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► To cite this version:

P. Werle. Analytical applications of infrared semiconductor lasers in atmospheric trace gas monitoring. Journal de Physique IV Proceedings, 1994, 04 (C4), pp.C4-9-C4-12. 10.1051/jp4:1994402 . jpa-00252540

HAL Id: jpa-00252540

<https://hal.science/jpa-00252540>

Submitted on 1 Jan 1994

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Analytical applications of infrared semiconductor lasers in atmospheric trace gas monitoring

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Abstract

Sensitivity, specificity, high time resolution and cost effective simultaneous measurements of several components using operational systems are the main requirements for atmospheric research and air pollution monitoring. Tunable diode lasers absorption spectroscopy (TDLAS) is increasingly being used to measure atmospheric trace gas concentrations down to low ppb-levels (10^{-9} volume mixing ratio). This optical technique fulfills the requirements for trace gas analysis in the atmosphere for most of the smaller molecules with resolved absorption spectra. Semiconductor lead salt diode lasers give access to the mid infrared spectral region, where the most important atmospheric constituents have strong rotational vibrational absorption bands. The application of high frequency modulation (FM) schemes can further improve sensitivity and detection speed of modern instrumentation.

Introduction

Modern measurements of atmospheric trace gases impose high demands on analytic instrumentation. Fast, accurate, rugged and operational instruments are needed for fast airborne measurements and sensitive and reliable field measurements. Ultrasensitive instruments free of interference by other atmospheric constituents are required to measure free radicals and other reactive species in the atmosphere. The great number of gaseous pollutants and their generally low variable concentrations with large local differences pose challenging requirements to analytical techniques. Thus, sensitive, selective and mobile or even portable instruments with large dynamic range are needed. Modern research in atmospheric chemistry requires highly sensitive techniques for measurement of concentrations of free radicals which determine the rate of photochemical destruction of most atmospheric pollutants.

Since the development of lasers with high spectral brightness and tunability over broad wavelength ranges, spectroscopic schemes are of growing interest. They are mostly based on absorption measurements. Since the absorption spectrum is characteristic for each molecule, these methods often permit the simultaneous detection of many substances. The list of molecules of environmental concern essentially includes volatile organic compounds (HCHO, HCOOH) yet as nitric oxides (NO, NO₂, N₂O), ozone (O₃), ammonia (NH₃), sulfur dioxide (SO₂), carbon oxides (CO, CO₂), etc. It is obvious, that the mid infrared from 3 to 20 μm , the so-called "fingerprint region", is the preferable wavelength range. According to Beer's law conventional absorption spectroscopy requires long absorption pathlengths for achieving high sensitivity. Table 1 shows a list of some molecules of interest and the calculated detection limits, which scale linear with the minimum detectable absorbance and the absorption pathlength. Higher sensitivities are expected at longer integration times.

Apart from flexibility as the molecule of interest is concerned, the ease of operation, the complexity of the apparatus as well as the usefulness for field applications have to be considered for practical evaluations. Tunable diode laser absorption spectroscopy (TDLAS) is being frequently used for measurement of trace gas pollutants in the atmosphere³. The TDLAS spectrometers usually work with multipass absorption cells to achieve high sensitivity. To alleviate problems by absorption line overlap, these absorption cells are usually operated at low pressure where the linewidth is Doppler limited. In most sensitive instruments the diode laser is repetitively tuned over an absorption line of a target molecule and the absorption spectra are averaged over a specified time interval. Additional modulation techniques are used to reduce the 1/f laser noise. With derivative spectroscopy using lock-in-detection at kHz modulation frequencies, typically, detection limits of the order of 0.1 ppbv were achieved for many molecules in the air with spectra averaging times of a few minutes⁴.

Gas	M [g/Mol]	$\tilde{\nu}_0$ [cm ⁻¹]	λ [μm]	$S/10^{-20}$ [cm ² /mole]	g [cm ⁻¹ /atm]	γ_V [cm ⁻¹]	γ_V [MHz]	$\sigma_0/10^{-18}$ [cm ² /mole]	c_{min}^{STP} [10 ⁸ /cm ³]	DL [pptv]	DL^{STP} [μg/m ³]
CO ₂	44.01	2270.290	4.405	3.358	0.0740	0.00351	105	3.50	42	160	0.31
O ₃	48.00	1052.848	9.498	4.2	0.0773	0.00264	79	5.30	28	100	0.22
N ₂ O	44.01	2236.224	4.472	100.4	0.0768	0.00355	106	103	1.4	5	0.01
CO	28.01	2169.198	4.610	46.15	0.0611	0.00363	109	48.9	3	11	0.014
CH ₄	16.04	3067.300	3.260	21.29	0.0616	0.00577	173	15.3	9.6	36	0.026
NO	30.01	1875.813	5.331	3.399	0.0620	0.00326	98	3.91	38	140	0.19
SO ₂	64.06	1371.695	7.290	4.855	0.1200	0.00386	116	4.11	36	130	0.38
NO ₂	46.01	1600.413	6.248	21.8	0.0670	0.00278	83	27.7	5.3	20	0.042
NH ₃	17.03	930.757	10.744	52	0.0750	0.00292	88	61.8	2.4	9	0.007
HNO ₃	63.01	1694.321	5.902	2.85	0.1100	0.00375	112	2.53	58	220	0.60
H ₂ CO	30.03	2781.035	3.596	11.86	0.1080	0.00517	155	8.41	17	65	0.087
H ₂ O ₂	34.01	1284.205	7.787	4.464	0.1000	0.00352	105	4.27	34	130	0.2
HO ₂	33	1411.182	7.086	1.2	0.090	0.00338	101	1.2	120	450	0.66

Table 1: calculated 1σ-Detection Limits DL for selected molecules and molecular absorption lines for a minimum absorbance of $OD_{min} = 10^{-6}$. Assumed are 30 mbar pressure in 25 m multi path cell @ 296 K. M = Molmass, S = Linestrength, g = Pressure broadening coefficient, σ_0 = absorption cross section at line center, γ_V = Voigt-HWHM, c_{min} = volume mixing ratio : 1 pptv = 10^{-12}

Although these detection limits are sufficient for many applications, still better detection limits are required by modern atmospheric research for the determination of concentrations of free radicals which play a decisive role in the destruction of almost all atmospheric pollutants and in the formation of tropospheric ozone. Substantial improvements of TDLAS detection limits were obtained by introducing the high frequency modulation technique^{4,5}. However, to achieve the sensitivity improvement using the FM technique and to build instruments for routine high sensitivity measurements and even sensitive field applications like trace gas flux measurements, many practical problems still have to be solved.

High frequency modulation spectroscopy

High frequency modulation technique (FM) applied to tunable diode laser absorption spectroscopy (TDLAS) has the potential to satisfy most of the requirements for sensitivity, specificity, detection speed and applicability for many smaller pollutant molecules. The FM technique which has been invented in 1979 by G. Bjorklund, determines the absorption or dispersion of a narrow spectral feature by detecting the heterodyne beat signal that appears when the FM optical spectrum of the probe wave is distorted by the spectral feature of interest⁵. A modified two tone modulation scheme has been introduced by Cooper and Gallagher⁵. A potential sensitivity improvement of up to two orders of magnitude in comparison to conventional derivative (2f) spectroscopy can be derived from wideband noise characteristics of lead-salt diode lasers⁶ for both FM-techniques. This sensitivity improvement can be achieved by increasing the modulation frequency from the 1/f noise dominated region (10 kHz) into a shot noise limited domain of beyond say 100 MHz. In terms of optical density the best detection limits obtained so far with a high frequency modulated TDLAS instrument with a multiple pass absorption cell were on the order of 10^{-6} with a detection bandwidth of 1 Hz^{7,9}. Since the detection limit in FM-spectroscopy is under these conditions proportional to the square root of the laser power on the detector, the laser output power should be as high as possible. This requirement is further stressed by the use of long absorption paths using multipass cells which strongly attenuate the incoming radiation. The theoretical square root dependence of the detection limit on detector incoming power is only valid under quantum limited conditions, which means that the shot noise has to be the dominating noise source in the system. While the shot noise level is dependent on the incident photon flux, the thermal noise is independent of the laser power. This means that the laser power available after passing through the absorption cell should be high enough to generate a shot noise current which is about one order of magnitude above the thermal noise level. With available detectors this requirement means that lasers for FM use should have an output power of at least 1mW. However, calibrated power measurements of most of the presently available lasers show values of about several hundreds of μW. Due to the limited power output, the FM instruments have to be operated at reduced absorption path length⁸.

Fig. 1 shows the basic setup of a FM-spectrometer. A rf current is superimposed to a current ramp with a dc-offset via a bias-tee to decouple the different current sources. A lead salt diode laser is driven by this current $i_L(t)$ and generates $E_1(t)$. The electromagnetic field interacts resonant with the rotational-vibrational absorptions of the molecules in the absorption cell. The interaction is described by the complex transmission function $T(\omega)$ which accounts for absorption and dispersion. The electrical field after the probe $E_2(t)$ induces a detector current $i_{rf}(t)$, which is fed into the rf input of a double balanced mixer for phase sensitive detection at the modulation frequency ω_{rf} . The time dependent demodulated signal $i_{IF}(t)$ at the IF port of the double balanced mixer is proportional to the concentration of the trace components in the absorption cell.

Fig 1 : Principle setup of a FM-spectrometer. For long optical absorption pathlength mostly White or Herriott cells are used.

The signal-to-noise-ratio (SNR) is a convenient way to describe the "cleanliness" of a given signal level. It is simply the signal voltage or power divided by the rms noise voltage (power). A spectrum obtained with a SNR of 100 or more is a very clean pattern, with negligible noise. An SNR of 10 is a little fuzzy, but the pattern is still very clear. A ratio of 3 is pretty bad, and at 1 the signal is nearly lost. If the noise in the detection system is the limiting factor for ultimate sensitivity, the detection limit (SNR^{-1}) of a spectrometer is proportional to the square root of the detection bandwidth and inverse proportional to the power incident upon the detector, P_D . Fig. 2 illustrates the dependence of the detection limit for a given set of experimental parameters :

$$DL \propto \sqrt{\Delta f} \cdot \sqrt{\frac{1 + P_0/P_D}{P_D}}$$

where P_0 is as system constant describing the power level where shot noise equals the noise of the detector preamplifier combination. There are actually two possible directions towards lower detection limits : increasing the laser power on the detector and bandwidth reduction, i.e. longer integration times. For a laser power $P_D \gg P_0$ the detection limit is proportional to $P_D^{-1/2}$, for $P_D \ll P_0$ it is proportional to P_D^{-1} . As far as laser power is concerned our work is limited to characterisation and selection of commercially available lasers. The second direction for further improvement of the sensitivity is digital signal averaging. A critical factor influencing the high sensitivity measurements is the system stability, especially at low optical densities below 10^{-5} . At these sensitivities interference fringes due to unwanted étalons are becoming the factor limiting further improvement of the detection limits^{7,9}. In principle, the problem of fringe limitation can be solved by subtraction of zero air spectrum from the measurement spectrum. Trace gas measurements near to the detection limit are, therefore, usually performed by measuring alternatively the spectrum of the ambient air and the spectrum of zero air, i.e. air devoid of the target substance. This procedure is based on the inherent assumption that within the time interval needed for the acquisition of both the measurement and the background spectra the fringes do not move. If this assumption is fulfilled, the subtraction of the background spectrum from the measurement spectrum would provide the absorption spectrum of the target species which, to a first approximation, is only subject to random noise.

Fig 2 : Minimum absorbance as a function of bandwidth and laser power.

Unfortunately, real systems are not stable forever and it is obvious that every real unstable system will have an optimum averaging time given by the drifts in the system such as temperature drifts, moving fringes, background changes etc. Therefore, a quality of the spectrometer can be described by the characteristics of the instrument stability⁹. To achieve the best possible sensitivity, the instrument should be made as stable as possible and the measuring time should be as short as possible. The real time signal analysis is made by a signal processing board using complex data reduction software. The instrument automatically provides signal, background and calibration spectra which can be averaged up to more than 10^4 individual spectra. Subsequently, a multiple linear regression is performed to fit the background and the calibration spectra simultaneously to the ambient air spectrum. A simultaneous multiple regression analysis also allows us to apply different filters. The Allan variance analysis⁹ predicts the optimum integration time to be about 60 s for this particular instrument. Within this time a complete measurement sequence consisting of the determination of the ambient air, zero air, and calibration gas spectra has to be completed. Ambient measurements were made with a NO_2 doublet line at 1600.413 cm^{-1} since its background was almost free of disturbance from pressure broadened H_2O lines nearby. A NO_2 concentration of 1 ppb in the following data corresponds to an optical density of about $5.3 \cdot 10^{-5}$. A characteristic spectrum is shown in Fig. 3. The spectra have been averaged 256 times within 740 ms to obtain a high SNR. The electronics bandwidth had been set to 1.5 kHz. In the subsequent regression analysis the measured spectrum has been fitted to the calibration spectrum. The fit reported a concentration of 1.17 ppb with an 1σ error of 31.5 ppt. The data (1.17 ± 0.0315 ppb) of Fig. 3, which are well above the detection limit, correspond to an optical density of $(62 \pm 1.7) \cdot 10^{-6}$ at 5.86 Hz bandwidth.

Fig. 3 : 1.17 ppb NO_2 -FM-signal from ambient air

The previous analysis shows that FM-spectroscopy is a very powerful tool for ultrasensitive trace gas analysis. It fulfils most of the requirements for atmospheric trace gas monitoring in ambient air, because it allows fast, sensitive and interference free detection of pollutants at sub-ppb levels. Nevertheless there are many other applications of this technique like quality control of high purity gases for semiconductor processing or breath analysis in medicine.

Acknowledgement

This work has been funded by the German Ministry for Research and Technology (BMFT) and by the Bayerische Staatsministerium für Wirtschaft und Verkehr.

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