Mid- and Near-infrared NICE-OHMS – Techniques for ultra-sensitive detection of molecules in gas phase

Thomas Hausmaninger

Akademisk avhandling

som med vederbörligt tillstånd av Rektor vid Umeå universitet för avläggande av filosofie doktorsexamen framläggs till offentligt försvar i N450, Naturvetarhuset, fredagen den 30 November, kl. 10:00. Avhandlingen kommer att förvaras på engelska.

Fakultetsopponent: Assistant Professor Kyle Crabtree, Department of Chemistry, University of California, Davis, USA.
Noise-immune cavity-enhanced optical heterodyne molecular spectrometry (NICE-OHMS) is a technique for ultra-sensitive detection of molecular absorption and dispersion. For highest performance, the technique combines cavity enhancement (CE) with frequency modulation (FM); while the former increases the effective interaction length between the light and the analyte by several orders of magnitudes, the latter removes the in-coupling of 1/f noise and makes the signals background free. The combination of CE and FM also gives the technique an immunity to amplitude noise caused by the jitter of the laser frequency relative to the cavity resonance frequencies. All these properties make the technique suitable for ultra sensitive trace gas detection in the sub-parts-per-trillion (ppt) range. The aim of this thesis is to improve the performance of the NICE-OHMS technique and to increase its range of applications.

The work in this thesis can be divided into three areas: Firstly, a mid-infrared (MIR)-NICE-OHMS instrumentation was developed. In a first realization an unprecedented white-noise equivalent absorption limit for Doppler broadened (Db) detection in the MIR of $3 \times 10^{-9}$ cm$^{-1}$Hz$^{-1/2}$ was demonstrated. This was subsequently improved to $2.4 \times 10^{-10}$ cm$^{-1}$Hz$^{-1/2}$ allowing for detection methane and its two main isotopologues (CH$_3$D and $^{13}$CH$_4$) at their natural abundance. Secondly, further development of an existing near-infrared NICE-OHMS system was performed. This resulted in an improved longtime stability and the first shot-noise limited NICE-OHMS system for Db detection with a noise equivalent absorption limit of $2.3 \times 10^{-14}$ cm$^{-1}$ detected over 200 s. Thirdly, models and theoretical descriptions of NICE-OHMS signals under strong absorption conditions and from methane under high laser power were developed. It was experimentally verified that the models allow for a more accurate evaluation of NICE-OHMS signals under a wide range of conditions.

**Keywords**
Spectrometry, NICE-OHMS, trace gas detection, acetylene, methane, isotopologues, near-infrared, mid-infrared, shot-noise, optical parametric oscillator