Novel laser-based techniques for monitoring of volcanoes

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Abstract
An overview of novel laser techniques suitable for volcanic monitoring, based on different kinds of infrared laser sources, is presented. Their main advantages and drawbacks are discussed focusing on the achievable sensitivity and precision levels in analysis of gaseous species. Some of the most recent experimental results obtained in laboratory development as well as in field tests of home-built laser spectrometers are reported. New perspectives in optical devices aimed at geochemical and geophysical applications are also considered.

Key words *diode laser – absorption spectroscopy – optical fiber*

1. Introduction

The analysis of volcanic gases is widely recognised as a powerful tool to validate geological models relevant to reliable predictions of volcanic events (Baubron *et al*., 1991; Notsu *et al*., 1993). Indeed, the chemical composition of certain gases, in volcanic effluxes, may provide direct information on deep magmatic processes and hydrothermal circulation (Chiodini *et al*., 2003). In particular, the absolute concentration and the isotopic content of some molecular species gives an indication of sources and sinks of volcanic gases, whereas its time variation may be a consequence of changes in the status of a volcano. These changes can be due to chemical reactions of magmatic gases with rocks or fluids occurring along their path to the surface.

With this in mind, the evolution of volcanic activity can be monitored using sensitive instrumentation for gas analysis (Chiodini *et al*., 2003). However, the compactness and ruggedness of field sensors are critical requirements for monitoring of volcanic areas, where the equipment is often exposed to high humidity, large temperature variations, and fumigation by corrosive gases. Furthermore, high precision and accuracy levels are necessary in order to retrieve significant information from experimental data. An ideal volcanic sensor would also allow for continuous, *in situ* gas concentration determination over long time periods, with unattended and remote operation.

So far, volcanic gases have been usually monitored by means of laboratory analysis methods, such as mass spectrometry and gas cromatography, which require *in situ* sampling, which is often impractical and hazardous. In addition, the time resolution of sampling-based methods may be not sufficient for some applications.

An alternative approach is given by optical techniques for remote-sensing, such as Differen-

tial Optical Absorption Spectrometers (DOAS), LIDAR (Svanberg, 2002) or open-path Fourier-Transform Infrared Spectrometers (FTIR) (Oppenheimer, 2002). The first two methods provided good results in field volcanic measurements, as in the case of Galle *et al.* (2003), and Weibring *et al.* (2002), although some of these apparatus are bulky and expensive, and often require a time-consuming post-acquisition data processing. More recently, new instruments, based on UV-correlation and DOAS techniques, have been developed in a more compact and user-friendly fashion (Porter *et al.*, 2002).

In the last few decades, the use of near-infrared room-temperature diode lasers for gas sensing has significantly increased (Werle, 1998). Compared to spectroscopic techniques that rely on incoherent sources as well as on lead-salt and solid-state lasers, semiconductor diode lasers offer the possibility to develop reliable and compact spectrometers, with reasonable costs. Also, they present several advantages in terms of tuneability, spectral selectivity and power consumption. The possible use of these devices in combination with optical fibers is particularly convenient for volcanic monitoring applications (Ginfrani *et al.*, 2000). Thanks to the great advances in semiconductor and optoelectronic technologies, most of these features have been recently transferred to the mid-infrared, with novel coherent radiation sources such as those based on difference-frequency generation and on quantum-cascade semiconductor structures (Tittel *et al.*, 2002). In this spectral region, several atmospherically relevant molecules, like H_2O, CO_2, CH_4 and SO_2, exhibit strong absorptions (Harvard Smithsonian Center for Astrophysics, 2003).

2. Near-IR spectroscopy using DFB diode lasers

Near-infrared diode laser sources, initially developed for telecom applications, are currently based on III-V semiconductor alloys. They operate in continuous mode, at room temperature, exhibiting single-mode emission in the 1-2 μm range, with linewidths in the order of 10 MHz and output power of several mW. A sup-

plementary DFB (distributed-feedback) structure also ensures very high spectral purity and mode-hop-free frequency tuning.

Diode-laser spectrometers rely on resonant absorption of coherent radiation by a gas sample, contained in an optical cell, whose transmission can be monitored by a pre-amplified room-temperature photodiode. According to Lambert-Beer Law, the transmitted power is related to the gas concentration N (in molecules/cm^3) and to the cell length L (in cm), via the equation

$$P(\nu) = P_0 \exp\left[-S(T)g(\nu - \nu_0)NL\right] \quad (2.1)$$

where P_0 is the incident power, $S(T)$ the transition linestrength (in cm/molecule), ν the laser frequency, ν_0 the line-centre frequency and $g(\nu-\nu_0)$ the normalized line shape function.

In the last decade, several experimental schemes, mostly based on modulation of laser frequency, such as Wavelength- (WMS) or Frequency-Modulation Spectroscopy (FMS), have been developed in an attempt to increase detection sensitivity. Using these techniques, the retrieval of quantitative information from the absorption spectrum of a gas sample can be achieved by comparison with that of a reference cell, containing a known mixture. In this case, the chemical composition and thermodynamic conditions of the reference cell must be exactly the same as those of the sample under investigation. Any such difference may induce a systematic error in the measurement process, thus affecting the achievable accuracy, in spite of the high sensitivity. This is of particular importance in the case of gases from volcanoes, where large temperature and pressure variations are possible. Different approaches, based on *a priori* calibration of WMS or FMS signals (Goldstain and Adler-Golden, 1993), exhibit limited precision levels and are difficult to implement, and are thus ill-suited to environmental applications.

Recently, we demonstrated that measurements of absolute gas concentrations with high precision can be efficiently performed using a very simple method, based on direct absorption, which does not require any frequency modulation technique or calibration cell (Gagliardi *et al.*, 2001). We employed an InGaAsP/InP DFB diode

laser, emitting at a wavelength of 2-μm and able to probe strong ro-vibrational lines of CO_2 and H_2O. A Herriott-type multiple-reflection cell, with a path-length of 50 m, was used as a gas cell. Absorption spectra were recorded for both species, and their concentration values were retrieved, through eq. (2.1), by measuring the integrated absorbances of the two absorption lines. This was possible after the product between the absorption pathlength and the linestrength had been measured using a certified gas mixture. Laboratory tests showed that a short-term reproducibility of 2‰ and an overall accuracy below 1% can be achieved in measurements in ambient CO_2, within a wide range of concentration values (Gagliardi *et al.*, 2002a). Simultaneous measurements of CO_2 and H_2O concentrations at similar precision levels were also demonstrated, a line pair of the two species being observed within one laser frequency scan.

One of the main advantages of such a near-IR laser spectrometer is its compatibility with telecom optical fibers, suitable for remote and *in situ* gas detection. Also, the principle of operation is completely independent of chemical composition and pressure of the gas sample. A portable version of the 2-μm spectrometer was

subsequently developed and tested to monitor gaseous emissions in volcanic areas, during a field campaign at Vulcano Island and Solfatara volcano, in Italy, during July and November, 2002 (Rocco *et al.*, 2004). The experimental set-up is schematically represented in fig. 1. The spectrometer is split into two parts, mounted on different breadboards, and connected by a telecom, single-mode, 30-m-long optical fiber. The laser source and collimating optics are mounted on one breadboard while the gas detection system on a another one, with a large hole in the centre which allows the gas to flow through the cell. In this way, remote measurements are possible at different sites across a volcanic area. In addition, a custom-built, open-path multiple-reflection cell, with a 20-m pathlength, was used for direct analysis of fumarolic effluxes without requiring any sampling procedure. Figure 2 shows an example of absorption spectrum. It corresponds to the $R(34)$ rotational line of the $\nu_1 + 2\nu_2 + \nu_3$ CO_2 combination band, and to the $15_{0.15} \rightarrow 14_{0.14}$ line of the $\nu_2 + \nu_3$ H_2O band, around 5000 cm^{-1}. The absorption signal was recorded at the Solfatara crater, directly on the flux of a small fumarole, scanning the laser frequency around a CO_2-H_2O line pair, while the
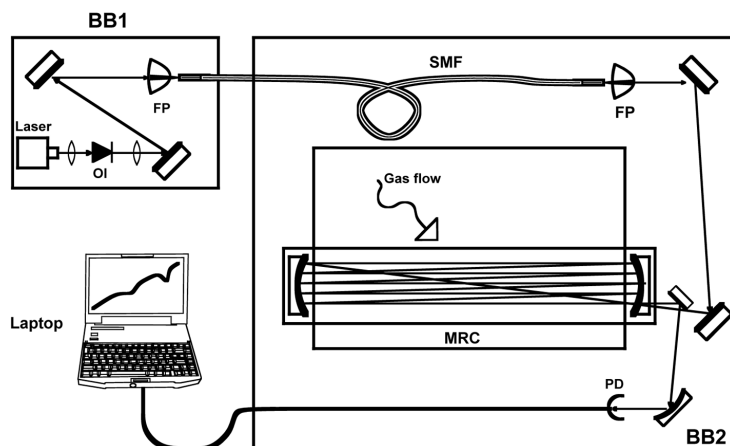
Fig. 1. Sketch of the experimental arrangement of the portable 2-μm spectrometer. OI – Optical Isolator; SMF – Single Mode Fiber; FP – Fiber Port; MRC – Multiple-Reflection Cell; PD – photodiode; BB1 – breadboard 1 (60×60 cm^2); BB2 – breadboard 2 (70×40 cm^2).
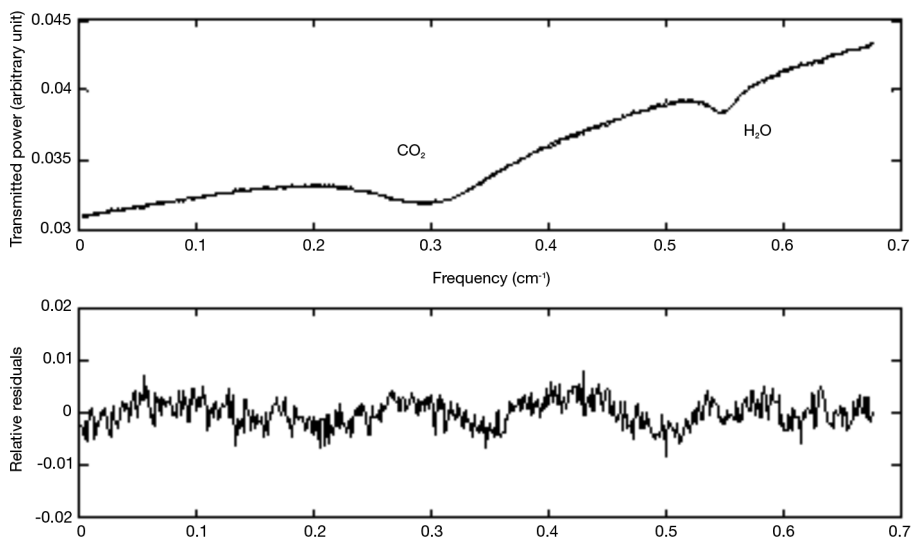
Fig. 2. Direct absorption measurement of CO_2 and H_2O performed for a small fumarole at the Solfatara volcano (Italy). The continuous line represents the Lorentian fit curve.

experimental spectra were continuously transferred to a laptop computer and analysed by a LABVIEW program. Furthermore, CO_2 and H_2O concentrations could be monitored in ambient air for several minutes, with a typical uncertainty of a few %, thus demonstrating real-time analytical capabilities of our spectrometer in hostile environmental conditions (Rocco *et al.*, 2004). Thanks to its low power consumption and ruggedness, the apparatus was transported almost everywhere in the selected volcanic sites. Indeed, substitution of optical or mechanical components was never necessary during operation in the whole campaign. The main drawback of our diode-laser based spectrometer is the influence of temperature fluctuations on measured concentration values. Due to the molecular linestrength dependence on Boltzmann distribution of population among energy levels, variations in the order of 3%/°C for water vapor, and less than 1‰/°C for carbon dioxide are expected. Nevertheless, the gas cell temperature was continuously monitored and acquired and, when necessary, its values were used to correct the corresponding small changes in the integrated absorbances.

## 3. Mid-IR spectroscopy with quantum-cascade lasers and difference-frequency based spectrometers

The advantages of direct absorption detection can be better exploited when one moves towards longer wavelengths. Indeed, most atmospheric molecules present stronger absorption bands, due to their fundamental vibrations, above 3 μm. That allows for sensitive detection of low abundance gases, like CH_4, SO_2 and N_2O, at their ambient concentration levels. For this reason, much effort has been directed towards the development of new coherent radiation sources emitting in the mid-IR spectral region. Among them are Quantum-Cascade Lasers (QCL), covering the interval from 3.5 to 24 μm, rare-earth-doped DFB fiber lasers, in the 1 μm to 1.5 μm range, and Optical Parametric Oscillators (OPO) or Difference-Frequency Generation (DFG) in periodically-poled crystals, between 2 and 5 μm.

Quantum cascade lasers were invented in 1994, at Lucent Technologies (Murray Hill, NJ) and are essentially based on a multiple miniband structure resulting from deposition of ultrathin alternating layers of semiconductor materi-

als. Electron transitions occur between different quantum well levels, in each mini-band, with many-photon emission (Faist *et al*., 1994). The major limitation of such lasers is the need for cryogenic cooling in order to have continuous-wave (cw) operation. Alternatively, they can be used at room-temperature in pulsed mode (Faist *et al*., 1998). Nevertheless, QCLs usually exhibit output power of 50-100 mW and intrinsic emission linewidth well below 1 MHz, with the possibility of a DFB design for high spectral purity and continuous wavelength tuning. Furthermore, cw operation of a quantum-cascade device, up to 246 K on a Peltier cooler, has recently been achieved (Hofstetter *et al*., 2001).

After the advent of quantum cascade lasers, several QCL-based spectrometers were successfully used, either in pulsed or continuous mode, for absorption spectroscopy as well as isotopic detection of species whose transitions are not accessible to conventional room-temperature diode lasers (Webster *et al*., 2001; Kosterev and Tittel, 2002). Our group recently developed a novel spectrometer relying on a cw DFB QCL at a wavelength of 8.06 μm, manufactured at Lucent Technologies Labs. In the experimental set-up, described in Gagliardi *et al*. (2002b), the laser was placed in a liquid-N_2 cryostat, and stabilised by an active temperature controller. The laser

beam was coupled to a 17-cm long absorption cell, filled with the gas sample, whose transmission was monitored by a liquid-N_2 cooled HgCdTe detector. The QCL spectrometer enabled us to detect the presence of very low CH_4 concentration. Indeed, several methane absorption spectra were recorded at sub-Torr pressures, in correspondence of the strong $P(10)$ $A2(1)$-$A1(1)$ line, belonging to the ν_4 fundamental band. Some of these spectra, with increasing absorbance, are shown in fig. 3, for different gas pressures in the cell. A wavelength-modulation spectroscopic technique, with phase-sensitive 1st-harmonic demodulation, was also implemented in order to detect CH_4 isotopomers. An example of simultaneous recording of $^{13}CH_4$ and $^{12}CH_4$, for natural isotopic abundance methane, is given in fig. 4. The spectra were observed within a single QCL frequency scan, amounting to 1 GHz. Furthermore, simultaneous detection of nitrous oxide and its isotopomers $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$ and $^{14}N^{14}N^{17}O$ was possible, in the same spectral region, with similar performances (Gagliardi *et al*., 2002b). An example is reported in fig. 5. In these operational conditions, a sensitivity level corresponding to a minimum detectable pressure of few mTorr was estimated, for pure methane and nitrous oxide, in a 1-m absorption pathlength. In addition, a signal repro-
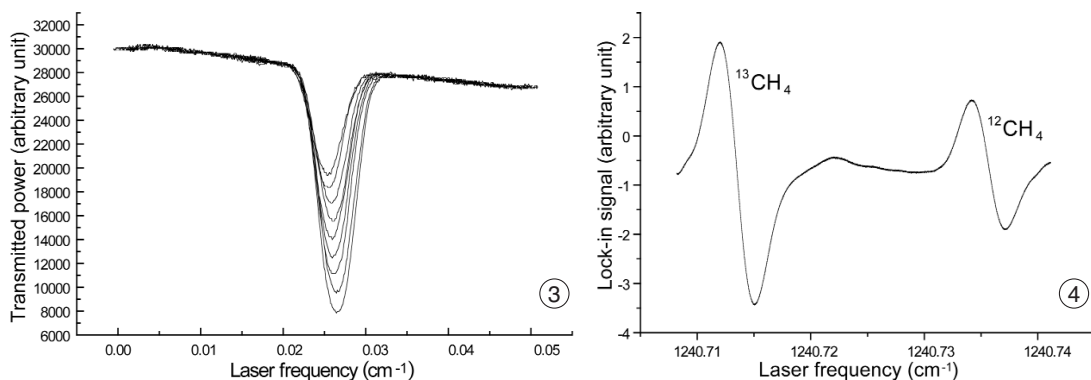
Fig. 3. Direct absorption spectrum of pure methane, around 1241 cm^{-1}. The gas pressure in the cell was varied from 100 to 400 mTorr.

Fig. 4. Simultaneous detection of $^{13}CH_4$ and $^{12}CH_4$, in natural isotopic abundance (1.1% and 98.9%, respectively), in the presence of 150 mTorr of pure methane.
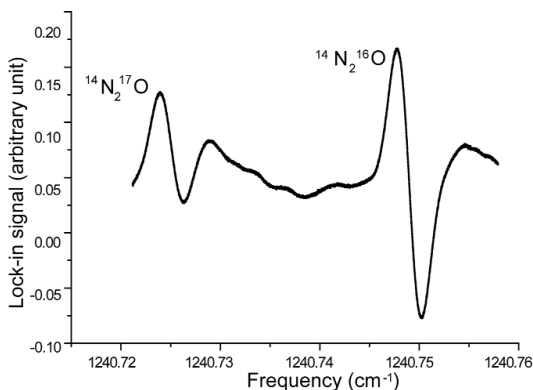
Fig. 5. First-harmonic absorption spectrum of $^{14}N^{14}N^{17}O$ and $^{14}N^{14}N^{16}O$ (0.37‰ and 99%, respectively). The N_2O pressure was equal to 80 mTorr.

ducibility better than 1 % was demonstrated in detection of all species. This feature is relevant to a possible use of the 8-μm spectrometer for measurements of the $^{13}C/^{12}C$ and $^{15}N^{14}N$, $^{18}O/^{16}O$, $^{17}O/^{16}O$ isotope ratios in CH_4 and N_2O, respectively.

Although the results obtained in our laboratory tests are encouraging, some drawbacks come from the use of a quantum cascade laser. For instance, the cryogenic system used for laser operation is bulky and expensive, while the high-current supply, usually needed for laser driving, makes its use somewhat difficult. As a consequence, considerable effort is still required in order to make this kind of spectrometer compact and well suited for field measurements.

A novel apparatus, based on difference-frequency generation in a periodically-poled lithium niobate crystal, is currently being developed in our lab. Mixing an Er-fiber-amplified diode laser, emitting at 1.55 μm, and an extended-cavity 1.05-μm diode laser, externally amplified by an Yb-fiber, we expect to produce coherent radiation around a wavelength of 3 μm, with powers up to 10 mW. Such a DFG spectrometer would satisfy some crucial requirements for spectroscopy, such as high spectral resolution, high power and wide tuneability. Indeed, its spectral coverage ranges from 2.9 to 3.5 μm. This is of great relevance if we consid-

er the current lack of laser sources in the region between 2.2 and 3.5 μm, where strong absorption bands of N_2O and CH_4 as well as of H_2O, NH_3 and NO_2 take place. It is worth noting that neither QCLs can presently cover this spectral window, due to manufacturing difficulties.

4. Conclusions and future perspectives

Several spectroscopic set-ups, based on different laser sources, have been reviewed. Some experimental results were presented on monitoring of CO_2 and H_2O emitted by volcanic fumaroles, using a compact and portable spectrometer operating at 2 μm. Using such a spectrometer, continuous, fast and *in situ* detection of these species was possible, measuring their concentrations with precision levels of a few %. For future developments, novel near-IR laser sources, such as Tm-doped fiber-based lasers, are also being considered as an alternative to diode lasers, especially in view of their possible integration in an optical fiber network for multiple-point, simultaneous monitoring of gas concentrations. Using the same fiber, the absorption spectrometer can also be combined with fiber Bragg-grating sensors for local measurements of strain and temperature (Rao, 1997). Such a network would be particularly relevant to the implementation of reliable methods for volcanic surveillance.

Alternative approaches for concentration measurements were also mentioned, such as Quantum-Cascade Laser (QCL) and Difference-Frequency-Generation (DFG) based spectrometers in the mid-IR. They exhibit significant advantages for analysis of gases whose natural abundance is extremely low. In particular, using a QCL at 8 μm, we demonstrated the potentiality of our spectrometer for detection of CH_4, N_2O and their isotopomers, with high sensitivity and resolution.

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