

MODIFICATION OF TIME-RESOLVED STEP-SCAN AND RAPID SCAN FTIR SPECTROSCOPY FOR MODULATION SPECTROSCOPY IN THE FREQUENCY RANGE FROM mHz TO kHz

D. Baurecht, W. Neuhausser and U.P. Fringeli, Institute of Physical Chemistry, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria

Introduction

FTIR-Spectroscopy provides several techniques to study time dependent phenomena^{1,2}. On the other hand modulation-spectroscopy can improve kinetic information and signal to noise ratio in experiments with reversible kinetics³. Most of FTIR modulation experiments performed up to now were done with Lock-In Step-Scan techniques (Fig. 1). Our aim was to modify time resolved Interleaved Rapid-Scan (Fig. 2) and time resolved Step-Scan techniques (Fig. 3) in order to use these techniques for modulation spectroscopy in the frequency range from Hz to kHz. We compare the new methods with the conventional Lock-In Step-Scan technique regarding measurement time and signal to noise ratio.

Materials and Methods

All FTIR techniques capable of sampling time slices (sampling point spectra) synchronous with the modulation period can be used to analyze modulation experiments⁴. In this case the demodulation of the time resolved sampling point spectra is done by software⁴ and allows to calculate both, the fundamental tone and higher order harmonics after the data sampling. For the analysis of slow kinetics (mHz) the sampling point spectra can be measured with the Fast-Scan technique⁵. Time-Resolved Step-Scan technique (TR-SS) and Interleaved-Rapid-Scan technique (IRS) on a Bruker IFS66 FTIR spectrometer are used to extend this technique to the kHz range. Nematic liquid crystals served as test samples. Polarized light and ATR-technique (Ge-plate) were used to study the properties of liquid crystals at the liquid crystal-Ge interface⁶.

Results and Discussion

Our results show that the measurement of time resolved sampling point spectra with post measurement demodulation is a transparent method for determining absolute phase angles and modulation amplitudes of absorption bands in modulation spectroscopy (Fig. 4a,b). Both methods (TR-SS and IRS) provide full information in the frequency domain (i.e. for 2D-IR-correlation analysis). Moreover, the two new techniques provide additional time dependent information of the absorbance during the stimulus period (time domain).

The highest possible modulation frequency is only determined by the sampling rate of the ADC-converter of the spectrometer (IRS and TR-SS, Tab. 1). In the IRS-mode the minimum modulation frequency (50 Hz with Bruker IFS66) is determined by the slowest possible mirror velocity of the scanner. In the SS-mode spectral artifacts increase below modulation

frequencies of 3 Hz. These artifacts could be attributed to instability of the mirror position and could therefore be improved using new digital control mechanisms. Considering same signal to noise ratios, the Interleaved Rapid Scan (IRS) and Time Resolved Step Scan (TR-SS) techniques lead to dramatically shortened measurement times compared to conventional Lock-In Step-Scan methods (Fig. 5a,b). At a modulation frequency of 100 Hz we got measurement times of 17 h for LI-SS, 2.4 h for IRS and only 31 min for TR-SS technique, respectively.

Tab. 1: Measurement parameters for Interleaved Rapid Scan Time Resolved Spectroscopy (IRS), Step Scan Time Resolved Spectroscopy (TR-SS) and Lock-in Step Scan (LI-SS) Modulation experiments (ADC converter with a time resolution of 5 μ s).

method	LI-SS	IRS	TR-SS
frequency range	continuous up to \sim 320 Hz	discrete 50 Hz - 12.5 kHz	continuous 1 Hz - 12.5 kHz
restriction for lower frequency limit	measurement time	slowest mirror velocity	spectral artifacts
restriction for upper frequency limit	phase modulation frequ.	ADC sampling rate	ADC sampling rate
spectra / period	not necessary	up to 16	limited by AQP
time resolution	-----	5 μ s (ADC)	5 μ s (ADC)
No. of scans (coadd.)	1 (60000)	100-3000 (1)	1 (5-40)
modulation spectra	measured by Lock-In	calculated by software	calculated by software
mirror modulation	yes	no	no
DC-coupling	no	no	yes
measurement time	17 h	15 - 270 min	7 - 616 min
signal to noise	17.7 - 18.2	37.4 - 38.2	28.9 - 43.6
drift of baseline	no	yes	no

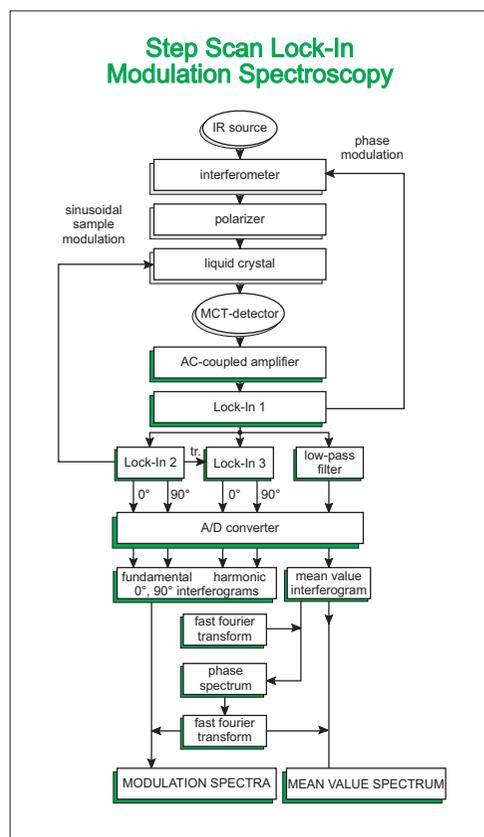


Fig. 1: System setup for Step Scan Lock-In modulation experiments. Phase modulation ("dithering" of the mirror) is used to modulate the IR beam (AC-coupled amplifier). Lock-In amplifier 1 demodulates the signal regarding the phase modulation frequency. Lock-In amplifier 2 provides the sinusoidal sample modulation. Lock-In 2 and 3 demodulate the in-phase (0°) and quadrature (90°) elements of the fundamental tone and first harmonic, respectively. The output of the low-pass filter provides the interferogram of the mean value spectrum.

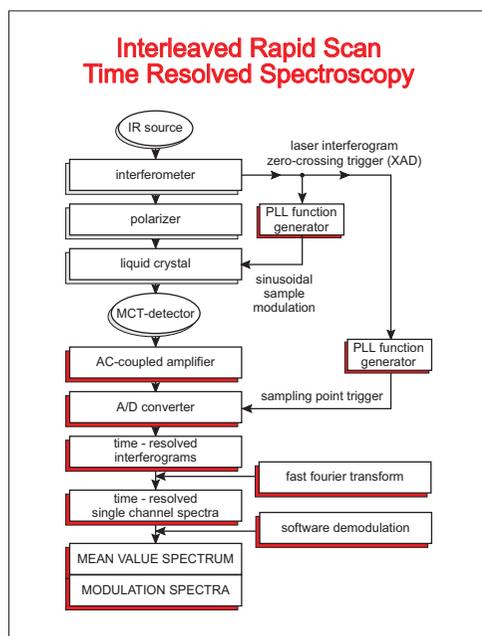


Fig. 2: Modification of Interleaved Rapid Scan (IRS) technique for modulation experiments. Time resolved interferograms are measured during the mirror movement. The synchronization of data sampling and sinusoidal sample modulation is done by two PLL (phase-locked-loop) circuits. The sampling process and calculation of the corresponding single channel spectra (Fourier transform) takes place in the acquisition processor of the spectrometer. The demodulation of the time resolved sampling point spectra is done by software and allows to calculate the mean value spectrum and modulation spectra of the fundamental tone and harmonics after the data sampling.

Abbreviations:
FFT Fast Fourier Transform, **LI-SS** Lock-In Step-Scan spectroscopy, **TR-SS** Time Resolved Step-Scan spectroscopy, **IRS** Interleaved Rapid-Scan spectroscopy, **ADC** Analog Digital Converter, **AQP** Acquisition processor of the spectrometer.

Correspondence:
 Dieter Baurecht (dieter.baurecht@univie.ac.at)

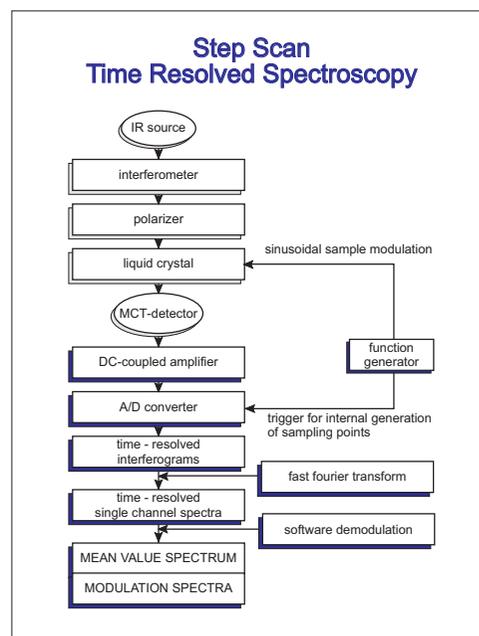


Fig. 3: Modification of Step Scan TRS technique for modulation experiments. A function generator provides the sinusoidal sample modulation and the trigger for the internal generation of sampling points. Sampling points must fit to the period of the stimulus. Time resolved interferograms are measured with the step scan technique (DC-coupled amplifier). The corresponding time resolved single channel spectra are calculated by a FFT. The demodulation of the time resolved sampling point spectra is done by software and allows to calculate the mean value spectrum and modulation spectra of the fundamental tone and harmonics after the data sampling.

References
¹ Sloan JJ and Kruus EJ (1989) In Clark RJH and Hester RE (eds) Time Resolved Spectroscopy, John Wiley & Sons, Chichester, England.
² Johnson TJ, Simon A, Weil JM and Hassis GW (1993) Appl Spec 47,9:1376-1381.
³ Fringeli UP (1992) In Mirabella FM jr. (ed) Internal Reflection Spectroscopy, Marcel Dekker, New York.
⁴ Fringeli UP (1997) Int. Patent Publication, PCT, WO 97/08598
⁵ Müller M, Buchet R and Fringeli UP (1996) J Phys Chem 100,25:10810-10825
⁶ Neuhausser W, Baurecht D, Schadt M. and Fringeli UP (1997) 11th International Conference on Fourier Transform Spectroscopy, Athens, Georgia USA

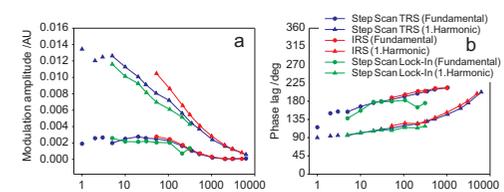


Fig. 4a, b: Comparison of Interleaved Rapid Scan (IRS), Step Scan TRS and Step Scan Lock-In ATR-FTIR modulation measurements. Frequency dependence of (a) absolute modulation amplitude and (b) phase lag for fundamental tone and first harmonic of the phenyl quadrant stretch (C=C) vibration at 1611 cm^{-1} . All three techniques lead to same results.

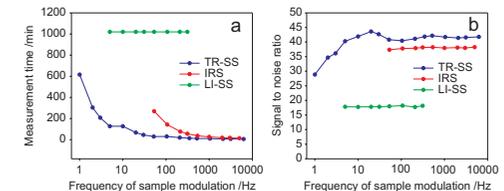


Fig. 5a, b: Measurement time and signal to noise ratio. **a** Measurement Time for FTIR-modulation experiments performed with IRS, TR-SS and LI-SS techniques. With the LI-SS technique no reduction of measurement time was possible (time constants of two Lock-In amplifiers). **b** Comparison of S/N for mean value spectra of the modulated liquid crystal assemble (wavenumber range: 1900-2100 cm^{-1}). Step Scan TRS - and IRS-technique show a significant higher S/N than Step Scan Lock-In despite higher resolution and shorter measurement time. Resolution: 4 cm^{-1} (IRS, TR-SS), 8 cm^{-1} (LI-SS).