INFRARED INTRACAVITY LASER ABSORPTION SPECTROMETER

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SUMMARY: A spectral sensing method is needed with sufficient sensitivity to detect vapors of low vapor pressure compounds, such as explosives. The opportunity is for ultra-trace molecular vapor recognition by Intracavity Laser Absorption Spectroscopy (ICLAS) at IR wavelengths. Our approach is based on multi-mode external-cavity quantum cascade lasers and a scanning Fabry-Perot spectrometer to analyze the laser mode spectrum in the presence of a narrow band intracavity absorber. Numerical solution of laser rate equations support feasibility of detecting 10 ppb molecular concentrations, which is comparable to the saturated vapor pressure of TNT. System design and first results are presented.

INTRODUCTION: A spectral sensing method with sufficient sensitivity to detect vapors of low vapor pressure compounds such as explosives would have great promise for defense and security applications. An opportunity is Intracavity Laser Absorption Spectroscopy (ICLAS) at Mid-IR (MIR, 3-5 μm wavelengths), Long-Wave IR (LWIR, 8-12 μm wavelengths) and Terahertz (THz 50-200 μm wavelengths). Applications include military and commercial screening for threat compounds and contraband having very low vapor pressures. Such compounds include explosives, chemical gases, biological aerosols, drugs, and banned or invasive plants or animals. Also, biomedical breath analysis and non-invasive law-enforcement searches are envisioned.

RESULTS:

1. Sensitivity Estimation: The sensitivity limit for a QCL-based intracavity laser absorption spectrometer has been estimated by numerical solution of the laser rate equations [1],

$$\frac{dM_q}{dt} = -\gamma M_q + B_q N(M_q + 1) + \gamma_q c M_q \quad \text{and} \quad \frac{dN}{dt} = P - AN - \gamma N - B_q M_q \quad , \qquad (1)$$

where γ is the broad band cavity loss, B_q the gain at the frequency of mode q, γ_q the absorption coefficient of intracavity absorption at the q^{th} axial laser mode, c the light speed, P the pump rate, and A the spontaneous decay rate of the upper laser level. These equations characterize the regimes of QCL laser build-up, namely the laser inversion N, the total photon number M, the photon numbers M_q in individual laser modes, and the final stability of the laser spectral output. The numerical solution of Eqs. (1) is presented as a time-integrated laser emission spectrum in Fig. 1 (left) for a THz QCL, where a weak intracavity absorption line has been included. The logarithmic abscissa represents the integration time, which can be interpreted as the laser-pulse duration. The logarithmic signal-strength color scale has blue for few photons and red for many. The vertical stripe at 2 μs corresponds to a 600 meter effective path. Fig. 1 (right) presents both the intracavity absorber line profile, having the very low peak value of just 2 x 10^{-4} cm^{-1} and the laser emission profile. In a conventional transmittance experiment using a 10 cm vapor cell, the absorption dip in the intensity would have been only 0.2%, which would be lost in the noise. In contrast, the ICLAS simulation achieves a nearly 100% deep absorption feature due to the extraordinarily long intracavity path length. Similar simulations for typical THz QCL parameters with 2 μs pulse duration suggest that absorptions as weak as 10^{-6} cm^{-1} might be detected. For and IR absorption cross section of 10^{-18} cm^2, the detection limit would be 10^{12} molecules per cubic centimeter, while the saturated vapor pressure of TNT is 3 x 10^{11}/ cm^3. In other words, the predicted sensitivity for a relatively short THz QCL pulse is within a factor of 3 needed to detect TNT in a confined space such as a shipping

container. Longer pulse duration improves sensitivity. In the THz, this may be achieved by cooling the laser below 77 K. Continuous wave QCLs are already available in the LWIR.

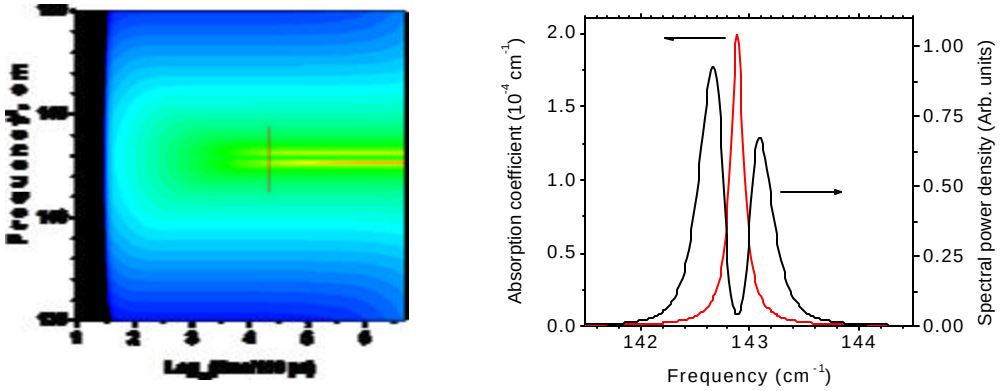

Figure 1. (Left) Time integrated laser emission spectrum. (Right) Weak intracavity absorption profile and its effect on the laser emission spectrum at 2 µs integration time

2. LWIR External Cavity: A key enabler for the proposed technology is an external cavity QCL. Fig. 2 (left) presents a schematic of a stable confocal cavity consisting of two 90° off axis gold coated parabolic mirrors and two flat mirrors. The QCL was placed at the common focal point of the two parabolic mirrors. A He-Ne laser was used to align the whole system before inserting the QCL. A small hole in the middle of the first flat mirror outcoupled laser emission from the cavity into a Fourier spectrometer. A photograph of the experimental set up is shown in Fig. 2 (right). Fig. 3 (left) presents the multimode laser emission of our LWIR QCL measured with the Fourier spectrometer. The emission spans 60 cm^{-1} with mode separation of ~1 cm^{-1} defined by optical length of the QCL crystal. Fig. 3 (right) presents a high-resolution spectrum of the external cavity QCL, where external cavity modes of spacing ~0.05 cm^{-1} appear. For ICLAS, the entire laser band width must be filled with these modes. This goal is impeded by the mode structure of the active crystal, demonstrating the need for anti-reflection (AR) coated QCL.

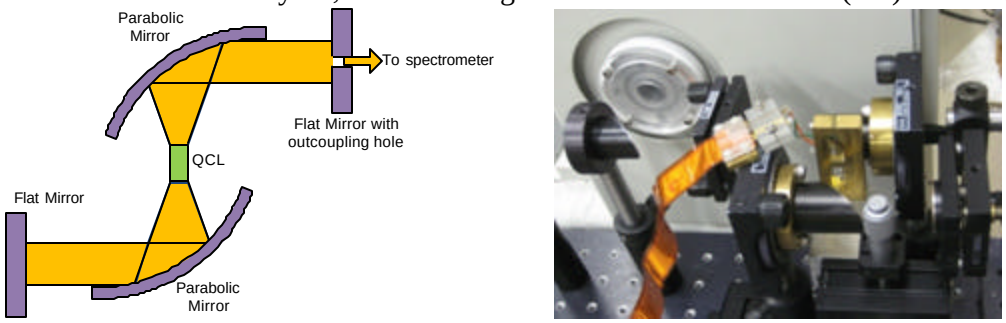

Figure 2. (Left) Schematic of confocal external cavity. (Right) Photograph of external cavity QCL. The QCL is housed in the rectangular brass holder. (One parabolic mirror and flat mirror are obscured by the laser mount and cable, respectively. A third parabola directs the emission into the spectrometer through a NaCl window.

3. Fabry-Perot Spectrometer: The second enabler is a real-time compact high resolution spectrometer. We have developed a scanning Fabry-Perot Spectrometer with a pair of mirrors formed from wedged (30-arcmin) ZnSe flats of 2 mm thickness, with high reflection coatings (97.5%) on the facing surfaces, and AR coatings on the other surfaces. Fig. 4 presents a photograph of the Fabry-Perot interferometer. One of the mirrors was fixed, while the other was placed in a mount with high-precision 3-axis alignment and piezo drivers. The piezo was controlled by a three-channel piezo driver. The 9.35 µm LWIR QCL (Alpes) was installed in the focus of the 90-degree off-axis parabolic mirror, which provided a collimated beam for the FP spectrometer. The signal transmitted by the FP was detected by a liquid nitrogen cooled MCT detector and was synchronously amplified. A linear ramp voltage of 0-10V at a rep rate of ~10 Hz controlled the piezo driver for the FP.

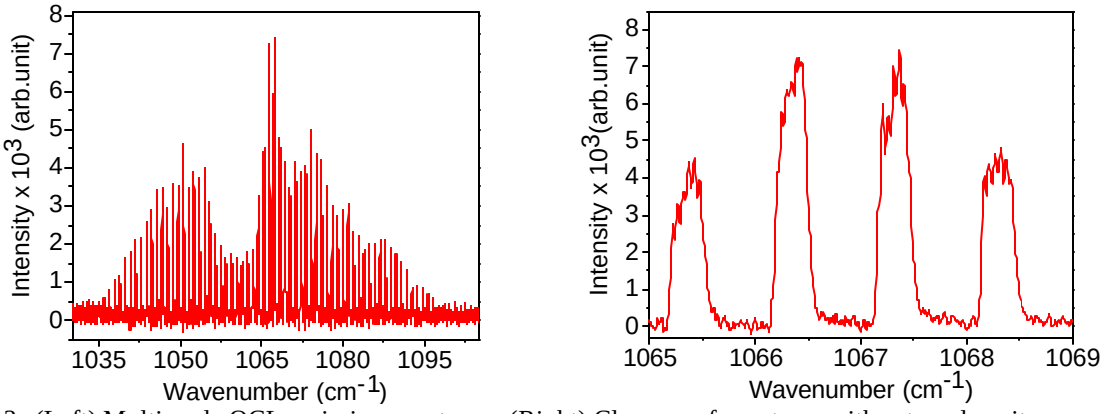

Figure 3. (Left) Multimode QCL emission spectrum. (Right) Close up of spectrum with external cavity.

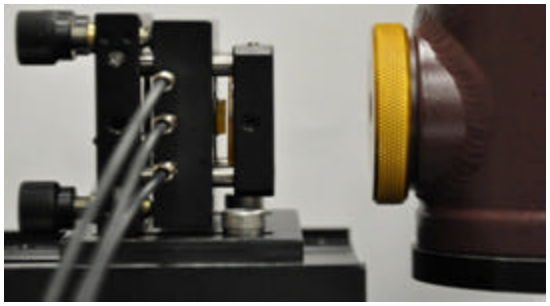

Figure 4. Picture of QCL and Fabry-Perot spectrometer. The MCT detector appears to the right.

The signal transmitted by the FP vs mirror displacement is presented in Fig. 5 (left) when the laser was operated under narrow band conditions. The spectrum corresponds to the 78th order of resonance. The spectrum was compared with the one obtained using a Fourier spectrometer at a resolution of 0.017 cm^{-1} showing good agreement. A similar experiment was done with the same laser operated under broadband conditions, which is necessary for ICLAS. The best compromise between free-spectral range and resolution was found at 25th resonance order (Fig. 5, right), when the different resonance orders just start to overlap, while individual modes are still resolved. This spectrum compares well with the high-resolution spectrum obtained with the Fourier spectrometer (Fig. 3). We estimate that here the achieved resolution is better than 0.5 cm^{-1}, which suffices for the expected pressure broadened vapor line widths of at least 0.2 cm^{-1}.

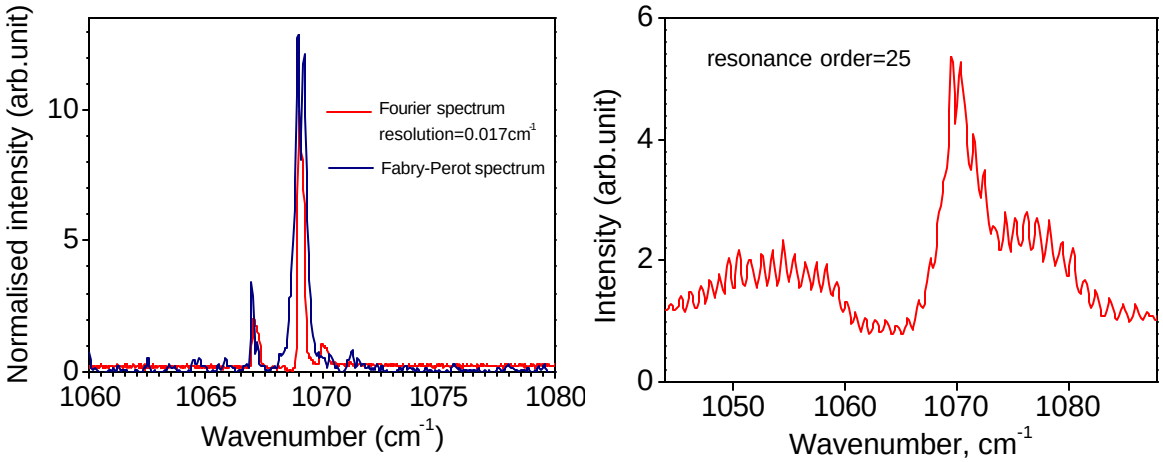

Figure 5. (left) Comparison of narrow-band QCL spectrum measured on Fabry-Perot and Fourier spectrometers. (Right) Fabry-Perot spectrum of broad-band QCL spectrum in 25th resonance order.

4. Vapor spectrum of TNT: The infrared spectrum of TNT vapor was measured using a Fourier spectrometer. Since TNT saturated pressure is only ~10^{-5} Torr at room temperature, vapors of TNT were generated by heating the sample inside a stainless steel cell, which was first purged for 10 minutes to reduce the water vapor before solid TNT powder was placed inside. The tube was heated with heating tape inside a copper shield. Temperature was monitored with a sensor directly connected to the surface of the tube. The ends of the tube were closed, but not sealed, with two 300-micron-thick, double-side-polished, high-resistivity, FZ silicon wafers. The windows were made to be the hottest part of the cell to prevent condensation of TNT on them. TNT spectra at different cell temperatures are presented in Fig. 6. Significant TNT absorption was observed in the 1000-3500 cm^{-1} spectral range when the temperature was raised above 140°C due to increased vapor pressure of TNT. The TNT spectrum is dominated by the symmetric and antisymmetric -NO_2 stretches at 1349 (7.41 μm) and 1559 (6.41 μm) cm^{-1} respectively[2]. The absorption lines grow rapidly with rising temperature. The measured linewidths were ~ 30 cm^{-1}, suggesting that for TNT a high resolution as 0.2 cm^{-1} for our ICLAS system is unnecessary. Room temperature linewidths will be lower, since all broadening mechanism increase with temperature. The main observation is that the QCL bandwidth needs to be at least 30 cm^{-1}.

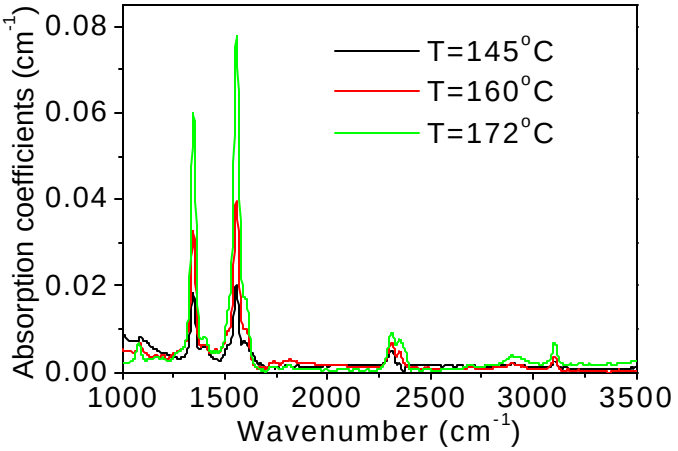

Figure 6: Measured absorbance spectra of TNT vapor in the 1000-3500 cm^{-1} wavenumber ranges.

CONCLUSIONS: The key enabling technology for a THz-LWIR ICLAS system is the multi-mode quantum cascade laser with external cavity that allows infusion of target vapors. Equally important is the Fabry-Perot spectrometer to measure the multi-mode emission spectrum at high resolution in real time. An external cavity QCL and a real-time scanning Fabry-Perot spectrometer with sufficient resolution for our application were demonstrated here. Additionally, a hot-cell system for measuring vapors of low-pressure solids was demonstrated with the successful measurement of the TNT vapor spectrum.

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