

# Coherent Control for Molecular Ultrafast Spectroscopy

**Tiago Buckup, Marcus Motzkus**

Physikalische Chemie, Philipps-Universität Marburg, D-35043, Marburg, Germany  
motzkus@staff.uni-marburg.de

**Jürgen Hauer**

Physikalische Chemie, Philipps-Universität Marburg, D-35043, Marburg, Germany  
Institute for Physical Chemistry, A-1090, Vienna, Austria

**Abstract** Quantum control spectroscopy (QCS) is a powerful modern experimental concept to disentangle complex dynamics in molecular quantum systems and combines coherent control methods with time-resolved optical spectroscopy. By manipulating the photo-induced reaction pathway with specifically tailored excitation light fields, it offers a new spectroscopic degree of freedom in addition to classic spectral and temporal coordinates. Particularly interesting in QCS is the excitation with well-defined pulse sequences which will be shown on two examples. In a first series of experiments the comparison of excitations with one or two pulses allows to unravel the complex energy flow network in all-*trans*- $\beta$ -carotene and its homologs. In a second experiment, we go a step further and use multipulse excitation via phase shaping in a prototype dye molecule to analyze the role of electronic coherence time for population and vibrational coherence enhancement.

**Keywords:** Coherent control, open-loop control, pulse shaping, carotenoids

## 1 Introduction

The modification of molecular quantum pathways by coherent control offers the possibility of a deeper insight into the involved dynamics (Rabitz et al. 2000; Brumer and Shapiro 1986, 1989; Tannor and Rice 1998; Lozovoy et al. 1999). The underlying principles can either be understood in a time approach (Tannor

and Rice 1998) or frequency domain scheme (Brumer and Shapiro 1989). Closed loop schemes based on evolutionary algorithms reveals the potential of coherent control experiments (Judson and Rabitz 1992; Bardeen et al. 1997; Assion et al. 1998), with successful optimization of dynamics even in complex biomolecules (Herek et al. 2002; Wohlleben et al. 2005; Prokhorenko et al. 2006, 2007). Differing from the often pursued goal of optimization, coherent control can also efficiently be used to trace the mechanisms of chemical reactions or photophysical processes. In contrast to mere optimization, such a quantum control spectroscopy (QCS) approach exploits the comparison between shaped and unshaped (Fourier-limited) pulses and focuses on specific shaped pulses typically in an open loop experiment to trigger theoretically well understood dynamics. The influence of multipulses on vibrational wave packet motion can be mentioned as an example of such a pulse shape (Weiner et al. 1990). Although open loop experiments are the more direct approach to QCS, the combination of mathematical analysis of generations (White et al. 2004) with the concept of phase and amplitude parameterization (Zeidler et al. 2001; Hornung et al. 2001) in a closed loop genetic algorithm can also lead to a better understanding of the involved mechanisms.

In QCS the application of shaped pulses should be seen as a spectroscopic degree of freedom beside classic spectral and temporal coordinates. This approach offers therefore evident parallels to modern pulsed NMR experiments, where a multitude of tasks ranging from protein structure elucidation (Wüthrich 1986) to imaging applications (Ciobanu et al. 2003) can be accomplished without general changes in the instrumentation used, showing the full potential of applying shaped excitation pulse sequences as a spectroscopic concept. The parallels between NMR and nonlinear optical spectroscopy become especially obvious in case of 2D-shaping based multidimensional optical spectroscopy (Tian et al. 2003; Wagner et al. 2005; Gundogdu et al. 2007; Brixner et al. 2005).

This article aims to discuss some generalizable examples of quantum control spectroscopy application in time-resolved experiments. In Section 2 the interaction of two excitation pulses in a transient absorption (TA) experiment is used to disentangle the complex ultrafast population dynamics of carotenoids. The idea behind this three pulse pump-probe (Fig. 1a), called pump-depletion-probe (Gai et al. 1997; Wohlleben et al. 2004; Buckup et al. 2004, 2005, 2006; Larsen et al. 2003), is to launch the system to an excited state and then interfere with its evolution at a point which is normally inaccessible with just one pump pulse. In Section 3, the interaction of a pulse train (Fig. 1b and c) is discussed. It will be shown that the precise control of the sub-pulse separation leads to tailoring of vibrational coherence and population transfer between the ground- and the excited-state (Hauer et al. 2006a, 2007a, b, 2008; Buckup et al. 2008).