Ultrafast time- and frequency-resolved coherent anti-Stokes Raman spectroscopy (CARS) with femtosecond excitation and picosecond probing

M. Lütgens, S. Chatzipapadopoulos, S. Lochbrunner
Institute of Physics, University of Rostock, Rostock, Germany (February 2014)

Application Note

Introduction

Coherent anti-Stokes Raman scattering (CARS) is a widely used and powerful method for the spectroscopy of vibrations. A combination of femto- and picosecond pulses can be used for broadband excitation and narrowband probing of simultaneously excited vibrational coherences and allows investigating their temporal evolution with high spectral resolution. This is helpful for the investigation of intermolecular interactions in liquids which lead to complex Raman spectra and dephasing processes associated with line broadening.

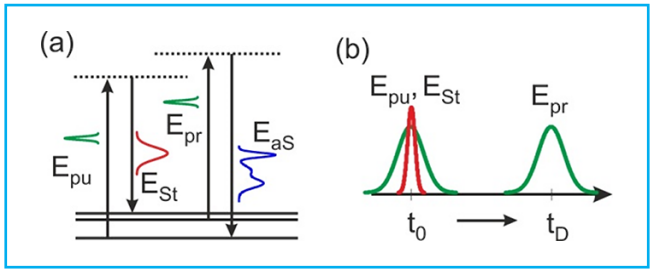

Fig. 1. (a) Energy level scheme of the multiplex CARS process. (b) time ordering of the pulse sequence.

CARS setup

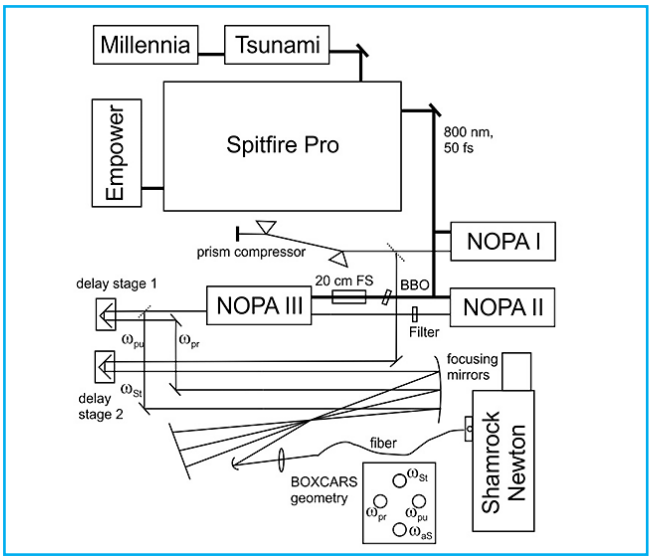

Fig. 2. Experimental design of the CARS setup. A regenerative Ti:Sapphire amplifier pumps three NOPAs. NOPA I and II deliver tunable femtosecond pulses. The outcome of NOPA II is spectrally narrowed and seeds the NOPA III, which is pumped by a stretched second harmonic of the fundamental of the Ti:Sapphire system. The narrowband pulses are divided in a pump and probe beam, respectively. Pump, probe and Stokes pulses are arranged in a folded BOXCARS geometry, and are focused with reflective curved mirrors into the sample. The anti-Stokes signal is collected in a multimode fiber and guide to the grating spectrograph Shamrock SR-500i-A; the frequency resolved signal is detected with the EMCCD detector Newton DU970P-BV.

The interacting laser fields are generated by non-collinear optical parametric amplifiers (NOPA) pumped by a Ti:Sapphire amplifier system. A conventional femtosecond NOPA (Fig. 2, denoted with NOPA I) is providing ultrashort sub-50 fs Stokes pulses. A two stage narrowband NOPA (denoted as NOPA II and III, respectively) delivers picosecond pulses for the CARS pump and probe beams. The narrowband NOPA consists of a conventional single stage NOPA (NOPA II), followed by a narrowband interference filter and a second stage (NOPA III) for parametric amplification of the filtered output of the first stage. NOPA III is pumped by stretched second harmonic pulses of the Ti:Sapphire laser. The resulting pulses are 1.0 ps long with a bandwidth in the order of 20 cm^{-1}. The three incoming beams are overlapped in a BOXCARS geometry and the time delay of the probe pulse with respect to the excitation pulses is scanned by a motorized linear stage. The CARS signal is detected time- and frequency-resolved by the spectrograph Shamrock SR-500i-A in combination with the thermoelectric cooled EMCCD detector Newton DU970P-BV (Fig. 2). The Shamrock with a focal length of 500 mm is equipped with a manual slit and a 1800 l/mm grating. The sensor of the Newton is a back illuminated EMCCD, optimized for visible light detection, and has 1600 x 200 active pixels with a size of 16 µm x 16 µm. The EMCCD comes along with a highly sensitive output amplifier and an electron multiplying mode. Due to the fast decaying CARS signals we need a high dynamic range to scan from very strong signals to weak signals with several orders less intensity. For the latter ones the sensitive output amplifier is most helpful. However, the electron multiplying mode should allow us to use CARS as probe process in pump-probe schemes, too. Here a shot-to-shot readout is desirable for better statistics.

Signal characteristics

The spectrally dispersed anti-Stokes signal is proportional to the squared Fourier transform of the nonlinear polarization which results from the interaction of the probe field with the coherently excited modes in the sample. In the limit of ultra-short excitation, justified by the femtosecond Stokes pulse, the coherence of a homogeneously broadened vibrational mode can be treated as a damped oscillator with a frequency ω_{vib} and a dephasing constant $\Gamma=1/T_2$. Additionally, non-resonant contributions during the pulse overlap of

Ultrafast time- and frequency-resolved coherent anti-Stokes Raman spectroscopy (CARS) with femtosecond excitation and picosecond probing

M. Lütgens, S. Chatzipapadopoulos, S. Lochbrunner
Institute of Physics, University of Rostock, Rostock, Germany (February 2014)

pump, probe and Stokes pulses have to be considered. The signal due to a single vibrational resonance shows a mono exponential decay with a line width essentially resembling the spectrum of the probe pulse. During the cross correlation interferences between the nonresonant and resonant contributions are observable. If the spectrum contains closely lying transitions within the spectral probe width, the modes interfere with each other leading to well known beating patterns at delay times after the cross correlation.

Results and discussion

The time- and frequency-resolved CARS spectrum of CH stretch vibrations of cyclohexane is shown in Figure 3. Cyclohexane exhibits three strong Raman bands around 2900 cm^{-1}. The mode at 2855 cm^{-1} is well separated from the other two contributions.

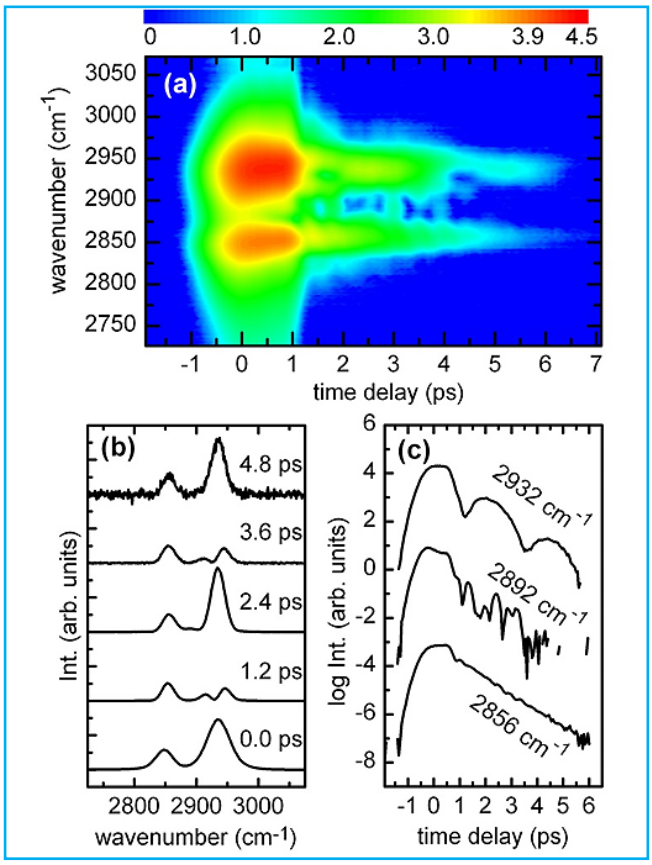

Fig. 3. (a) CARS signal of the CH vibrations of cyclohexane shown in a logarithmically scaled contour plot. (b) Selected spectra at different delay times. The line shape of the mode at 2855 cm^{-1} does not change after cross correlation; the two modes around 2930 cm^{-1} are beating with each other. Time traces for different wavenumbers are plotted in (c).

Application Note

Fitting an exponential function to the data for delay times after the cross correlation reveals a time constant of 0.6 ps which reflects a dephasing time of 1.2 ps for this mode. The other two contributions around 2930 cm^{-1} behave quite differently and the temporal evolution of the two Raman bands is dominated by beating phenomena. The beating period of 2.3 ps can be extracted directly from the time trace in the overlap region. This time constant is related to the frequency spacing of the two beating modes. Between these both features caused by the so far discussed three modes additional beating occurs (see Figure 3c, the time trace at 2892 cm^{-1}). This beating pattern indicates vibrational contributions in the sampled region which are not resolved in the spectra (Figure 3b).

Summary

In this article we presented a new CARS setup and demonstrated its capability to extract vibrational parameters by measurements on the CH stretch vibrations of cyclohexane. The setup equipped with a Shamrock spectrograph and a Newton EMCCD detector is suitable to measure different vibrational contributions in broad bands and to study dephasing processes of these modes. Since typical dephasing times in liquids are in the picosecond range or even faster, a sensitive setup is absolutely essential to extract reliable dephasing parameters. This requirement is even more necessary for CARS experiments utilizing picosecond instead of femtosecond pulses for probing.

References

[1] M. Lütgens, S. Chatzipapadopoulos, and S. Lochbrunner, Opt. Express 20, 6478 (2012).
[2] M. Lütgens, S. Chatzipapadopoulos, and S. Lochbrunner, EPJ Web of Conferences, XVIIIth International Conference on Ultrafast Phenomena 41, 05007 (2013).

Contact

Prof. Stefan Lochbrunner
Institute of Physics
University of Rostock
18051 Rostock,
Germany

Phone: +49 (381) 498-6960
E-mail: Stefan.lochbrunner@uni-rostock.de
Web: http://web.physik.uni-rostock.de/dynamics/