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Infrared laser spectroscopic trace gas sensing

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Chemical sensing and analyses of gas samples by laser spectroscopic methods are attractive owing to several advantages such as high sensitivity and specificity, large dynamic range, multi-component capability, and lack of pretreatment or preconcentration procedures. The preferred wavelength range comprises the fundamental molecular absorption range in the mid-infared between 3 and 15 μ m, whereas the near-infrared range covers the (10-100 times weaker) higher harmonics and combination bands. The availability of near-infrared and, particularly, of broadly tunable mid-infrared sources like external cavity quantum cascade lasers (EC-QCLs), interband cascade lasers (ICLs), difference frequency generation (DFG), optical parametric oscillators (OPOs), recent developments of diode-pumped lead salt semiconductor lasers, of supercontinuum sources or of frequency combs have eased the implementation of laser-based sensing devices.

Sensitive techniques for molecular absorption measurements include multipass absorption, various configurations of cavity-enhanced techniques such as cavity ringdown (CRD), or of photoacoustic spectroscopy (PAS) including quartz-enhanced (QEPAS) or cantilever-enhanced (CEPAS) techniques. The application requirements finally determine the optimum selection of laser source and detection scheme.

In this tutorial talk I shall discuss the basic principles, present various experimental setups and illustrate the performance of selected systems for chemical sensing of selected key atmospheric species. Applications include an early example of continuous vehicle emission measurements with a mobile CO₂-laser PAS system [1]. The fast analysis of C1-C4 alkanes at sub-ppm concentrations in gas mixtures is of great interest for the petrochemical industry and was recently achieved with a new type of mid-infrared diode-pumped piezoelectrically tuned lead salt vertical external cavity surface emitting laser (VECSEL) [2]. Another example concerns measurements on short-lived species like nitrous acid (HONO) with a QCL-based QEPAS system where the small gas sampling volume and hence short gas residence time are of particular importance [3]. A true analysis of gas mixtures has been performed with a widely tunable DFG system in a medical application that could also be adapted to atmospheric species [4]. It is demonstrated that a laser-based narrowband system with broad tunability combined with an appropriate detection scheme is feasible for the chemical analysis of multi-component gas mixtures even with an a priori unknown composition. Most recent examples will further confirm the great potential of infrared laser-based devices for trace species sensing.

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