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Review

Tunable diode laser spectroscopy as a technique for combustion diagnostics

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ABSTRACT

Tunable diode laser absorption spectroscopy (TDLAS) has become a proven method of rapid gas diagnostics. In the present review an overview of the state of the art of TDL-based sensors and their applications for measurements of temperature, pressure, and species concentrations of gas components in harsh environments is given. In particular, the contemporary tunable diode laser systems, various methods of absorption detection (direct absorption measurements, wavelength modulation based phase sensitive detection), and relevant algorithms for data processing that improve accuracy and accelerate the diagnostics cycle are discussed in detail. The paper demonstrates how the recent developments of these methods and algorithms made it possible to extend the functionality of TDLAS in the tomographic imaging of combustion processes. Some prominent examples of applications of TDL-based sensors in a wide range of practical combustion aggregates, including scramjet engines and facilities, internal combustion engines, pulse detonation combustors, and coal gasifiers, are given in the final part of the review.

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1. Introduction

Tunable diode lasers (TDLs) are sources of coherent light that are widely used in different areas of science and technology. TDLs have been successfully applied in high resolution molecular spectroscopy [1–7], atmospheric trace gas analysers [8–10], plasma diagnostics [11, 12], biomedical applications [13,14], industrial sensors [15–17], and so on. During the 1990s there were great hopes and expectations that tunable diode laser absorption spectroscopy (TDLAS) would be a good choice for elemental analysis because of their many attractive features: narrow linewidth (below 0.001 cm^{-1} or below 30 MHz), high spectral brightness, simple and fast tuning of the wavelength, compactness, robustness, and relatively low cost compared to other types of lasers.

The first successful applications of TDLAS for elemental analysis were reviewed in [18,19]. The advantages of TDL over classical hollow cathode lamp (HCL) were discussed in detail and specific applications for different atomizers — graphite furnace, plasmas, and flames were presented. The narrow spectral line of the TDLs enables isotope selective analysis. For the elements with relatively large isotope shifts (like Li or U) isotope selectivity can be achieved even in a one-step excitation scheme. For medium weight elements (e.g., Sr and Ca) two-step excitation by TDLs can provide isotopic selectivity up to $10^4 — 10^6$. The basic approaches for isotope selective analysis using TDLs were discussed in [20]. For example, the combination of laser ablation followed by TDL based absorption and fluorescence probing of the ablated plume was reported in [21–23] for the isotope selective detection of uranium. TDLAS was used as selective detector in combination with different separation techniques like liquid or gas chromatography. Speciation analysis of Cr (CrIV/CrVI) and Mg (CMT/MMT/CCMT) was demonstrated in [24–27]. A review of TDLAS as element selective sensor for gas chromatography can be found in [28].

Unfortunately, the lack of reliable and compact TDLs for the spectral range below 300 nm limited the application of TDLAS for elemental analysis. Because most resonance absorption lines of the great majority of elements lie below 300 nm, only a few alkaline elements could be detected by TDLAS using the fundamental frequency of a TDL. During the last decade great improvements in application of non-linear optics methodology for generation of uv-radiation were achieved. By generation of harmonics and sum frequencies of fundamental TDL radiation the UV extreme of TDL radiation was extended down to 220 nm. Several papers demonstrated the detection of elements with absorption lines below 300 nm [29,30]. On the web pages of different manufactures (see for example [31,32]) one can find information on the different types of such sources — sum and difference frequency generators (SHG, DFG). However, it should be pointed out that all these sources lose the TDLs in terms of price, compactness and robustness. Another serious limitation of TDL was the narrow range of fast wavelength tuning (about 1 cm^{-1}), which excluded the analysis of several elements with one laser. The use of a number of TDLs for detection of the number of analytes is evidently not practical. Besides, the inductively coupled plasma with optical emission or mass spectrometric detection occupied the leading position in elemental analysis. Since then analytical spectroscopy with TDL has moved away from the main scope of *SAB*.

TDLAS is widely used in diagnostics of different types of plasma. The characterization of a microplasma by TDLs is presented in [33]. A small, low-pressure dielectric barrier discharge used as a detector for the analysis of halogenated hydrocarbons was studied by TDLAS of excited plasma atoms [34]. The diagnostic of argon microplasmas by TDLAS in the 1–760 Torr pressure range was reported in [35,36]. TDLAS was used for the detection of absolute number densities of He in four different plasma based ambient sources [37].

TDLs were and still are successfully used not only in elemental analysis and plasma diagnostics but also in basic physical research areas like atom cooling, atomic optics, atom traps and other areas of fundamental physics [38,39]. The measurements of the fundamental atomic parameters such as life time of the specific states, collision broadening, energy transfer rates and so on were fulfilled using TDLs. A review of these applications of TDLs is outside the scope of this Review.

At the same time, TDL successfully penetrated into the large area of gas chemistry and combustion diagnostics. The aim of this review is to give *SAB* readers some impressions on the state-of-the art of the TDL applications in this area.

Combustion takes a significant position in investigations because of its extremely broad applications — a great variety of engines are based on combustion. For many decades the development of combustion diagnostics has been a growing field of multidisciplinary researches: fundamental and applied spectroscopy, physical chemistry, laser spectroscopy, and so on. The results of combustion diagnostics (temperature, concentrations of key molecules, and flow velocity) provide engineers with valuable information for improving the operation and performance of the engines.

Any type of combustion is characterized by the main parameters: the temperature, total pressure, and partial pressures of the gas components. Different diagnostic techniques used for combustion characterization are reviewed well in [40–46]. Among these are coherent anti-stocks Raman scattering (CARS) [47–53], laser-induced fluorescence (LIF) [54–58], laser light scattering [59–61], and so on. These techniques, which provide valuable data for specific types of combustion and a specific range of combustion parameters, have some limitations. The LIF technique is very sensitive to quenching of the excited states by gas components and also needs a large solid angle of light collection. The CARS technique provides quite accurate temperature measurements for relatively high temperatures (up to 3000 K) and pressure (above 1 MPa), but for low pressure flames, CARS sensitivity is not sufficient for accurate measurements. Besides, the technique needs very sophisticated and expensive laser instrumentation and skilled personnel.

TDLAS is also one of the widely used spectroscopic techniques for detection of the parameters of the hot zones. Measurement of the temperature and concentrations of species in combustion flows by detection of the absorption of a probing monochromatic laser beam was first proposed in [62].

This technique provides remote, non-perturbing measurements of the parameters of a hot zone with time resolution in the microsecond to millisecond range depending on the specific experimental conditions. The technique is usually based on the measurements of the ratio of the absorption line intensities of a test molecule. If the Boltzmann distribution of the energy levels is established, the ratio of the line intensities depends only on the kinetic temperature of the object.

TDLAS possesses many attractive features as a diagnostic technique. The spatial coherence of TDLs enables a narrow laser beam to be delivered to a probing zone without noticeable divergence, which makes remote sensing possible. In contrast to any kind of optical emission-fluorescence technique, TDLAS does not need a large solid angle of light collection; all of the information which can be deduced from the absorption signal is “frozen” in a narrow laser beam of low divergence. Therefore the thermal emission of an investigated hot zone and laser stray light can be eliminated by a set of diaphragms and lenses. Last