Final report to Ångpanneföreningens Forskningsstiftelse for project (Ref. nr 10-180): *Construction for a compact laser detection system for in-situ toxic gas sensing in harsh environments*

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Abstract

The ability of remote sensing at molecular level of a reacting gas plume with non-intrusive optical techniques is of pivotal important in understanding the detail chemical processes and consequently improving the practical technologies crucial for energy utilization and environmental protection. The focus of this project has been the development and construction of a compact laser gas sensing system for in situ detection of toxic gases and some small hydrocarbon molecules in harsh environments of strong relevant to energy utilization and environmental protection.

The project has been performed through a close collaboration with a laser company, GWU-Lasertechnik. We work together in developing and spectroscopic characterizing a prototype infrared OPO system designed by GWU, namely versaScan-L 1064/200, partly by the visiting of Mr. Guido Göritz, a senior product specialist from GWU to our laboratory. The results indicated that this compact OPO system can be efficiently pumped by a laser system available in our lab with relatively low pulse energy lasing at 1064 nm, which provides the possibility of building a compact system with sufficiently laser output at mid-infrared spectral range. A preliminary degenerated 4-wave mixing measurement has been performed. A single-shot based spectral characterization system was built in our lab, which provides for the first time the possibility to analysis the longitudinal mode structure of the mid-infrared laser pulse, based on which a collaborative efforts with GWU has been putting on injection seeding the infrared OPO with DFB diode lasr to narrow the linewidth of the compact infrared laser system.

Instroduction

As a common knowledge, the ability of remote detection of molecular compositions and concentrations, and temperature of a reacting gas plume with non-intrusive optical techniques is of pivotal important in understanding the detail chemical processes and consequently improving the practical technologies crucial for energy utilization and environmental protection. However, the detection of trace level molecular species of most small hydrocarbons, some toxic species like HF, HCl and HCN using the most prevail laser spectroscopic techniques encounter fundamental limitations due to the lack of proper electronic transitions to be probed in the UV/visible spectral range. Although good potential has been invented through probing molecular rovibrational transitions in the mid-infrared spectral range with nonlinear techniques like polarization spectroscopy [1,2] and degenerated 4-wave mixing (DFWM) [3], the complexity and bulky laser system commercially available in providing tuneable mid-infrared laser pulses with high peak power have prevented its practical applications. The focus of this project has been the development and construction of a compact laser detection system for in situ detection of toxic gases and some small hydrocarbon molecules in harsh environments of strong relevant to energy utilization and environmental protection.

The project has been performed through a close collaboration with a laser company, GWU-Lasertechnik from Germany, who has special expertise in OPO (optical parametric oscillator) laser design and manufacturing. We work together in developing and spectroscopic characterizing a prototype infrared OPO system designed by GWU namely, versaScan-L 1064/200, partly by the visiting of Mr. Guido Göritz, a senior product specialist in GWU, to our lab. The results indicated that this compact infrared OPO system can be efficiently pumped with relatively low-power laser available in our lab lasing at 1064 nm. This provides the possibility of building a compact system with sufficiently laser output at mid-infrared spectral range. A preliminary DFWM measurement has been performed. A single-shot based high resolution spectral characterization system was built in out lab, which provides for the first time the possibility to analysis the longitudinal mode structure of individual pulse of the mid-infrared laser, based on which a collaborative efforts with GWU has been putting on injecting seeding the infrared OPO with a DFB diode lasr to achieve single mode operation of the compact infrared laser system, with Fourier transform-limited linewidth.

Performance and achievements

IR OPO setup

The goal of the OPO system was to build a compact laser system that could deliver tunable single-longitudinal mode laser light in the mid-infrared around 3 μm. This type of laser could be used for *in situ* detection of trace molecules in combustion environments by DFWM and IRPS.

The OPO as shown in figure 1 consists of a resonator with 2 mirrors that can be tilted, a KTP crystal for frequency mixing and a telescope to change the beam diameter of the pump laser. The cavity length can be controlled with a piezo element (see the blue box in figure 1, which is the electronic controller of the piezo). The OPO is pumped by the fundamental frequency of a Nd:YAG laser (part of the YAG laser can be seen on the up-right corner of figure 1) at 1064 nm with approximately 290 mJ pulse energy. The frequency-mixing will produce a signal beam at around 1600 nm and an idler beam at around 3200 nm. The resonator mirrors are adjusted to reflect the signal beam. The single- longitudinal mode radiation will be achieved by seeding the OPO laser with a

DFB diode laser with 1603 nm. The seed laser will pass into the cavity through the rear mirror and will trace the signal beam path.

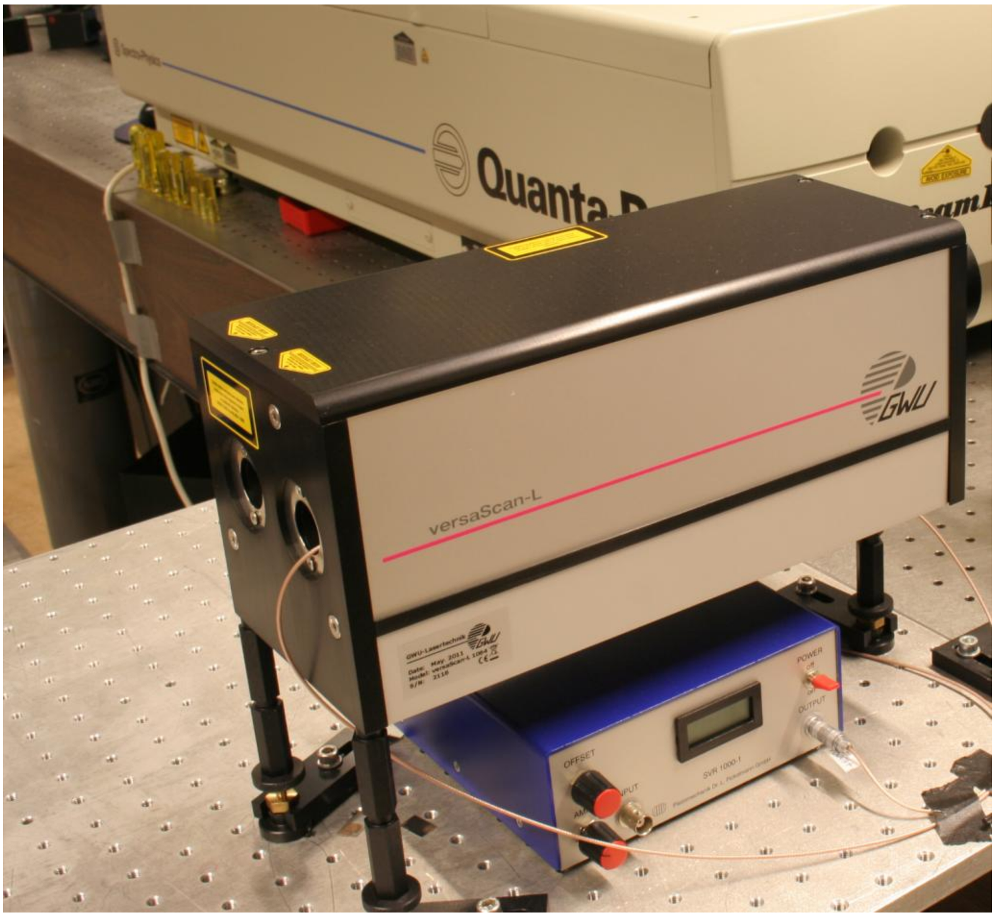

Figure 1. Photograph of the IR OPO with the rear mirror piezocystal controller, and the pumping Nd:YAG laser.

The OPO is aligned in a non-collinear geometry. The principle of the phase matching is shown to the right in the figure 2. This means that the signal and idler beams can be easily separated since they don't follow the same beam path.

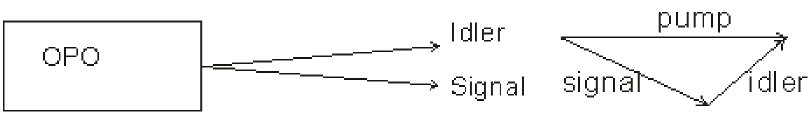

Figure 2. schematic of the OPO laser and its principle.

Multi-mode laser

Without the seed laser, the OPO is a multi-mode laser with a bandwidth of about 5 cm^{-1}. The mode structure of the idler beam was studied by dispersing the beam on a grating with 600 g/mm and focusing the dispersed light on a nitrogen-cooled CCD-camera. The single-shot images recorded (see figures 3) show that the beam has large mode fluctuations from shot-to-shot.

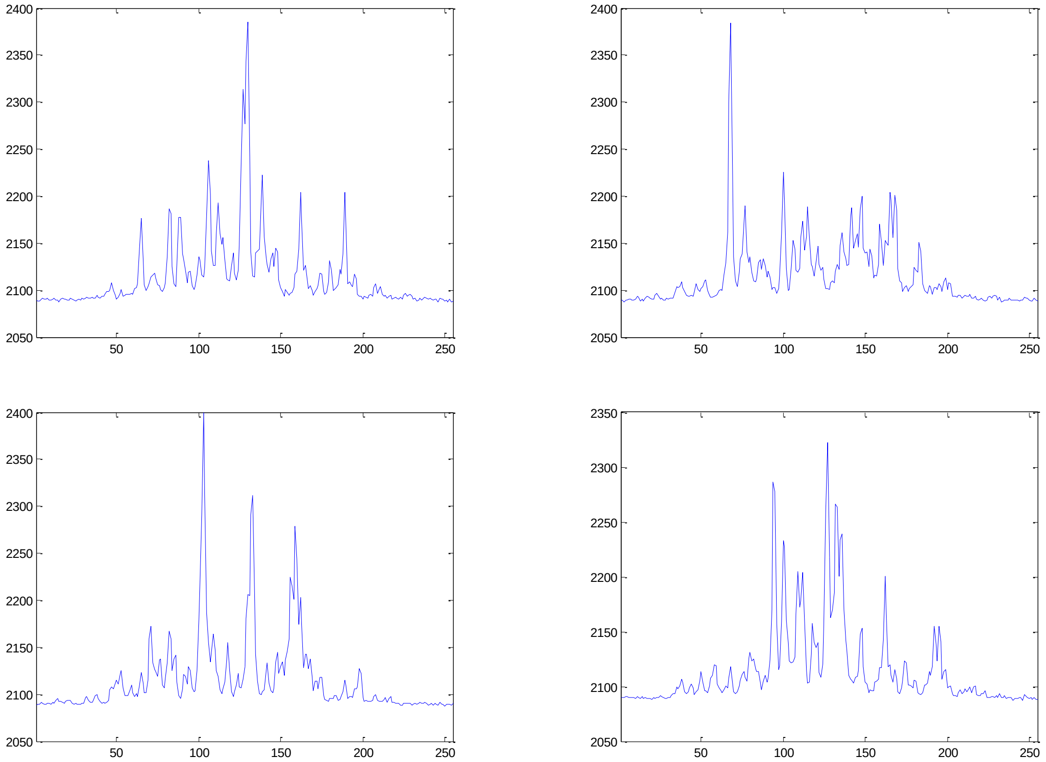

Figure 3. spectrally dispersed mode structure of single-shot laser pulses.

An average of 500 shots shows a regular mode structure that can be repeated. The larger periodicity in the left figure 4w is also repeated. When multi-mode pump light is used, the mode structure disappears and only the larger periodicity remains, see the right figure 4.

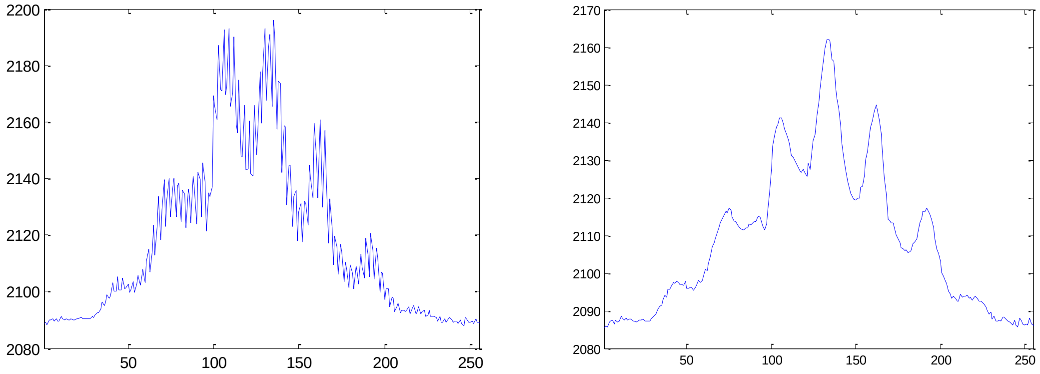

Figure 4. spectrally dispersed mode structure of an avarage of 500 pulses.

To test the possibility of broadband DFWM for single-shot measurements with the idler beam, the absorption spectrum of C_2H_2 has been taken up with this laser in a gas flow. The results were performed with a multi-mode pump since this gives a smoother line-shape in averaged spectra. The measurement is an average over 500 shots and in these measurements the stronger absorption lines of C_2H_2 are clearly visible. The recorded spectrum is shown in figure 5.

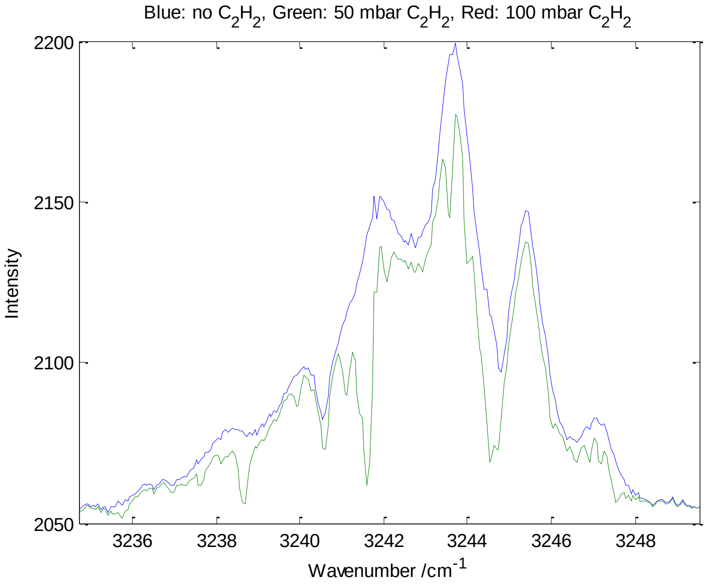

Figure 5. Recorded absorption spectra using the IR OPO pumped with the multi-mode Nd:YAG.

Broadband DFWM preliminary results

We applied this broadband IR OPO as the mid-infrared laser source to test degenerated four-wave mixing (DFWM) spectroscopy of acetylene (C2H2) molecules. The detail description of our DFWM setup can be found in [3]. Briefly, using this novel setup the laser beam was split into four parallel locating on the four corners of a rectangle, and three of these four beams were focused into detection volume to generate DFWM signal. In the measurements, the center wavelength of OPO was tuned to 3265 cm^{-1}, and the laser radiation covered P_{7e} and P_{13e} ro-vibrational lines of C_2H_2 as well as its other relative weak absorption lines. The OPO output energy was about 4.5 mJ/pulse. The testing gas flow was 0.76% C_2H_2 mixed in nitrogen.

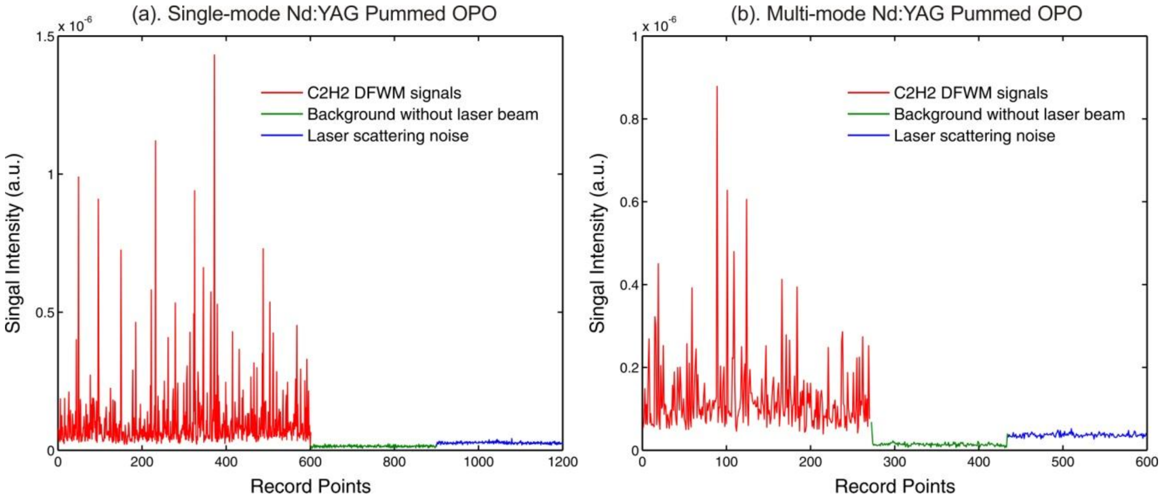

Figure 6. Signals of DFWM of C_2H_2 measured with the IR-OPO pumped by Nd:YAG fundamental output operating in single-mode (a) and multi-mode (b), respectively.

The preliminary results are shown in Fig. 6. Since a point-detector, liquid N_2 cooled InSb, was used to collect the signal, there are no spectral information in the spectra. Two tests were performed: IR-OPO pumped (a) by single-mode Nd:YAG and (b) by multi-mode Nd:YAG. In both cases, DFWM signals from C_2H_2 were distinctly appeared as shown in Fig. 6. The DFWM signal was a little bit stronger in Fig. 6(a) than that in Fig. 6(b). This might be due to the mode-smooth effect when the OPO laser was powered by the multi-mode pump source. In addition, the DFWM signal had strong fluctuation because of the mode-jump of OPO output. Unstable mode output always results in strong fluctuation of signal intensity, especially in nonlinear spectroscopy. In Fig. 6 comparing the DFWM signal intensity (in red) and the background noise (in blue), it can be concluded that using this OPO laser we can obtain DFWM signal for C_2H_2 (<1%) with a high signal-to-noise ratio.

Seeding of the OPO

The principle of the seeding setup is shown in figure 7. The light from a DFB diode laser is coupled into an optical fiber, collimated and sent into the OPO in a path that overlaps the back reflection of the signal beam transmitted through the rear mirror of the cavity.

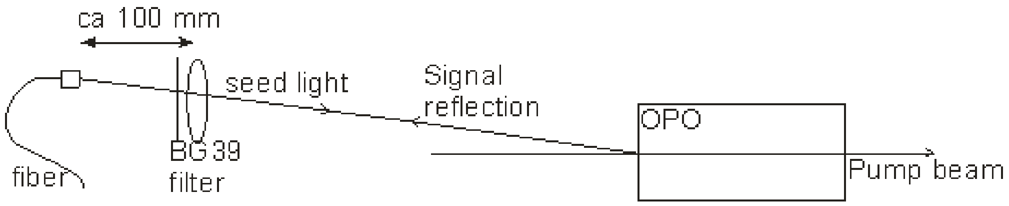

Figure 7. schemetic setup of injecting seeding to the IR OPO.

To simplify the alignment a HeNe-beam, as shown in figure 8, was overlapped with the signal beam in front of the OPO and sent through the OPO. It was checked that the HeNe-beam had not changed direction through the OPO, but was still overlapped with the signal back reflection. Overlapping the seed laser with the HeNe-laser should give a good overlap between the signal and seed.

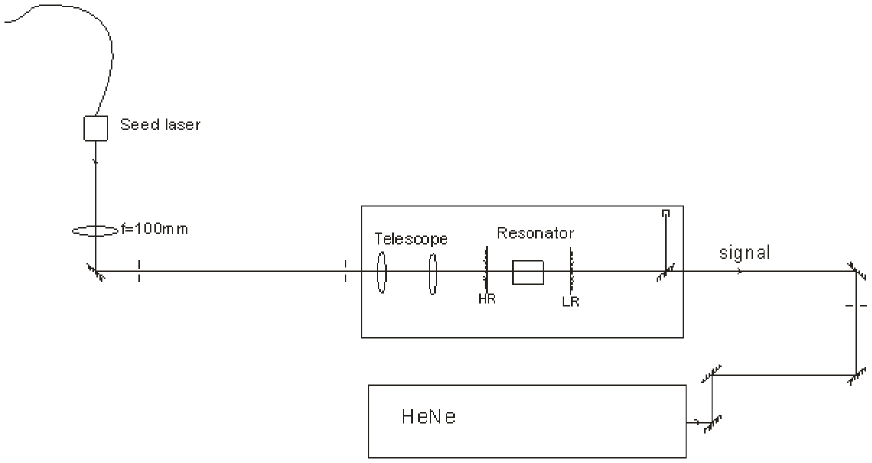

Figure 8. schemetic setup of the HeNe laser alignments.

To achieve a proper seeding, the wavelength of the seeder laser should match the wavelength of one of the modes in the cavity. When the seeding works, one mode in the cavity will become much stronger than the others and the adjacent modes will be suppressed. This has been attempted with the help from Mr. Göritz from GWU. Unfortunately, no seeding has been achieved up to this moment. Further effort includes:

- Improving the seeder laser power

- Change the rear mirror reflectivity to enable more coupling of the seeder laser power to the cavity
- Optimize the alignment of the system

Use of the grant

The grant from ÅF up to 220 kSEK was used mostly for paying the prototype IR OPO laser, versaScan-L 1064/200, from GWU, to bring it in-house to our lab. It costs 22.953EUR. Some travel cost for Mr. Göritz was also covered by the grant.

Future plans

More efforts will be put in achieving single mode operation of the IR OPO laser. Multiplex DFWM for multi-species gas sensing and temperature measurement with the un-seeded IR OPO will also be performed.

Acknowledgments

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References

[1] Z.S. Li, Changhong Hu, J. Zetterberg, M. Linvin and M. Aldén, '*Mid-Infrared Polarization Spectroscopy of OH and Hot Water in Low Pressure Lean Premixed Flames'*, **J. Chem. Phys.127**, 084310 (2007).

[2] Z. W. Sun, M. Försth, Z. S. Li, B. Li and M. Aldén, 'Mid-infrared polarization spectroscopy: A tool for in situ measurements of 3 toxic gases in smoke-laden environments', **Fire and Materials 35**, 527-537(2011).

[3] Z.W. Sun, Z. S. Li, B. Li, M. Aldén and P. Ewart, '*Detection of* C_2H_2 *and HCl with mid-infrared degenerate four-wave mixing with stable beam alignment: towards practical in situ sensing of trace molecular species*', **Appl. Phys. B 98,** 593-600 (2010).