Selective trace gas detection of complex molecules with a continuous wave optical parametric oscillator using a planar jet expansion

Anthony K. Y. Ngai, a) Stefan T. Persijn, and Frans J. M. Harren
Life Science Trace Gas Facility, Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University, P.O. Box 9010, NL-6500 GL Nijmegen, The Netherlands

Harald Verbraak and Harold Linnartz
Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University, P.O. Box 9513, NL-2300 RA Leiden, The Netherlands

(Received 21 December 2006; accepted 20 January 2007; published online 23 February 2007)

The authors present a trace gas detection method for complex molecules using continuous cavity ring-down spectroscopy in combination with a continuous wave optical parametric oscillator (tunability wavelength: 2.8–4.8 μm; power: 1 W) sampling a supersonic planar jet expansion (nozzle dimension: 3 cm × 80 μm). The improved molecular selectivity allows simultaneous detection of larger numbers of complex molecules. With a total optical path length of 180 m in the planar jet, a detection limit for methanol in an air expansion was determined at 70 ppbv, corresponding to a minimal detectable absorption of 2.2 × 10−8 cm−1 (over 90 s). © 2007 American Institute of Physics. [DOI: 10.1063/1.2709515]

Trace gases are distinctive markers of biological processes that occur in plants, animals, and humans. An excellent method for highly sensitive and selective detection of these volatile organic compounds (VOC’s) is laser spectroscopy. A combination of a laser source in the midinfrared “fingerprint” region and a sensitive trace gas detection method, such as photoacoustic spectroscopy 1–3 or cavity ring-down (CRD) spectroscopy, 4,5 provides the means to detect multicomponent gases at sub-ppbv (parts per 109 by volume) levels. Trace gases such as nitric oxide, methane, ethylene, and ammonia 6–8 have been detected in a number of applications. However, a problem arises when trace gas detection is extended to larger, more complex molecules, which represent the majority of VOC’s. At room temperature, molecules such as isoprene and methanol exhibit very broad and complex absorption patterns. Because of their lack of symmetry, these molecules tend to have a high degree of vibrational and rotational freedom, resulting in complex spectra consisting of a multitude of overlapping lines. This complicates the spectral identification considerably and it also effectively decreases the state density, i.e., detection sensitivity.

One way to tackle this problem is to measure molecular absorptions at multiple points spread over entire absorption bands of gases. 9,10 The required scan range typically spans several hundreds of wave numbers, thus requiring widely tunable coherent sources such as CO and CO2 lasers, sources based on difference frequency generation, or optical parametric oscillation (OPO). For successful detection the coherent light source has to be properly combined with the sometimes limited detection method. In general, direct absorption spectroscopy suffers from low sensitivity, photoacoustic spectroscopy requires a long measuring time (due to relaxation effects and acoustical build up), cavity enhancement methods are limited by mirror coating properties, while wavelength or frequency modulation works best only for relatively sharp absorption features. In addition, the method of recording broad absorption bands is mainly applicable to a restricted number of compounds; an increased number of gases will definitely result in a reduced sensitivity and accuracy.

Therefore, we introduce a method of detecting traces of complex molecules based upon a combination of continuous cavity ring-down spectroscopy using a continuous wave (cw) infrared OPO system sampling a supersonic planar jet expansion. Supersonic slit jet expansions, both cw and pulsed, are well known in the field of molecular spectroscopy, particularly for high-resolution studies of van der Waals complexes, 11 cluster ions, 12 and molecular transients. 13 They have, however, never been applied in the field of trace gas detection. A planar expansion combines a Doppler-free environment with a relatively large absorption path length and low final rotational temperatures. The adiabatic cooling compresses the population distribution of a complex species into the lowest quantum states. Broad, complex, and overlapping absorption patterns thus become distinctive with linewidths that are principally determined by the residual Doppler broadening. Relatively short scans over tenths of wave numbers are sufficient to unambiguously identify and quantify multiple compounds with high sensitivity (ppbv’s) and short scan times (seconds).

For this experiment a homebuilt cw OPO (Fig. 1) is used, which has previously been described in detail by Ngai et al. 14 The OPO covers the midinfrared wavelength region between 2.8 and 4.8 μm, where the majority of gases have strong, characteristic absorptions. It provides high power (~1 W), continuous tunability with complete coverage, and a very narrow linewidth of 7 kHz over 20 μs and 4.5 MHz over 1 s. The OPO consists of a magnesium-doped periodically poled lithium niobate crystal with seven periods ranging from 28.5 to 31.5 μm (HC Photonics) and a singly resonant bow-tie cavity which is resonant for the signal. A 0.4 mm thick yttrium aluminum garnet (YAG) etalon in the cavity serves as an additional wavelength-selective element.

The OPO is pumped by a 10 W cw Nd:YAG laser (Lightwave MOPA 6000) with 1.3 cm−1 continuous tunability. Af-
For trace gas detection a continuous planar jet is used by expanding gas mixtures at a stagnation pressure of 400 mbar through a long and narrow slit nozzle (3 cm × 80 μm).\(^\text{15}\) The latter is located in a large stainless-steel ISO 160 six cross piece which forms the main expansion chamber. In order to guarantee stable gas expansion conditions, a roots blower with a total pump capacity of 4500 m³/h is used resulting in background pressures in the expansion chamber lower than 0.2 mbar during jet operation.

The ring-down cavity is incorporated into the expansion chamber such that the optical path traverses the full length (3 cm) of the jet expansion parallel to the slit (Fig. 1). The OPO beam intersects the expansion typically 1.5 mm downstream of the orifice. The total cavity length amounts to 60 cm. The length of the ring-down cavity is periodically modulated at 30 Hz covering two free spectral ranges of the cavity to assure a ring-down event during each period. An acousto-optic modulator (AOM) is used to block the cavity as soon as the cavity becomes transparent for the infrared light, resulting in typical ring-down events with ring-down times of the order of 12 μs. This corresponds to a total absorption path length of more than 3.6 km in the full cavity and an effective absorption path length of at least 180 m through the jet expansion. The used CRD spectroscopy mirrors have a radius of curvature of 1 m and 99.98% high reflective (HR) coating with a center frequency around 3000 cm\(^{-1}\) (Los Gatos Research). Even though the mirrors are almost 30 cm removed from the actual expansion, the use of He curtains directly in front of the mirrors is necessary to prohibit contamination of the high reflective coatings.\(^\text{13,15}\) Since OPO, molecular jet, and detection method are cw, there is no need for more complex trigger and timing schemes.

We chose the important trace gas methanol\(^\text{16,17}\) to demonstrate the potential of trace gas detection in a jet expansion. The methanol gas mixture was produced by flowing a water circuit.

The wavelength and power stability of the OPO system are further enhanced by embedding the OPO cavity into a monolithic aluminum block, maintained at 30 °C using a closed water circuit. The methanol gas mixture was produced by flowing water through the jet expansion. The used CRD spectroscopy mirror is used to monitor cold complex species in a planar expansion in direct absorption.

FIG. 1. Schematic of the experimental setup for improving trace gas detection of complex molecules. A cw optical parametric oscillator is used as a tunable infrared source and cw CRD is used to monitor cold complex species in a planar expansion in direct absorption.

laboratory air through the headspace of a cuvette containing liquid methanol. By maintaining a constant gas flow with a mass flow controller and by carefully determining the begin and end weights of the liquid methanol during the measurement time, methanol gas concentrations have been determined accurately. This method also allows varying the methanol concentration by using different gas flow rates. At room temperature CRD measurements result in a complex absorption feature with an intricate absorption pattern. To illustrate this, part of the CH stretching region of methanol (Q branch, \(K=1\leftarrow 0\), −→→−→\) with (a) 125 ppmv methanol in 10 mbar laboratory air without jet, (b) an expansion of 60 ppmv methanol in a 525 l/h laboratory air flow, and (c) an expansion of 1250 ppmv methanol in 25 l/h air mixed with 500 l/h argon. For each data point 16 ring-down events were averaged over a data acquisition time of 1 s.

FIG. 2. cw CRD spectra of the CH stretch fundamental region of methanol (\(Q\) branch, \(K=1\leftarrow 0\), −→→−→\)) with (a) 125 ppmv methanol in 10 mbar laboratory air without jet, (b) an expansion of 60 ppmv methanol in a 525 l/h laboratory air flow, and (c) an expansion of 1250 ppmv methanol in 25 l/h air mixed with 500 l/h argon. For each data point 16 ring-down events were averaged over a data acquisition time of 1 s.
central selectivity in the present setup. Since the population distribution of methanol is compressed into the lowest vibrational and rotational levels, absorption efficiencies are derived that are up to three times higher than at room temperature. This enhancement partially compensates the decrease in effective absorption path length, 3 cm as compared to the 60 cm length of the full ring-down cavity, as well as the lower effective geometrical coverage as the OPO beam (waist: 0.85 mm) is narrower than the width of the expansion (3 mm). To determine the detection limit of the present system, full advantage has been taken of the acquired wavelength-dependent absorption. By performing a Gaussian fit on the $Q(4)$ peak and using the area as a measure for the concentration, a detection limit $(S/N=1)$ of 70 ppbv is derived over a time period of 90 s. This corresponds to a minimum detectable absorption of $2.2 \times 10^{-8}$ cm$^{-1}$. A Gaussian fit with the same fitting parameters was performed in an expansion of pure argon and the fit area taken as a measure for the noise.

Laboratory air is not an effective cooling gas due to the presence of $N_2$ and therefore an additional spectrum has been recorded of 1250 ppmv methanol in laboratory air (25 l/h) mixed with argon [500 l/h, see Fig. 2(e)]. The addition of argon substantially improves the cooling properties of the expansion and a final rotational temperature of 17 K is achieved. In addition, absorption lines with a further reduced FWHM of 79 MHz are obtained. This provides a further gain in spectral purity but reduces the detection limit for methanol to 350 ppbv because of the 20 times weaker mixture. Nevertheless, the gain in state density due to the stronger rotational cooling limits the sensitivity decrease to a factor of 5 only.

The best results have thus been acquired in an air cooled jet with a minimum detectable absorption of $2.2 \times 10^{-8}$ cm$^{-1}$. The higher population of the lowest rotational levels improves the detection sensitivity. The limited absorption path length through the expansion and the lower effective geometrical coverage of the OPO beam in the expansion, however, result in detection limits that are two orders of magnitude lower than found in the CRD experiment using a gas cell filled at 10 mbars. Trace gas detection in the jet expansion, however, strongly improves the molecular selectivity and allows the simultaneous detection of different complex molecules without the necessity to scan over wide wavelength ranges. A logical extension of the present experiment is to use a pulsed planar expansion. This allows higher molecular densities in the expansion at even lower final rotational temperatures with reduced gas consumption and substantially smaller pump capacities. Even though this will complicate the trigger scheme it will make a setup more sizable and usable for research, with application in atmospheric and life sciences.

The authors thank the Dutch Technology Foundation (STW), the EU-NEST program “the Optical Nose,” the Dutch Foundation for Fundamental Research on Matter (FOM), and the research school NOVA for financial support.