Feature Article 堀場雅夫賞受賞者論文

Masao Horiba Award

Ultra-sensitive in-situ molecular detection of reactive chemicals based on laser dispersion effects.
レーザー分散効果を応用した大気中の反応性化学種の高感度その場計測技術

Gerard Wysocki

An ideal solution for sensitive spectroscopic sensing would be an optical method that combines simplicity and robustness provided by conventional direct laser absorption spectroscopy with high-sensitivity and background-free nature of indirect spectroscopic sensing approaches (such as chemiluminescence or photoacoustic sensing), while avoiding common problems with induction of intermediate physical processes (such as non-radiative quenching or slow V-T relaxation). Molecular dispersion sensing is a very promising approach to achieve these goals. This research work is focused on development of new dispersion sensing techniques, which provide background-free measurement capability that is also immune to laser power fluctuations, offers gas-free calibration based on first principles, and enables high dynamic range concentration measurements. Examples of dispersion spectroscopy techniques currently under studies will be given here.

理想的な高感度分光検出法として，従来の直接的レーザ吸収分光法の簡便さ・堅牢さに，化学発光や光音響分光法のような間接的分光検出の利点である，高感度でバックグラウンドの影響を受けない点を兼ね備えた分光法が考えられる。ただし，直接・間接両分光法に共通する，無輻射失活や，振動-並進緩和といった検出過程に起こる物理現象の回避が課題となる。分子の異常分散検出が，これらの物理現象を回避し理想的な分光検出法を実現する有望な手法と考えられる。私の研究は，バックグラウンドの影響やレーザ強度のゆらぎのない，新たな分散検出手法開発に焦点を当てたもので，第一原理に基づく標準ガス不要の校正と，広いダイナミックレンジの濃度測定を可能とする技術の開発です。分散分光技術を使った測定例も紹介する。

Introduction

Since the invention of the laser in 1950's[1] and its first demonstration in 1960[2] the laser spectroscopy of atomic and molecular species has become one of the major tools for studying physical, quantum and chemical properties of the matter. This includes investigation and quantification of molecular/atomic systems by absorption[3] and/or fluorescence[4] measurements, studies of ultra-fast processes with pico- and femto-second laser sources[5], or exploration of new laser matter interactions using non-linear optical processes with high-intensity lasers. Majority of these studies require large laboratory configurations and highly specialized personnel. Due to relatively low complexity of the optical set-up and well understood physics of the absorption process, laser absorption spectroscopy (LAS) has been adopted and is extensively used to high-sensitivity and high-specificity chemical sensing outside the laboratory[3]-[7]. Dynamic expansion of LAS techniques in field applications has been observed after an advent of compact laser sources (especially electrically pumped semiconductor lasers)[7]. This trend continues and although no major breakthroughs have been made in the fundamental LAS, incremental improvements in this technology result in over 100 publications per year since 1990's.

Direct LAS offers excellent sensing capabilities that include detection limits down to pptv (parts-per-trillion

by volume) levels[8], fast in-situ non-destructive sensing[9]-[11] and remote detection capability[12]. However there is several fundamental limitations, which degrade the performance of sensor systems based on this technology. By nature of the absorption process governed by Beer-Lamberts Law, the useful signal is determined from transmission through the sample of interest. This involves measurements of small changes in total laser intensity arriving at the detector, which basically requires quantification of small signal on the top of a large (often fluctuating) background. Laser amplitude noise and other intensity fluctuations (e.g. interference effects) are therefore the main source of measurement error.

Significant suppression of such effects can be achieved with indirect methods that offer background-free molecular/atomic signal generation. Those methods are taking advantage of secondary processes induced by the laser radiation. One popular method that uses laser excitation followed by non optical detection is photoacoustics[13]-[15], which measures acoustic wave produced by laser radiation modulated at audio frequencies and absorbed by the sample. Another entirely optical indirect method is laser induced fluorescence (LIF) that measures spontaneous emission from molecules excited with the laser light[4]. Although proved to be extremely sensitive the indirect methods often suffer from limitations associated with the physics of the secondary processes used for sensing. For the two examples given above the most pronounced drawbacks would be: 1) limited efficiency of the energy thermalization in photoacoustics e.g. through the V-T (vibration-translation) relaxation process and 2) a nonradiative quenching mechanism affecting the LIF signal. Such intermediate processes can be additionally affected by the measurement conditions such as pressure, temperature or even presence of other molecules in the sample.

Molecular Dispersion Sensing

An interesting alternative to absorption measurements is the detection of refractive index changes inherent to molecular absorption, which lead to anomalous dispersion in the vicinity of the target transition. The measurement of the molecular dispersion, although very challenging, can provide significant advantages over the absorption sensing. It provides an ideal solution for sensitive spectroscopic sensing, because it actually is an optical method that combines advantages of simplicity and robustness provided by direct LAS with high-sensitivity of background-free indirect spectroscopic sensing, while avoiding common problems with induction of intermediate physical processes. The most prominent capabilities of molecular dispersion sensing include:

a) Zero-baseline detection: One of the most important features is the background-free nature of molecular dispersion. This allows for exploration of true baseline-free measurement techniques that will have advantage of being strongly immune to fluctuations of the laser power incident on the detector. This makes it very attractive to remote sensing applications or in-situ sensing of turbulent media with high content of particulate matter (furnaces or smoke stacks).

b) Gas-free calibration: The anomalous dispersion can be easily calculated using absorption coefficient data and Kronig-Kramer's transformation. Similarly to LAS system calibration by using line-by-line absorption calculation based on Beer-Lambert's Law the calculation of the dispersion spectrum can be easily applied to perform sensor calibration based on theoretical models and avoid equipment-, cost-, and labor-intensive calibrations based on certified gas mixtures. This is particularly attractive for long-term field deployments and for applications in large area distributed trace-gas sensor networks, in which the autonomous, consumable-free operation is critical.

c) High dynamic range in concentration measurements: Another fundamental advantage of dispersion measurements over absorption sensing is high dynamic range of this purely optical measurement. Unlike the absorption process, which becomes strongly non-linear above ~10% absorption due to the exponential character (Beer-Lamberts Law), the dispersion can be measured with high accuracy even when absorption is high. With the optical heterodyne interferometric methods studied in this work, the sample dispersion will be measurable as long as the power arriving at the detector is above the detection limit. It is also anticipated to obtain shot noise limited performance in the mid-IR with the proposed new coherent detection schemes, which will represent a significant advancement with respect to measurement techniques used conventionally in LAS.

d) Potential for etalon fringe suppression: Finally the dispersion information does not have to be used alone, but it might be used in combination with the absorption measurement to further enhance the chemical sensing capabilities. By using both the dispersion and the absorption information simultaneously it will be possible to identify molecular spectral features and distinguish them from etalon fringes present in the system.

While dispersion line shapes have often been used for laser stabilization[16], spectroscopic molecular sensing

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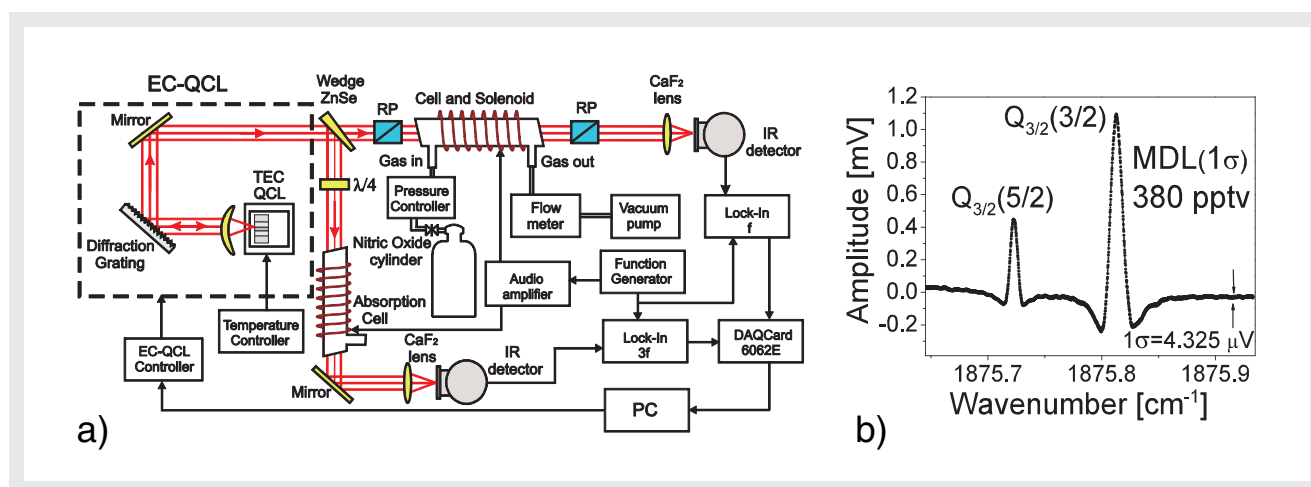
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Figure 1 a) Schematic diagram of an EC-QCL based FRS experimental setup. RP - Rochon polarizer, $\lambda/4$ - quarter wave plate, PC - personal computer; b) Faraday rotation spectrum of $Q_{3/2}(3/2)$ and $Q_{3/2}(5/2)$ transitions of NO centered at 1875.8 cm^{-1} measured for 96 ppbv in N_2 mixture at 40 Torr with a liquid nitrogen cooled InSb photodetector [18].

applications have not been realized frequently. Several special cases of dispersion spectroscopy exist which clearly demonstrate its tremendous potential to chemical sensing. One of the special cases is the Faraday Rotation Spectroscopy (FRS)[17]-[18] that can be applied only to paramagnetic species and by taking advantage of magnetic circular birefringence (MCB) of the sample inserted in magnetic field ultra-sensitive concentration measurements can be performed.

a. Faraday Rotation Spectroscopy

We have previously conducted studies on the development of a transportable, autonomous, cryogen-free FRS system targeting nitric oxide (NO). This work has demonstrated the best performance obtained to-date with FRS NO sensing systems with sensitivities of 380 ppt for 1 sec lock-in time constant and only a ~44 cm long active optical path[17]-[18] .The schematics of the optical setup as well as an example spectral measurement of NO transitions at 1875.8 cm^{-1} is shown in Fig 1 a and b respectively.

The system was configured as an extractive sensor that requires no sample preparation, but still needed the air sample to be introduced into the system. Such an approach would not be effective in monitoring of molecules such as OH-radicals, which are one of the most important atmospheric oxidants and are known to "cleanse" the atmosphere by starting the photochemical oxidation process for a large majority of atmospheric pollutants (especially those related to energy production

and use, like hydrocarbons and other volatile organic compounds - VOCs). OH-radicals are extremely reactive and the loss of the species due to sampling procedure would strongly affect the quality of the measurement. Despite the importance of OH radicals in atmospheric chemistry, measurements of this species are incredibly challenging due to its extremely low concentration typically below 10^7 cm^{-3} (below ~10 parts per trillion by volume, pptv; and down to less than 10^4 cm^{-3}, or ~0.01 pptv during nighttime[19]), short atmospheric lifetime (< 1 s), and high reactivity[20].

Therefore we are currently developing a new approach to ultra-sensitive detection of paramagnetic species using new FRS technique enhanced by an optical heterodyne detection. This concept is directed towards development of an open path FRS system for in-situ monitoring without a need of extractive gas sampling. The optical laser heterodyne detection is used to shift the detection to radio-frequencies (RF) >30MHz where the laser excess noise is significantly lower and will allow for FRS measurements close to theoretical shot noise limit (which is several orders of magnitude lower than thermal noise of the detector). Additionally to perform FRS measurements at atmospheric pressures high magnetic fields are required to provide sufficient Zeeman splitting of the target transitions. In this case one can take an advantage of strong permanent magnets (e.g. based on rare earth elements such as Neodymium) and instead of modulated approach that require powerful electromagnets a static magnetic circular birefringence of the gas sample can be probed. This will provide a preferable solution for field deployable sensor systems. This idea has been initially

studied using diode lasers operating at 760nm and targeting molecular oxygen absorption bands[21]. An example spectrum of oxygen at atmospheric conditions (no extractive sampling) collected using DC magnetic field is shown in **Fig 2**. The sensor uses our custom ultra-low power spectroscopic sensor control electronics[22], a compact 3.5 meters Herriott multipass cell and electromagnetic coil for static magnetic field generation. In the next implementation permanent magnets will be used in place of electromagnetic coil to reduce the total power consumption. If the power dissipated in the electromagnet is excluded (~20W) a working laser system is dissipating only ~0.3W and provides a minimum oxygen detection limit of 37ppm in the atmospheric air.
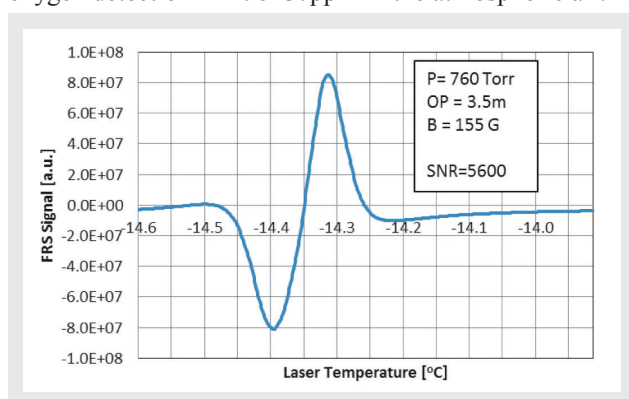

Figure 2 A static field FRS spectrum of O_2 recorded as a function of VCSEL laser temperature at atmospheric conditions. Based on the signal-to-noise ratio a (1σ) minimum detection limit to molecular oxygen is 37ppm (P - pressure, OP- optical path, B - magnetic field, SNR - signal-to-noise ratio).

b. Chirped laser molecular dispersion spectroscopy (CLaDS)

It is clear that the FRS approach works only for paramagnetic molecules and similar method based on molecular dispersion capable of concentration measurements of dia-magnetic molecules would be an extremely valuable approach to chemical detection. In collaboration with Dr. Damien Weidmann from Rutherford National Laboratories in the UK we have developed a sensing technique based on two-color dynamic interferometric heterodyne detection[23]. This chirped laser molecular dispersion spectroscopy (CLaDS) method similarly to FRS utilizes two frequency shifted dispersion curves, but instead of single frequency laser and Zeeman split dispersion envelopes (as in the FRS), a two-color laser beam probes a single dispersion line. The dispersion signal demodulation is done in the frequency domain using coherent optical heterodyne scheme, which gives the measurement high immunity to laser power fluctuations (by analogy FM radio signal shows similar noise immunity when compared to AM transmission). The method does not require any particular molecular properties (e.g. magnetic dipole moment) and will be applicable to a wide range of molecular species.

CLaDS provides several other advantages valuable to sensitive trace-gas sensing. For example when detecting high concentration samples (yielding $\geq$ 10% absorption), the Beer-Lambert law becomes highly non-linear and small changes in concentration can no longer be measured. This fundamentally limits the achievable accuracy for high sample concentration using conventional absorption methods. The measurement of dispersion is a completely linear process and allows for large dynamic range of concentration measurements. This capability is presented in in **Fig. 3(a)** depicting measurements of nitric oxide mixed with nitrogen using both absorption as well as dispersion spectroscopy technique. The amplitude of dispersion signal is confirmed to be proportional to the sample NO concentration. Another capability is related to
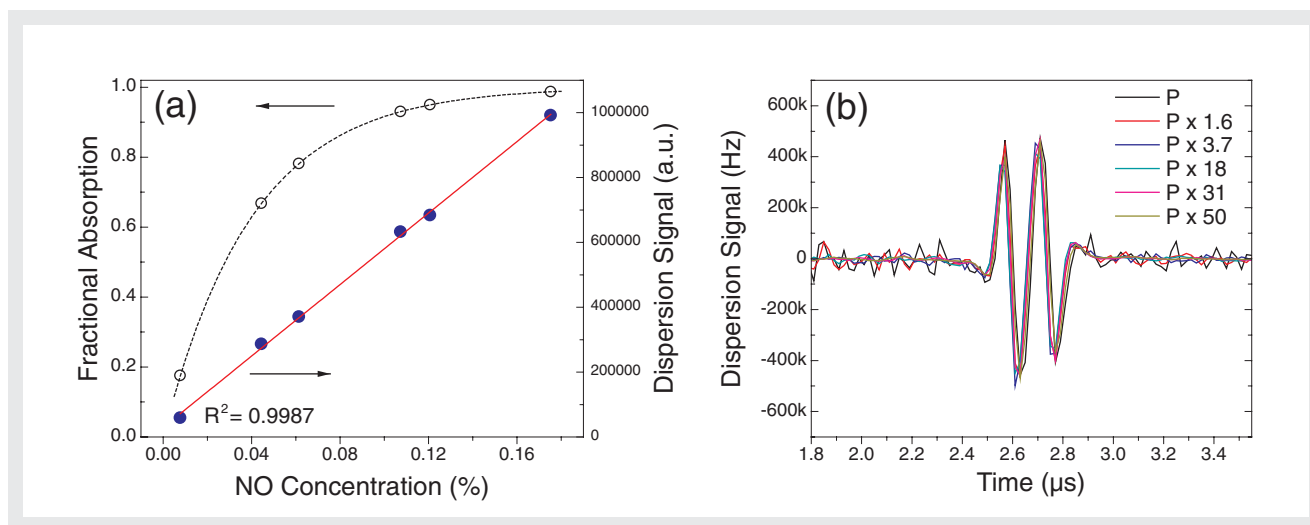

Figure 3 (a) Comparison of direct absorption (left axis) and dispersion signals (right axis) for a range of NO concentrations.
(b) Single shot dispersion signals for various power levels incident on the detector (1% NO at 5 Torr, 15 cm path length).
(P is arbitrary detected power level increased up to 50 times)[23]

immunity of CLaDS spectra to detected intensity fluctuations as mentioned above. Fig. 3(b) shows the dispersion signal for various incident powers on the detector. Power variations have small effect on the dispersion spectrum as long as the detected power at the detector has sufficient carrier-to-noise ratio. Decrease in the CLaDS signal-to-noise ratio is visible only for the two lowest laser power levels.

Presently we conduct research towards implementation of CLaDS to remote sensing of atmospheric pollutants. This system will not require sampling or sample preparation and will allow for truly versatile spectroscopic sensing method that can be implemented for remote detection of majority of chemicals with well resolved mid-infrared spectral features. CLaDS allows application of pulsed quantum cascade laser sources which provide high peak-powers and large chirp rates, which enhance CLaDS signal. High intensity lasers combined with high immunity to intensity fluctuations shown by CLaDS (e.g. due to particulate matter or atmospheric turbulence) make the new technology ideally suited for remote chemical sensing. A complete studies and series of experiments demonstrating the system performance with hard target stand-off detection using variety of scattering surfaces and retro-reflectors will be carried out in the next years.

Summary

In a long term within approximately a 5-year time-frame the molecular dispersion sensing technology that is currently in the stage of laboratory research and development is expected to lead to first field deployments of the prototype sensing instrumentation. Systems based on mid-infrared spectroscopy of anomalous molecular dispersion (both CLaDS as well as heterodyne FRS) are expected to be used in actual application testbeds outside the laboratory. The next challenging research steps of the FRS and CLaDS techniques investigations will be focused on scaling down the laser based sensing platform that includes integration of devices at the chip-level. This will require exploratory research of molecular dispersion sensing using the Goos-Hänchen effect and evanescent field interactions in planar and photonic crystal waveguides. Such integrated sensors are expected to provide unique and high impact technology for broad spectrum of chemical sensing applications.

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