The Application of Femtosecond Four-Wave Mixing Techniques for the Investigation of Excited State Dynamics

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In the experiments presented in this work, third-order, time-resolved spectroscopy was applied to the investigations of electronic relaxation processes in various chemical and physical systems subsequent to excitation by ultrashort laser pulses.

The development of different strategies within the framework of time-resolved, four-wave mixing (FWM) spectroscopy for addressing the problem of vibronic coupling began with the experiments on gaseous iodine. This simple, well investigated molecular system was chosen in order to unambiguously characterize the effect of Raman resonances on four-wave mixing processes. It could be shown that Raman resonances determine the selectivity with which these FWM processes prepare and interrogate nuclear dynamics in different electronic states.

With the insight gained into the relevance of Raman resonant processes in FWM spectroscopy, an experimental scheme was devised that utilizes this effect to selectively interrogate the dynamics of a specific vibrational mode within a polyatomic molecule during the dynamics of radiationless electronic transitions such as internal conversion (IC). This is accomplished by integrating coherent anti-Stokes Raman scattering (CARS) as a probe mechanism in a femtosecond time-resolved pump-probe scheme. This configuration employs four femtosecond laser pulses. It will be shown that within this experimental arrangement it is possible to identify the electronic states participating in an IC and gain information about vibrational modes of the transient electronic states. The principle of these experiments is illustrated by exploring the influence of different normal modes on the rate of the S_1-S_0 internal conversion in β-carotene, an active chromophore in photosynthesis and the redistribution of vibrational energy between different modes of Stilbene 3 taking place after photoexcitation. Time-resolved CARS was also used to identify shifts of normal mode positions in the S_1 excited state of Stilbene 3 in comparison to the ground state.

Furthermore, femtosecond time resolved population gratings were employed for the characterization of radiationless transitions in various biologically relevant molecules e.g. to study the *pump* wavelength dependency of excited state processes in phycocyanobilin (PCB) which is considered to be a good model for the chromophore of the biological photoreceptor phytochrome.

The results demonstrate that the applied four-wave mixing techniques are powerful tools for gaining insight into complex molecular dynamics by utilizing the effect of optical as well as Raman resonances.

Additionally spin dephasing dynamics in CdSSe quantum dots (QDs) embedded in a glass matrix have been investigated to derive information about QD asymmetry by studying the polarization properties of time-resolved four-wave mixing spectroscopy.

Overall the presented experiments nicely demonstrate the wide applicability of four-wave mixing techniques for the characterisation of excited electronic states of molecular systems, clusters and solids.