Mid-IR laser based photothermal sensing of gases, liquids and imaging

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Advances in Instrumental Analytical Chemistry are often linked to technological developments in neighbouring disciplines. This is the case with respect to recent advances in Mid-IR quantum cascade lasers (QCLs) which are increasingly used as a new light source in mid-IR spectroscopy. QCLs offer high spectral power densities, fast amplitude and frequency modulation possibilities, polarized and coherent radiation. Based on these properties a range of new sensing schemes, often clearly outperforming established FTIR based analysers, have been developed recently. This presentation will centre on photothermal sensing schemes for trace analysis of gases, liquids as well as label free mid-IR imaging with nanometre spatial resolution. As opposed to established mid-IR absorption spectroscopy based on Beer´s law, mid-IR photothermal spectroscopy is an indirect method where the generated analytical signal scales directly proportional to the laser power. In one way or another it detects temperature induced changes (refractive index changes, sample expansion) in the sample matrix which are caused by absorption of the mid-IR photons by the analyte present in the sample under investigation.

After introducing the general concept of QCL based photothermal spectroscopy in comparison to absorption spectroscopy, applications will be shown covering different fields. For trace gas sensing interferometric cavity assisted photothermal spectroscopy (ICAPS) will be introduced [1]. This technique uses a Fabry-Perot interferometer to read out temperature induced refractive index changes in gaseous samples and achieves single digit ppb sensitivities (1 sigma, 1 second) for SO2, CO and similar IR active gases. ICAPS employs CW operated frequency tuneable distributed feedback QCLs as an excitation source to target isolated ro-vibrational transitions of the target gas molecule and an NIR probe laser to monitor the induced refractive index changes. Recent developments include a fibre coupled readout system and locking of the diode probe laser to the inflection point of transmission function. Because the thermal wave is heavily damped it is possible to develop effective balanced detection schemes in a small sensor architecture. A typical sensing configuration is shown in the Fig 1 below.

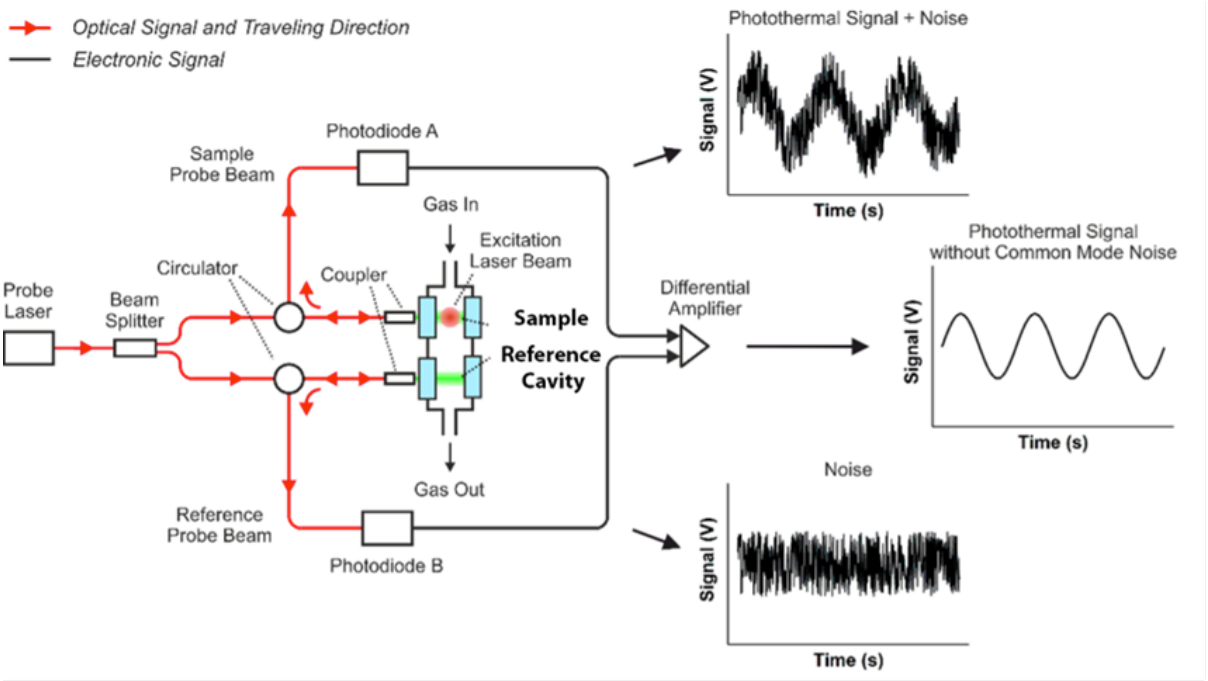

Fig. 1. Principle of balanced-detection ICAPS monitoring the reflectance of the interferometers in an all fibre-coupled probe laser configuration; the probe beam is split into two equal parts – a sample probe beam and a reference probe beam – and coupled by a collimator into two separate but identical interferometers. The sample beam probes the photothermal signal, which is superimposed by noise, whereas the reference beam probes only noise. The reflected light is again collected by the coupler and separated from the forward propagating light coming from the probe laser by a circulator, routing the beam to a photodiode. By subtraction of the two photodiode signals, the photothermal signal is received along with high rejection of common mode noise.

With respect to the analysis of liquids trace analysis of water in organic solvents will be shown and introduced as an alternative to Karl Fischer titration. This technique uses a broadly tuneable pulsed external cavity QCL for measuring the characteristic bending vibration of condensed water. The sample is illuminated by a pulsed mid-IR excitation source causing a periodical heating and cooling of the sample. The resulting photo-induced thermal gradient ΔT can be probed as a consequent refractive index change (Δn) by means of a second laser source, a so called “probe laser”. The challenge lies in detecting the smallest Δn. To do that, we use an interferometric approach. In particular, our liquid PTS IR sensor consists of a Mach-Zehnder Interferometer (MZI) able to sense sub-nm phase shifts $\Delta\varphi$ between its two arms. For that we use a HeNe probe laser and an external cavity (EC)-QCL pump laser tuneable from 1730 to 1565 cm^{-1}. The stability and linearity of our system are ensured by temperature stabilization and holding the MZI in its quadrature point using a PID controlled piezo electric transducer (PZT) glued directly on a mirror in one arm of the MZI. Some of the relevant obtained results are reported in Fig. 2. Achieved limits of detection are in the low ppm region [2].

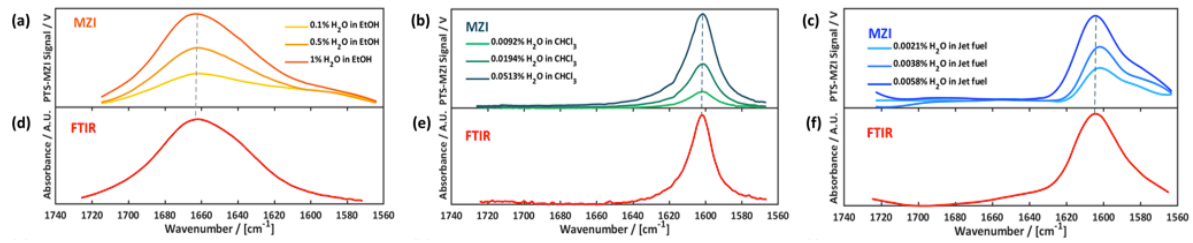

Fig. 2. PTS spectra of the water bending vibration as recorded using the Mach Zehnder Interferometer (MZI) and compared to the those recorded on a standard FTIR spectrometer. **(a),(d):** water in ethanol, **(b),(e)** water in chloroform and **(c),(f)** water in jet-fuel. The differences in the spectral shape result from different H-bonding of the water molecule in the studies solvents and solvent system (jet-fuel).

Nanometre spatial resolution in mid-IR imaging is achieved by coupling an atomic force microscope to a broadly tuneable pulsed EC-QCL source (AFM-IR). After a short introduction to this technique data obtained using tapping mode AFM-IR for the analysis of a PE/PP recyclate blend will be shown. The analysed sample derives from a post-consumer waste stream containing PE, PP, and a rubber component. Using tapping mode AFM-IR for recording spectra and images, and chemometric models for data analysis, we are able to locate the rubber component at the interface of the PE and PP and to detect the presence of other polymer contaminants. The AFM-IR data obtained through spectra and chemical images are in agreement with each other as well as with data obtained from conventional methods (SEM and soluble fraction analysis). The results obtained thus demonstrate that AFM-IR is a valuable tool for the nanoscale analysis of recycled polymer blends. A representative AFM-IR image of a region of only 1,5 µm x 1,5 µm is shown in Fig 3. Plotting the ratio of the characteristic C-H bending vibrations of PP and PE allows detection of small PP inclusion in PE in a direct and label-free way.

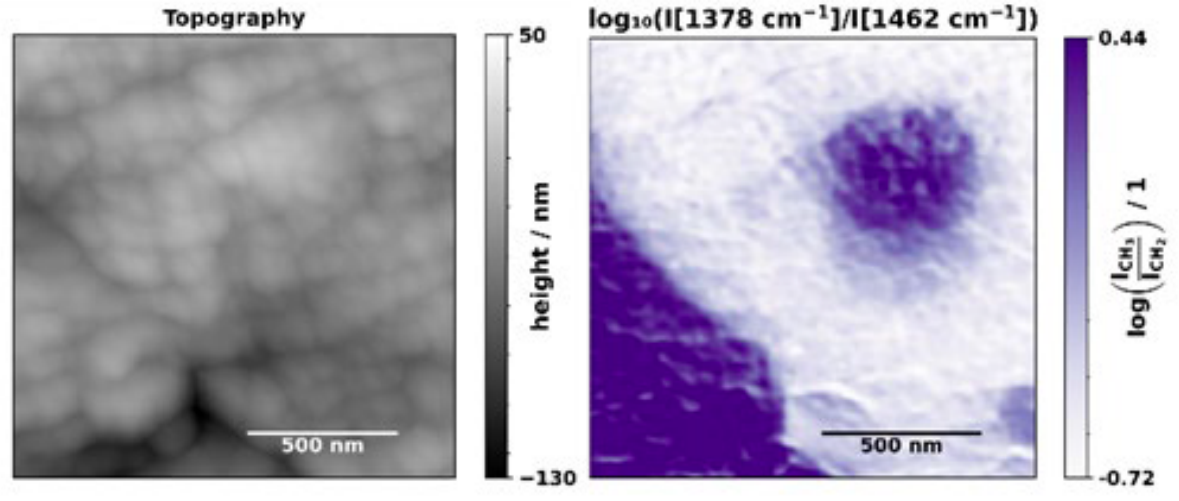

Fig. 3. Topography and band ratio of the bands corresponding to deformation vibrations of CH_2 and symmetric deformation of CH_3 groups (1.5 µm x 1.5 µm).

References

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