Coherent Control of Molecules: Technical Challenges, Fundamental Aspects and New Applications

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Tailoring of the optical phase, amplitude and polarization is an important branch of ultrafast spectroscopy. It has helped overcome technological challenges in femtosecond optics, given detailed fundamental insight into molecular dynamics as well as complex light matter interactions, and has also contributed to novel applications in spectroscopy. In this contribution, I will present our recent results with respect to these three directions, which could give an explanation as to why it is difficult to achieve control in learning loops, and why many coherent control experiments conducted previously were unsuccessful.

Liquid crystal spatial light modulators (LC-SLM) are a useful tool to modulate the phase, amplitude and polarization of femtosecond laser pulses. A reliable and stable modulation of the LC-SLM is crucial for successfully performing experiments for coherent control, in which small changes due to modulated laser fields are detected. However, using 12 fs pulses in the visible range shaped by an LC-SLM, we observed unstable pulses making reliable femtosecond control experiments challenging and often unsuccessful. A systematic study showed that one of the key parameters towards maximizing pulse stability, and minimizing noise effects, lies in the careful control of the SLM operating temperature. This phenomenon was observed for two different LC-SLMs from two different manufacturers. Based on the experimental data we developed a physical model to give a deeper understanding of the influence and level of noise arising from the shaper. The improvement of the pulse stability, through cooling the LC-SLM, allows us to perform extremely phase sensitive coherent control experiments.

To steer photochemical reactions into selected channels, or controlling molecular quantum phenomena, the tailoring of molecular vibrations is a fundamental control knob. For example, population of vibrational states and vibrational coherence of the ground state can be manipulated by using chirped pump pulses, which induces intrapulse stimulated Raman scattering. Additionally, electronic near-resonant excitation with multipulses has been shown to enhance vibrational coherence in the excited state. These two important mechanisms of mode selective control can be found as the major mechanisms in many control experiments. We combined these two processes and studied the interplay of single transform limited and chirped pulses, as well as transform limited and chirped multipulses, on vibrational coherence and population in the electronic excited and ground state. These studies were conducted over a range of excitation spectra in order to develop general rules for successful control. Our results show a strong dependence on the resonant and off resonant tuning of the excitation pulse. For example, a blue-detuned multipulse enhances the vibrational coherence, and when a negative chirp is applied to each multipulse the effects add up. On the other hand, the effects for resonant and red-detuned excitation, are in general less pronounced, and do not follow the same trend as for the blue-detuned pulses. For a better understanding of the underlying process, and the assignment of ground and excited state contributions, a numerical density matrix based model was developed to simulate the changes of population, vibrational and electronic coherence due to several pulse shapes

Finally, the possibility to exploit shaped, ultrabroadband pulses for molecular control offers a simple implementation of numerous nonlinear spectroscopic methods. In particular, the combination of these nonlinear optical modalities in one setup, such as coherent Raman microscopy, second harmonic generation or two-photon fluorescence, which have been previously applied separately in various applications for both the material and life sciences could be possible. Here, we discuss the experimental realization of this concept for multimodal nonlinear microscopy and show in detail the successful implementation of adaptive spectral focussing schemes for Raman and mid-IR spectroscopy, allowing the detection of these two orthogonal modalities within a single setup.