

Vibronic Coupling in Excited Electronic States Investigated with Resonant 2D Raman Spectroscopy

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Abstract. The coupling between molecular vibrational modes in the excited state is investigated by resonant Raman two-dimensional time resolved spectroscopy. Resonant 2D Raman exploits electronic resonances to enhance fifth-order signals. We apply this approach to several (bio-)chromophores in solution.

1 Introduction

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 $\chi^{(3)}$ 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 carotenoids [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 $\chi^{(3)}$ -contributions are strongly suppressed.

2 Experimental Implementation

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_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_5 excitation beams, and to suppress cascaded $\chi^{(3)}$ -artifacts. Polarization of the incident beams can be independently varied and different $R^{(5)}$ -terms can be selected or specifically suppressed.

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

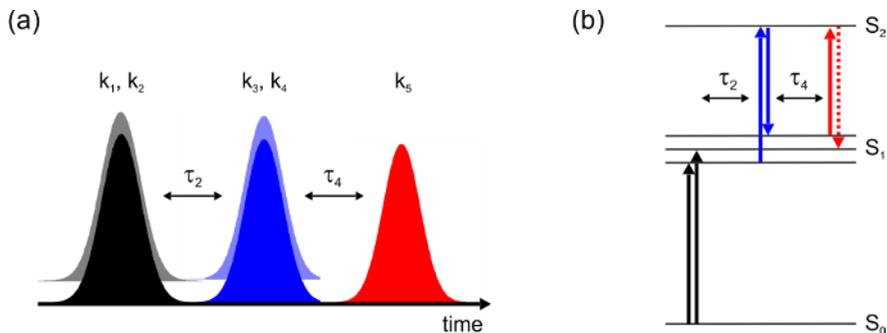


Fig. 1. Scheme of resonant 2D Raman method. (a) Time ordering for the excitation pulse pairs (black and blue) and probe pulse (red). (b) Excitation scheme of Raman modes in the excited state S_1 . Dotted red arrow represents the signal.

3 Resonant 2D Raman Spectra

The resonant 2D CARS spectra are obtained by scanning the probe delay τ_4 while varying the delay τ_2 (Figure 1). After removing the slowly-varying contributions from population terms, the 2D time-resolved signal is Fourier transformed along the τ_2 and τ_4 coordinates. The calculated Fourier spectra are shown along the respective frequency axis, ω_{τ_2} and ω_{τ_4} . Peaks in the diagonal are expected if the respective vibrational coherence is induced in both delay times τ_2 and τ_4 . 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-induces 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 τ_2 would not be observable during delay τ_4 . Besides, due to the applied homodyne signal detection, cross-peaks between solvent and solute Raman active modes can also be detected.

4 Results and Discussion

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 cm^{-1} , which are two well known Raman active modes of rhodamine-dyes. The asymmetric peak form for both Raman modes suggests that during τ_4 delay time the dephasing of such modes is much faster than in the τ_2 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).

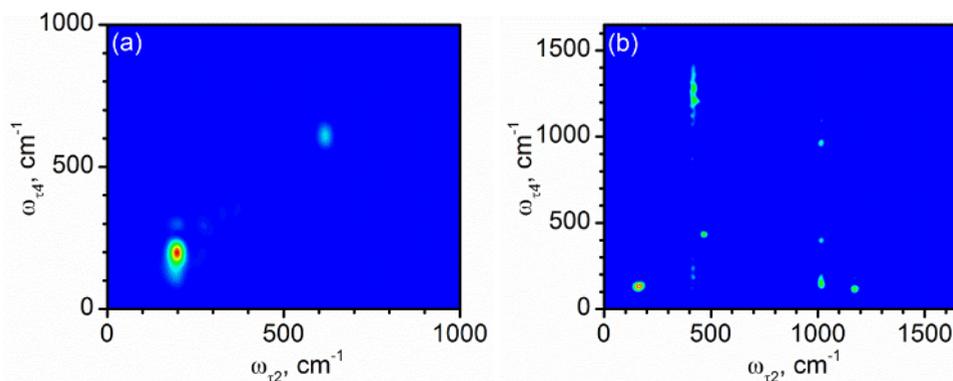


Fig. 2. 2D Raman spectra of (a) rhodamine B in methanol and (b) β -carotene in benzonitrile. The integrated resonant 2D Raman signal of rhodamine B shows two main diagonal peaks. The signal of β -carotene in benzonitrile at 610 nm shows a more complex 2D Raman spectrum with several off-diagonal contributions.

A more complex resonant 2D Raman spectrum can be observed for β -carotene in benzonitrile (Figure 2(b)). In this case, the spectrally resolved $R^{(5)}$ signal was obtained by tuning k_1/k_2 resonant to the S_0 - 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 β -carotene, while the contribution at about 1000 cm^{-1} (CH_3 -rocking mode) contains both solute and solvent information. The low-frequency modes of β -carotene 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 β -carotene in benzonitrile, which suggests strong coupling between modes from the low-frequency and fingerprint region in the excited-state of β -carotene.

4 Conclusion

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 References

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