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# Detection Of Formaldehyde Using Off-Axis Integrated Cavity Output Spectroscopy With An Interband Cascade Laser

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**Abstract** A continuous-wave, mid-infrared, distributed feedback, interband cascade laser was used to detect and quantify formaldehyde ( $\text{H}_2\text{CO}$ ) using off axis, integrated cavity output spectroscopy in gas mixtures ranging from  $\approx 1$ -25 ppmV in  $\text{H}_2\text{CO}$ .

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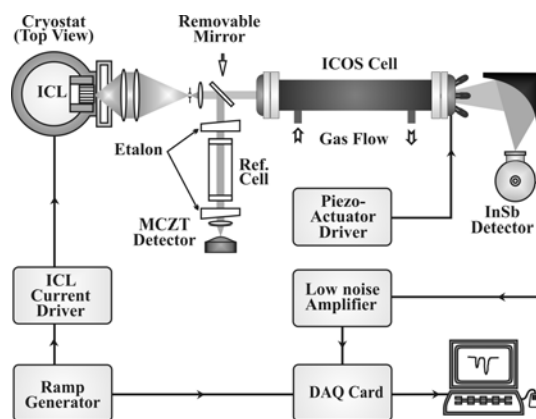
OCIS codes: (120.3940) Metrology (300.6340) Spectroscopy, infrared

## 1 Introduction

### 1.1 Formaldehyde and its detection

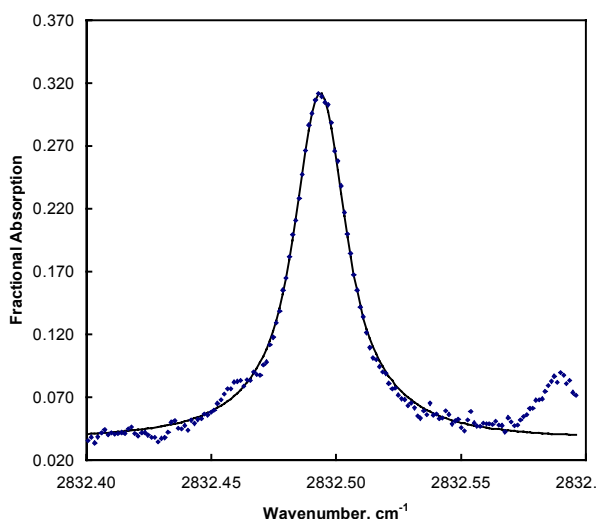
Formaldehyde ( $\text{H}_2\text{CO}$ ) is widely used in the manufacture of building materials and numerous household products. It is also an important intermediate in the oxidation of hydrocarbons in both combustion systems and in the troposphere. Thus,  $\text{H}_2\text{CO}$  may be present in substantial concentrations in both indoor and outdoor air samples. Tropospheric  $\text{H}_2\text{CO}$  concentration measurements provide a means of validating photochemical model predictions that play a key role in our understanding of tropospheric ozone formation chemistry [1]. Formaldehyde is a pungent-smelling, colorless gas that causes a variety of effects (including watery and/or burning eyes, nausea, and difficulty in breathing) in some humans exposed to  $\text{H}_2\text{CO}$  levels of only 100 ppbV. Known to cause cancer in animals, it is also a suspected human carcinogen.

To quantify  $\text{H}_2\text{CO}$  concentrations, several different chemical [2, 3] and physical detection methods have been used. Chemical analyzers, which employ coloration of a formaldehyde-sensitive reagent, are sensitive at ppbV levels but they suffer from cross-interference effects by other aldehydes and require long sampling times (i.e. minutes or more). To overcome these limitations, laser-based spectroscopic sensors have been developed. Several different tunable, *cw* laser sources have been employed to access  $\text{H}_2\text{CO}$  absorption lines, including lead-salt lasers [4], difference frequency generation (DFG) [5] sources, CO overtone gas lasers [6], and optical parametric oscillators (OPOs) [7, 8]. The best  $\text{H}_2\text{CO}$  detection sensitivity reported [9] ( $< 50$  pptv) was achieved using lead salt diode laser based absorption spectroscopy in a multipass optical cell with an effective optical path length of 100m.



**Figure 1.** Experimental arrangement used in OAICOS detection of formaldehyde.

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**Figure 2:** Experimental fit to formaldehyde feature at  $2832.48 \text{ cm}^{-1}$ . Formaldehyde concentration is 26.57 ppmV. Fit uses a Voigt line shape function

### 1.2 Interband Cascade Lasers

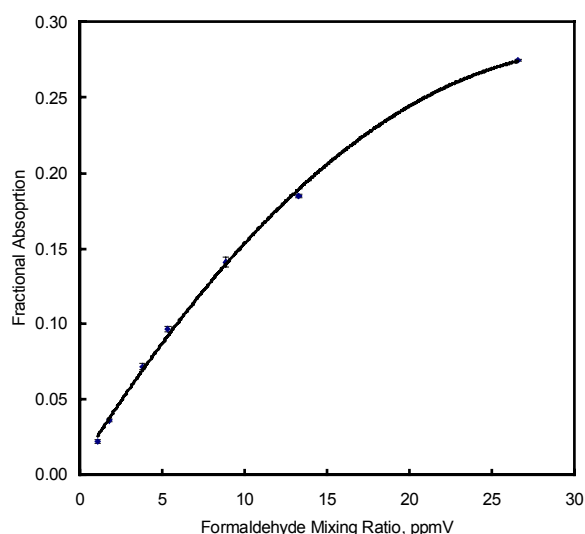
Recently, distributed feedback (DFB) interband cascade lasers (ICLs) [10] have been constructed that can access wavelengths between  $3.0$  and  $4.5 \mu\text{m}$  [11], a spectral region which has been difficult to cover with intraband quantum cascade lasers (QCLs). ICLs employ transitions between the conduction and valence bands as in bipolar diode lasers, but instead of losing an electron to the valence band it is recycled through interband tunneling into the conduction band of the next cascade stage. This is made possible with the type-II broken gap alignments in InAs/GaInSb quantum well structures. Because the conduction and valence bands have opposite dispersion curvatures, fast phonon scattering loss is circumvented in ICLs, which results in a more efficient operation with a low threshold current density. The emission wavelength of ICLs can be tailored in a wide spectral range, particularly on the shorter-wavelength side due to a large band offset between their constituent materials. Presently, continuous-wave (cw) operation of ICLs is obtained at relatively low temperatures (up to  $237 \text{ K}$ ). However, cw operation of ICLs at room-temperature

is projected to be feasible by improving thermal management on the current devices [10].

### 1.3 Integrated Cavity Output Spectroscopy

Absorption spectra resulting from methods such as tunable diode laser absorption spectroscopy (TDLAS) with wavelength or frequency modulation, and FTIR are typically easy to interpret and are not limited by species selectivity. However, they may be orders of magnitude less sensitive than techniques such as GC/MS, laser induced fluorescence (LIF), or resonant ionization methods (REMPI). Cavity ringdown spectroscopy (CRDS) is a sensitive absorption technique that is capable of monitoring a wide range of species. In cw-CRDS, a beam from the diode laser is injected into an optical cavity formed between two highly reflective mirrors. Only light with a frequency that matches a cavity transmission mode is coupled into the cavity due to constructive interferences. The energy of light at these resonant frequencies builds up in the cavity over time. When the energy reaches a set threshold, the input beam is shut off and a ringdown is recorded. The CRDS technique, while very sensitive, depends on fast electronics both for shuttering and for the data acquisition process needed to capture and store the ringdown waveform that is on the order of microseconds.

Integrated Cavity Output Spectroscopy (ICOS) provides enhanced cavity sensitivity using a less complex setup than CRDS [12, 13]. With this method, the transmitted output of the cavity is time-integrated to provide an absorption spectrum as the wavelength is scanned through the region of interest. The spectrum is then converted to absorbance through the Beer-Bouguer-Lambert Law. Off-axis ICOS (OAICOS), in which the laser beam is directed at an angle with respect to the cavity axis, provides



**Figure 3.** Dependence of fractional absorption on formaldehyde concentrations. Several spectra were acquired at each concentration. Error bars (barely discernible here) show standard deviations within the fits for these groups.

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increased spectral density of cavity modes and thus minimizes the noise in the resulting absorption spectra [13, 14].

### 2. Experimental

A schematic of the apparatus used in this study is shown in Figure 1. Briefly, light from a ICL was directed into an ICOS cell and detected with an InSb detector. The IC laser, housed in a liquid-nitrogen cryostat, provided single-mode output powers of up to 12 mW at 3.53  $\mu\text{m}$ . The output is tunable from 2831.8  $\text{cm}^{-1}$  to 2833.7  $\text{cm}^{-1}$  by varying injection current. The low threshold current operation of ICLs requires a current source with relatively high precision (an ILX Lightwave model LDX 3220 was used in this study). With the ICL operating at  $\approx 80$  K it is possible to access several formaldehyde absorption lines. For these measurements the OAICOS signal for an absorption line at 2832.483  $\text{cm}^{-1}$  was analyzed. A gas standard generator (Kin-Tek model 491M) based on a permeation tube was used to provide  $\text{H}_2\text{CO}$  concentrations ranging from 0.5 to 25 ppmV in a diluting gas (such as  $\text{N}_2$ ). The formaldehyde gas mixture was introduced into a custom, 50 cm OAICOS cell equipped with 50 mm diameter, high reflectivity mirrors (Novawave Technology). Cavity modes were randomized by imposing a 300 Hz modulation on one set of the cavity mirrors using three piezo actuators.

### 3. Results and Discussion

Spectra were collected for mixtures of formaldehyde in nitrogen. To mitigate effects of formaldehyde stickiness, spectra were collected in ascending concentrations ranging from  $\approx 1$  to 25 ppmV. Several spectra were collected for each concentration. Figure 2 shows part of the OAICOS spectrum for a 26.57 ppmV mixture of formaldehyde in nitrogen. Also shown is a fit of the data using a Voigt line shape function. Figure 3 shows the dependence of the fractional absorption at line center on formaldehyde concentration. The standard deviation in fractional absorption determined for this calibration curve was 0.15% equivalent to a formaldehyde detection limit of  $< 100$  ppbV.

### 4. Acknowledgement

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