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14. ABSTRACT
A hand-held sensing and alarm system is needed for ultra-trace concentrations of chemical gases, biological aerosols, and explosive vapors. Unprecedented sensitivity is required due to low concentrations and low vapor pressures for many targets of interest. Zyberwear has identified intracavity laser absorption spectroscopy (ICLAS) as a promising solution. Our working name "Hyperdog" anticipates its sensing capabilities for trace vapors. Hyperdog provides greater than kilometer effective optical path lengths in a device with centimeter dimensions. Innovations include the use of room-temperature

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Report developed under topic #A08-75, contract W911NF-10-C-0030.

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Zyberwear, Inc.

"THz intracavity laser absorption spectrometer"

Final Report, SBIR Phase II
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Period 18/11/09 to 18/11/11
15 January 2012

Motivation for the work

A hand-held sensing and alarm system is needed for ultra-trace concentrations of chemical gases, biological aerosols, and explosive vapors. Unprecedented sensitivity is required due to low concentrations and low vapor pressures for many targets of interest. Zyberwear has identified intracavity laser absorption spectroscopy (ICLAS) as a promising solution. Our working name "*Hyperdog*" anticipates its sensing capabilities for trace vapors. Hyperdog provides greater than kilometer effective optical path lengths in a device with centimeter dimensions. Innovations include the use of room-temperature semiconductor quantum cascade lasers (QCL) in wavelength regions rich in molecular signatures.

The simple low-power compact Hyperdog for spectral sensing of explosive vapors, chemical gases, and biological aerosols will have immediate application in Army operations. Additional industrial, bio-medical, and atmospheric science applications give Hyperdog tremendous commercial potential. Anticipated low vapor concentration creates the need for extreme sensitivity. Hyperdog provides this by combining kilometer effective absorption path lengths with the extreme sensitivity of the laser spectrum to intracavity absorption.

Goals of the work

The three enabling hardware components of Hyperdog are an open external cavity for the QCL, a Fabry-Perot spectrometer to characterize the laser mode spectrum, and electronics. Fig. 1 presents a schematic of the first two components and how they operate together.

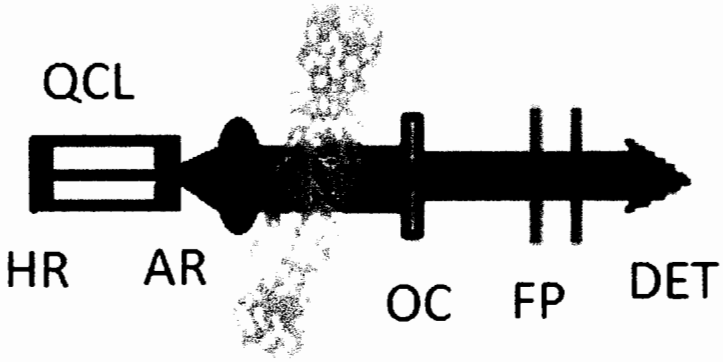

Fig. 1. (left) Schematic of Hyperdog. A LWIR QCL at room temperature has HR and AR coatings and an external cavity is formed using a collimating optic (orange) and an output-coupling flat mirror (OC). The cavity is open to the flow of target vapors (green) with characteristic sharp absorption lines. The outcoupled mode spectrum is analyzed using a scanning FP spectrometer. The signal is detected using a room temperature piezo-electric detector.

Work done in this period:

Summary:

We developed a scanning Fabry-Perot spectrometer for spectral analysis.
We built a breadboard structure of the Hyperdog vapor sensor, and determined the sensitivity of the system to acetone vapors inside the cavity in CW operation.
The experimental results were compared with the numerical simulation to quantify the sensitivity.
Projections of sensitivity limits were made.
We purchased and prepared for installation new QCL from Maxion, Inc.
A hand held enclosure was fabricated to contain the whole cage system and control the ambient.
We assembled the prototype Hyperdog trace-vapor sensor, and demonstrated its ultra-trace sensitivity, for the example of acetone vapor.

Sensitivity estimation:
We made quantitative sensitivity estimates. Fig. 2 demonstrates how the CW laser emission spectrum reacts to the presence of acetone vapor inside the cavity. The concentration of acetone vapor has been chosen below the level when remarkable drop of the laser intensity occurs. In this experiment the acetone concentration inside the cavity was not quantified, but subjectively it was slightly above human nose sensitivity (41 ppm [1]). In response to the vapor, the laser emission shifted by 6 cm^{-1} away from the absorption toward higher frequencies, even to a region where no laser emission was previously observed. This strongly non-linear behavior demonstrates the extreme sensitivity of the system to frequency-dependent intracavity absorbers.

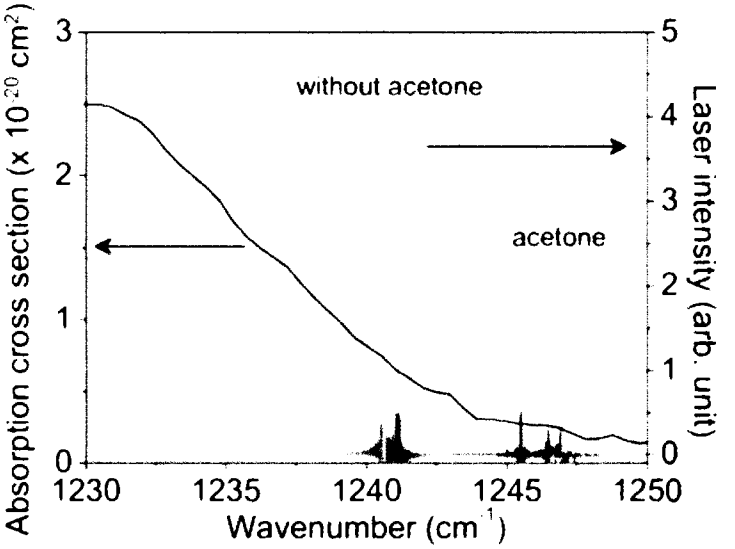

Fig 2. Emission spectrum of the external cavity QCL together with absorption cross section of acetone. The QCL was operated CW at 940 mA excitation current. The spectral resolution of the spectrometer is 0.5 cm^{-1}. Two separate laser spectra are plotted, one without, and one with acetone vapor in the cavity. When the open laser cavity is exposed to acetone vapor, the spectrum blueshifts, as indicated by the arrow.

Numerical simulation of the laser rate equations demonstrates the temporal evolution of the QCL emission spectrum. The spectrum of the acetone absorption cross section ! taken from [2] was fit to a 2^{nd} order polynomial to obtain a smooth function for the calculations. The maximum and minimum cross-sections in the 1235-1250 cm^{-1} wavenumber region were 1.75×10^{-19} and 0.15×10^{-19} cm^2, respectively. The absorption coefficient at the q^{th} laser mode was determined using $K_q = n\sigma_q$, and the value of n taken to be 5.4×10^{15} cm^{-3}, or ~217ppm, which is consistent with qualitative concentration level used in the experiment. This corresponds to an acetone vapor pressure of 165 mTorr.

QCL parameters used in numerical simulation were either estimated, or taken from the literature where available. The active layer length L is taken to be 3 mm. We estimate a beam waist of 4 μm, which gives a cavity mode volume $V_C = 3.7 \times 10^{-10}$ cm^3. We estimate a value for the gain per round trip per unit time $B_O = c\sigma_S/V_C$ of 0.5 by assuming a stimulated emission cross-section $\sigma_S \sim 10^{-20}$ cm^2 (typical laser emission cross-section). The value of A is estimated as 7.1×10^6 s^{-1} assuming spontaneous decay time τ_{SP} of 1.4×10^{-7} s [3]. The broadband cavity loss is obtained from $\psi \approx -(c/2L)\ln[R(1-T_i)^2]$ where T_i is the waveguide fractional loss per pass (due to diffraction, scattering, and absorption loss in the active medium), and *R* is the fractional cavity output coupler reflectivity [4]. Estimating reasonable values of $T_i = 0.25$ and $R = 0.8$, we found $\psi \sim 3.9 \times 10^{10}$ s^{-1}. The normalized pump rate $\eta = 18$ and the spectral width of the gain is *Q* (HWHM) = 4000.

Fig. 3 (next page) shows the calculated laser emission spectrum with and without acetone inside the cavity. The spectra plotted correspond to an integration time of 52 μs from the beginning of the laser excitation. The plot clearly shows a 6 cm^{-1} shift toward higher wavenumbers, which is in agreement with the experiment.

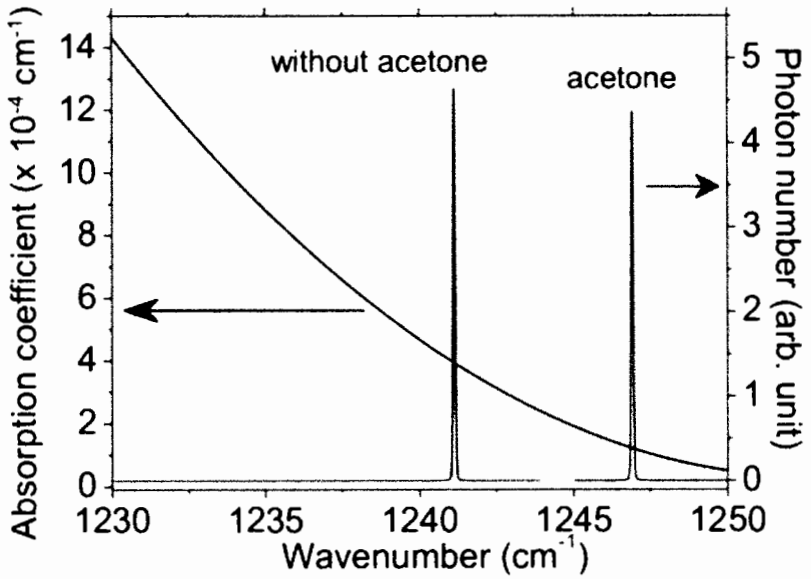

Fig 3: Calculated laser emission spectra without (left) and with (right) acetone inside the cavity. The acetone profile was quadratic with a concentration of 5.4 x 10^{15} cm^{-3}, or 165 mTorr pressure. The spectrum with acetone shows a clear 6 cm^{-1} shift to higher wavenumbers.

Assuming a minimum detectable shift of 0.03 cm^{-1}, which is the observed external cavity mode spacing [13], the sensitivity limit for acetone using the given set-up is estimated from similar calculations to be ~320 ppb. This is improved somewhat to the value 240 ppb by (numerically) shifting the QCL with emission wavelength closer to the peak of the acetone absorption.

In other words, the system described in this report is probably 3 orders of magnitude more sensitive to the presence of acetone then was actually demonstrated.

To further elaborate the sensitivity question, we studied the dynamics of the QCL spectrum in external cavity operation in long pulse mode. This showed that spectrum stabilizes after 0.5 to 1 ms from the beginning of the pulse. At times shorter than 1 ms from the beginning of the pulse fast temperature drift cause mode instability and as a result pour repeatability of the spectrum dynamics. After 1 ms temperature drift slows down and the emission spectrum becomes very stable, adiabatically shifting due to slow drift of the active chip temperature. It is important that this adiabatic shift of the emission spectrum is very repeatable from pulse to pulse, which can't be said about the spectrum on the times shorter than 1 ms.

This fact allowed us to substitute for power consuming CW regime of QCL operation with long pulse operation. Optimal typical pulse durations were defined as 5-10 ms. With a repetition rate of 10-20 Hz (reasonable for data acquisition) this corresponds to ~ 10% duty cycle. This allowed us to reduce power consumption by the laser - as well as by the cooling system - by an order of magnitude without losing sensitivity of the

system; this makes battery operational prototype quite feasible.

Slow drift of the laser gain spectrum due to temperature drift in the time interval from 1 to 10 ms from the beginning of the pulse, allows us to keep the Fabry- Perot (FP) interferometer at the fixed position (instead of scanning the FP in CW laser operation mode). This allows us to eliminate expensive and power- and space-consuming piezo drives and supporting electronics for the FP interferometer. In this configuration the FP interferometer works as a monochromatic filter for an adiabatically tuned emission spectrum of the external cavity laser system.
It was demonstrated that in this configuration the system is sensitive to the presence of water vapor in the ambient air in the lab, even though the QCL wavelength does not coincide with the water absorption band. Estimated observed sensitivity to intracavity markers corresponds to absorption coefficient $3*10^{-7}$ cm^{-1} or an absorption length of 27 km.

Together, these provide an ***acetone sensitivity at the wavelength of the test QCL chip of some 60 ppb***, which is remarkably better than previously obtained sensitivity levels at CW operation mode.

8.1 micron QCL:
We purchased a new QCL to replace the old laser. The center wavelength of the new QCL is at 8.1 microns. The QCL has one face with high reflection (HR) coating while the other is coated for anti-reflection (AR). A new design of the external cavity was also implemented as shown in the schematic in Fig. 4. Instead of the previously used 90^{o} off axis parabolic mirror, a collimating lens at our QCL wavelength was used. We procured a 1" focal length ZnSe plano convex lens with AR coating optimized for 8-12 microns, for this purpose.

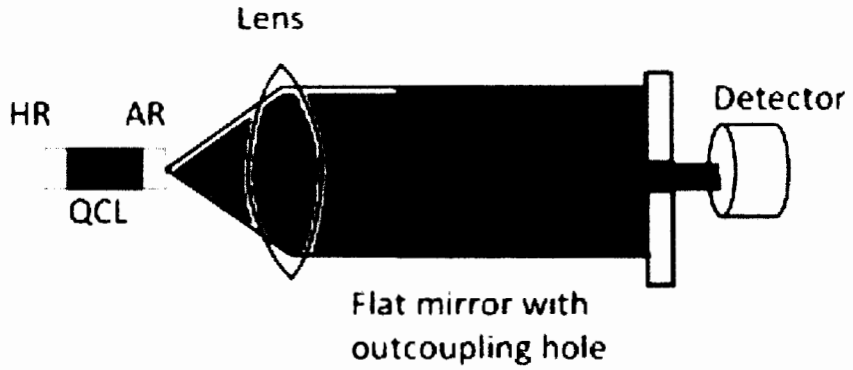

Fig 4: Schematic of external cavity QCL using a lens system.

Air sealed enclosure:
An air sealed enclosure was built, to avoid hyperdog's exposure to ambient air and to allow more accurate sensitivity estimates. A photograph of the enclosure is shown in Fig. 5 on the next page. The QCL was mounted on thermoelectric cooler (TEC) and the combined system was then mounted on a water-cooling aluminum plate. From previous

measurements the system shows better sensitivity at around 14^{o}C. The TEC controls the temperature of the aluminum plate and thus the QCL. The QCL divergence beam is collimated by the ZnSe lens working at 8.1 microns. The aluminum enclosure in the middle of the picture contains the required gas (air sealed gas cell). This box has gas inlet and outlet ports (not shown in the picture), which are controlled externally. The right end of the enclosure has a flat mirror with an outcoupling hole in the middle (not seen in the picture) which passes the cavity signal to the Fabry- Perot and thence to the detector.

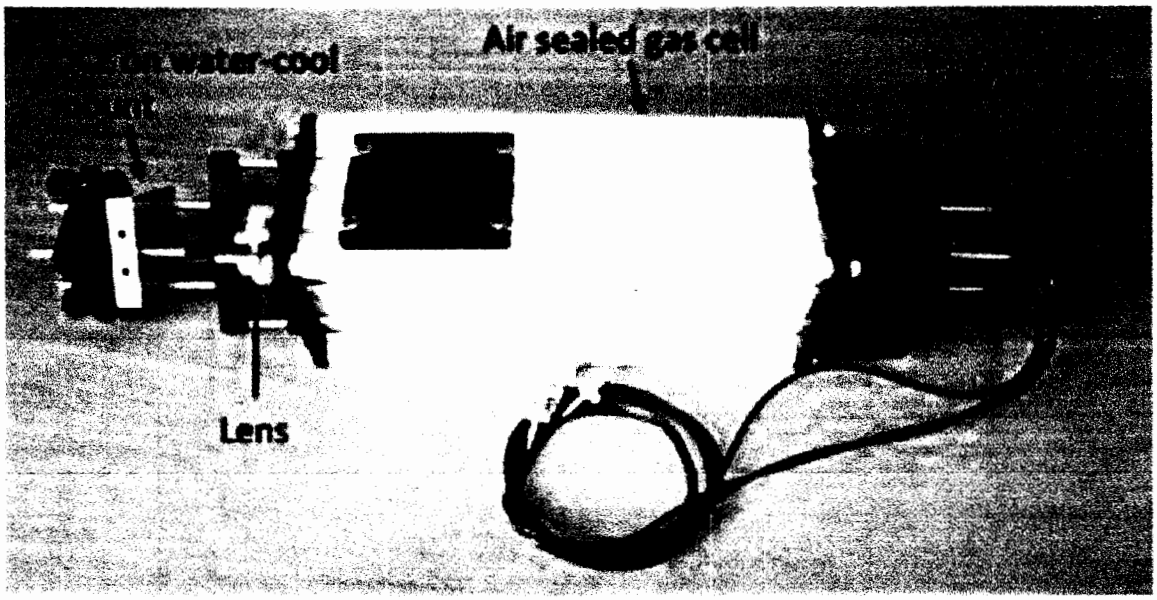

Fig 5: Schematic of the hyperdog system with gas enclosure.

A cold finger was also made to repair a tiny leak (one drop in one month), which posed a contamination risk to the laser optics. This new cold finger was mounted with a retaining ring on the mirror mount instead of the previously designed fixed screw method.

RESULTS:
Effectiveness of the Hyperdog trace-vapor sensor was demonstrated, detecting the presence of acetone vapor at approximately 25 PPB in air.

Participants:
Zyberwear: Oliver Edwards, Dr. Andrei Muraviev, Himanshu Saxena. University of Central Florida: Prof. R. E. Peale, Gautam Medhi, Chris Fredricksen

References:
[1] C.J. Wysocki, P. Dalton, M.J.Brody, H.J. Lawley, "Acetone odor and irritation thresholds obtained from acetone-exposed factory workers and from control (occupationally unexposed) subjects", American Industrial Hygiene Association Journal 58, 704-12 (1997).

[2] R. E. Peale, A. V. Muravjov, C. J. Fredricksen, G. D. Boreman, "Spectral Signatures Of Acetone Vapor From Ultraviolet To Millimeter Wavelengths", Proc. Intl. Symp. Spectral Sensing Research, Bar Harbour ME June (2006). [3] Q.K Yang, B. Hinkov, F. Fuchs, W Bronner, K. Kohler, J. Wagner, R. Maulini, "Rate equation analysis of external cavity quantum cascade lasers", Journal of Applied Physics 107 043109 (2010). [4] A. Kachanov, A. Charvat, F. Stoeckel, "Intracavity laser spectroscopy with vibronic solid-state lasers: I. Spectro-temporal transient behaviour of a Ti:sapphire laser", J. Opt. Soc. Am. B 11 (12), 2412 (1994). [5] G. Medhi, A.V. Muravjov, H. Saxena, C.J. Fredricksen, T. Brusentsova, R.E. Peale, O. Edwards, "Intracavity laser absoption spectroscopy using mid-IR quantum cascade laser", Proc. SPIE 8032, 12-19 (2011).

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