Optical CCD lock-in device for Raman difference spectroscopy

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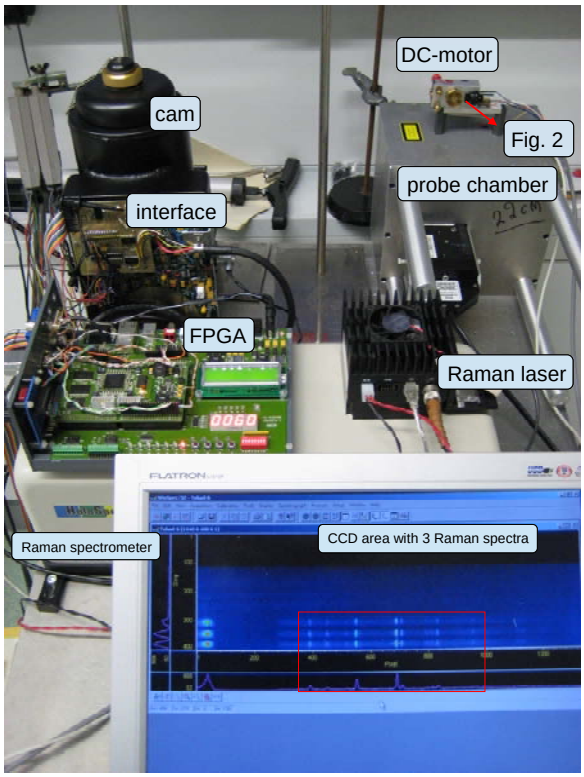
A new multi-channel lock-in technique for the detection of periodically varying Raman spectra is presented. Bacteriorhodopsin difference spectra demonstrate the capabilities of the scheme which incorporates sub-pixel precision spectra while avoiding environmentally induced drift. The modular VHDL-design enables chip-level compatibility with modern high-end liquid-cooled CCD camera devices.

1 Introduction

Raman difference spectroscopy (RDS) is a proven technique to compare i.e. the spectra of a sample probe against a reference. A common method is to use a rotating cell filled with two or more different samples.

2 Instrument setup

The setup in Fig. 1 shows the nitrogen cooled "Spec-10:400" camera from Princeton Instruments/Acton equipped with a front illuminated



1340x400 pixel chip.

Fig. 1 *The Raman difference spectrum setup in the laboratory*

The front cover of the electronic housing is detached to control and interface the timing of the CCD via the FPGA-based electronic board. The FPGA-board acts as the core-controller, switches the Raman laser and references the phase-locked-loop motor control which drives a small DC-motor Fig. 2.

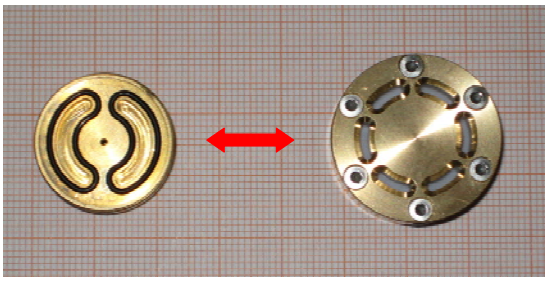


Fig. 2 *The brass sample disk containers are driven by a PLL-controlled DC-motor. Left the two-cell and right the six-cell containers are shown. The six-cell container is filled and arranged in pairs with three different samples in a special sequence to avoid spectra mixing on the CDD-chip.*

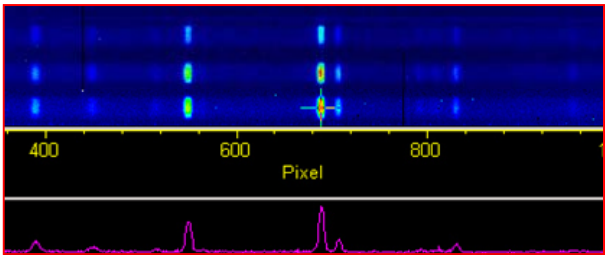


Fig. 3 *Magnified detail of the triple toluene spectra shown in the setup. Three spaced spectra are measured with the six-cell container. At pixel number 440 and ~780 two CCD-defects are recognized.*

3 CCD Raman difference spectroscopy (RDS)

Fig. 4 gives an overview of the instrument design. The main task of the FPGA-board is to provide a proper periodic timing to shift the CCD charges from the different Raman spectra up and down

synchronized with the different probes [1],[2]. Depending on the position of the rotating samples the Raman laser is chopped on and off phased by the FPGA-board. In order to improve signal-to-noise ratio one Raman measurement can contain up to 10000 cycles of optically accumulated signals from the same sample position. In order to gain maximum flexibility many important parameters like the number of accumulations and the shifting distance can be chosen by the user.

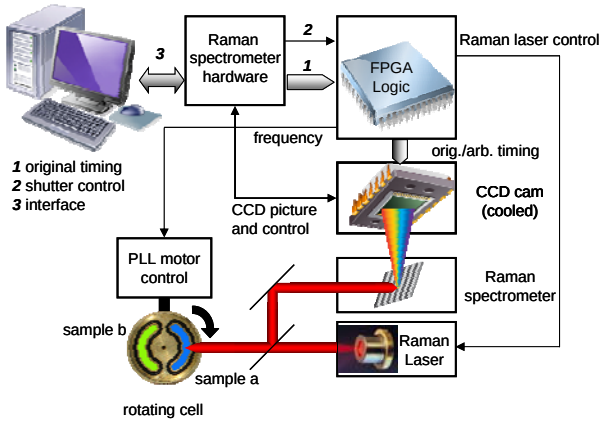


Fig. 4 *The FPGA-logic is the heart of the suggested system. Signals from an ordinary Raman spectrometer are observed and the different timing and reference signals are processed in real-time.*

4 Results

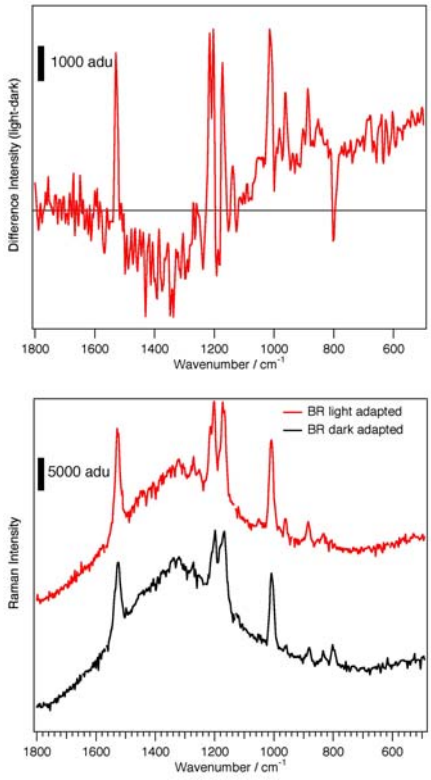


Fig. 5 *Shows the simultaneously detected forms (below) and the (light-dark) Difference spectrum (above). Note the change in terms of absolute intensity.*

As a performance check a light activated and a dark Bacteriorhodopsin sample was measured with the two-cell disk Fig. 5.

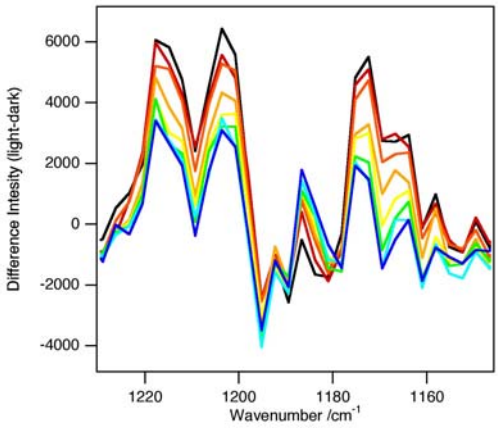


Fig. 6 *Time development of the difference spectra. For better clarity a selected spectral region is shown.*

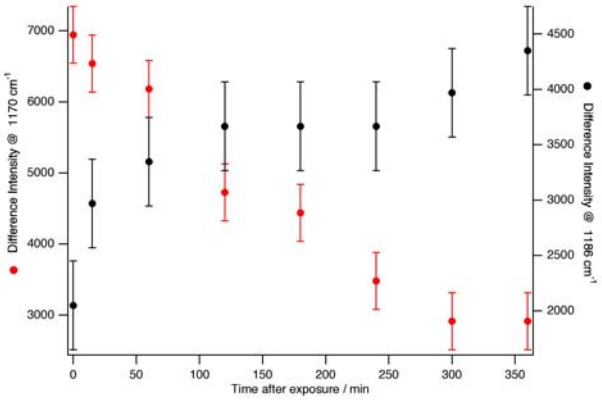


Fig. 7 *Two bands that exhibit the decay and increase of the difference intensity, respectively.*

The results in Fig. 6 and Fig. 7 demonstrate the capabilities of the technique. In particular when only small intensity and frequency shifts occur. The precision of the method is much higher than comparable setups, because temperature drift and laser intensity changes between measurements are avoided. Furthermore, sensitivity variations on the detection chip are cancelled, as always the same region is used for the acquisition. Last not least, the general scheme of the method can be easily applied to the detection of all periodically varying signals.

References

[1] V. Deckert, W. Liebler, R. Eck, W. Kiefer, „New Device for Raman Difference Scpectroscopy with Multichannel Detection“, Appl. Spectrosc. **51**, 939 (1997)

[2] H. Povel, C.U. Keller, I.-A. Yadigaroglu, „Two-dimensional polarimeter with a charge-coupled-device image sensor and a piezoelastic modulator“, Appl. Optics **33**, 4254 (1994)