy. Resonant 2D Raman spectra contain information on anharmonically-coupled modes, in particular on the strength and on the relaxation mechanism of the coupling.

### 5 H I H U H Q F H V

128 < 7 D Q L P X U D 6 0 X N D P H O - R X U Q D O R I & K H P L F D O 3 K \ V L  
 \$ 7 R N P D N R I I \* 5 ) O H P L Q J - R X U Q D O R I & K H P L F D O 3 K \ V  
 < / / L / + X D Q J 5 - ' 0 L O O H U 7 + D V H J D Z D < 7 D Q L  
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 0 6 0 D U H N 7 % X F N X S 0 0 R W J N X V - R X U Q D O R I 3 K \ V L F