

# Laser Absorption Spectroscopy

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Laser absorption spectroscopy (LAS) is an absorption spectroscopic method that employs a laser as the light source and measures the chemical concentration based on detection of a variation of laser beam intensity after transmission along the optical path.

Keywords: laser absorption spectroscopy ; gas detection ; infrared laser ; tunable laser ; standoff detection ; remote sensing ; environmental monitoring ; combustion diagnosis ; security early-warning

## 1. Overview

Laser absorption spectroscopy (LAS) is an absorption spectroscopic method that employs a laser as the light source and measures the chemical concentration based on detection of a variation of laser beam intensity after transmission along the optical path. LAS is proven one of the most sensitive technologies for quantitative measurement of gas-phase chemicals because nearly every molecule possesses a unique spectroscopic “fingerprint” in the infrared spectral region [1]. Compared with conventional absorption spectroscopy using broadband incoherent radiation sources, LAS based chemical sensing offers a highly desirable combination of high-sensitivity and high-speed detection, and the collimated laser source with high brightness allows beam propagation over large distances.

There are several different modes of operation for LAS. Direct absorption spectroscopy (DAS) is the most common technique for the simple-optical configuration, -signal processing, and potential absolute measurement. DAS often suffers from low-sensitivity (absorbance  $\sim 10^{-3}$ ) for the interference from  $1/f$  noise in the system and laser power fluctuation. There are basically two ways to improve sensitivity on the situation: 1) to reduce the noise in the signal, 2) to increase the absorption. The former can be achieved by using modulation technique [2], e.g. wavelength modulation spectroscopy (WMS) and frequency modulation spectroscopy (FMS), with a typical sensitivity of absorbance  $\sim 10^{-5}$ - $10^{-6}$ . Whereas the latter can be obtained by placing the gas inside a cavity in which the light passes through multiple times to increase the interaction length, e.g. multiple-pass or long path absorption cells, and cavity enhanced absorption spectroscopy (CEAS) [3]. CEAS can achieve a very ultra-sensitive of absorbance  $\sim 10^{-7}$ - $10^{-9}$ . The both ways of reducing noise and increasing absorption can be further applied at a same system, e.g. cavity enhanced wavelength modulation spectrometry [4] and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) [5][6]. NICE-OHMS can realize an extraordinary sensitivity of  $\sim 10^{-11}$ - $10^{-13}$ .

The purpose of LAS is frequently to find out details on the measured substances, but in other cases one utilizes known details of substances for other purposes. For example, LAS is often used for realizing optical frequency standards, e.g. by stabilizing the wavelengths of a laser to a precisely defined absorption transition. The realization of all these goals depends on a standard spectral database. HITRAN (**H**igh **R**esolution **T**ransmission) database [7] is the recognized international standard, containing line-by-line parameters of 49 small gas molecules currently. For quantitative detection of large molecules with broadband feature, PNNL (Pacific Northwest National Laboratory) database [8] can be referred for absolute or calibration-free measurement. Alternatively, one can measure high-resolution and high-accuracy broadband absorption spectrum of the target substance in the laboratory for reference of the subsequent quantitative measurements [9][10][11]. Furthermore, for the measurement of large molecules with broadband absorption features using WMS, some methods or procedures can be used to ensure the detection sensitivity and selectivity, including but not limited to optimizing modulation index [12], varied modulation amplitude [13], removing fringes and noise interferences [14], multicomponent spectral fitting [15] and artificial neural networks [16].

## 2. Principles of LAS for Quantitative Measurement

The fundamental theory lying behind absorption spectroscopy is the Beer-Lambert law, which describes the relationship between the transmitted intensity  $I_t$  and the incident intensity  $I_0$  through the gas medium. Its expression is presented in Equation (1) with multiple forms [17]:

$$I_t(\nu) = I_0(\nu)\exp(-\alpha_\nu) = I_0(\nu)\exp(-k_\nu L) = I_0(\nu)\exp(-n\sigma_\nu L) = I_0(\nu)\exp(-S\phi_\nu P\chi_i L) \quad (1)$$

where  $\alpha_\nu$  is the spectral absorbance,  $k_\nu$  [ $\text{cm}^{-1}$ ] is the spectral absorption coefficient,  $L$  [cm] is the absorption pathlength,  $n$  [ $\text{molecule}/\text{cm}^3$ ] is the number density of the absorbing species,  $\sigma_\nu$  [ $\text{cm}^2/\text{molecule}$ ] is the absorption cross section,  $S$  [ $\text{cm}^{-2}/\text{atm}$ ] is the absorption linestrength of an individual transition line,  $\phi_\nu$  [cm] is the frequency-dependent lineshape function,  $P$  [atm] is the total gas pressure, and  $\chi_i$  is the mole fraction of the absorbing species  $i$ . The subscript  $\nu$  denotes the spectral dependence of the parameter on the light frequency  $\nu$ .

Different forms express the gradual expansions of the total absorbance  $\alpha_\nu$ . The first three forms are applicable to absorption spectroscopic measurements in general. When knowing the absorption cross section  $\sigma_\nu$ , one can obtain the number density of the absorbing species according to the third expression. However, the last form is more demanding because it contains a lineshape function. Therefore, it is suitable for the measurement of small gas molecules with narrow absorption features, which can be described by an analytical expression. The narrow spectral lines can be obtained by wavelength scanning of tunable lasers with rather narrow linewidth, so that quantitative measurements are performed to determine the chemical concentration of interest via the measured ratio  $I_0(\nu)/I_t(\nu)$ .

### 3. System Configuration

A typical LAS consists of a laser, a photodetector, and an optical configuration for light interaction with gas. For modulation-based LAS, there are additionally a laser modulator and a signal demodulator, the later usually by a lock-in amplifier.

The laser is LAS's key component, which usually need to be continuously tunable mode-hop-free, reliable, single frequency with narrow linewidth (typically  $<1$  MHz), and low intensity noise. Recently, great progress in laser technologies brings many types of excellent lasers [1], i.e. quantum cascade lasers QCLs, external cavities based (EC-) QCLs, interband cascade lasers (ICLs), optical frequency combs..., which undoubtedly promotes the development of LAS.

High-sensitive and low-noise detectors are essential for trace gas detection. Both Indium Gallium Arsenide (InGaAs) and Germanium (Ge) photodiode detectors are commonly used to measure optical power in the near-infrared (NIR) range. While in the mid-infrared (MIR) detection, the most popular commercial one is mercury-cadmium-telluride (MCT, or HgCdTe) photoconductive semiconductor based detector. MCT detector enjoys a very wide spectral response (2 to 25  $\mu\text{m}$ ) and higher speed of detection. Its main limitation is that it needs cooling to reduce noise due to thermally excited current carriers. Alternatively, newly developed quantum heterostructure detectors could take a vital part in the future infrared detection [18].

The optical configuration provides interaction between light and gas, the interaction length directly relates with the sensitivity of gas detection. Thus, long interaction length is desired to achieve high sensitivity. Multiple-pass cells (MPCs) and open long path are commonly used in LAS to measure low-concentration components or to observe weak spectra in gas. Traditional MPCs, such as White or Herriott gas cell, are still widely used, but the requirements of compact, small sample volume, and fast response time have stimulated the development of new type of gas cell. Recently, modified MPCs [19][20][21], circular multi-reflection (CMR) cells [22][23][24], and hollow waveguide (HWG) based gas cells [25][26][27] hint the glorious prospective of compact integrated sensors. On the other hand, the need for open-path gas detection, e.g. leak detection, aroused the development of standoff remote sensing with or without a retroreflector [17].

### 4. Applications of Laser Absorption Spectroscopy

Methods of laser absorption spectroscopy are commonly used for quantitative measurements of concentrations of gases or vapors. But not limited to this, LAS based techniques are also employed for detecting the composition of liquids [28], solids [29] or plasma [30]. Some application areas are summarized as follows.

**Environmental monitoring** [17]: The temporal and spatial distribution of greenhouse gases, such as  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{O}_3$ , etc., is of great concern to those who study climate change. Moreover, Detection of some other atmospheric constituents ( $\text{NH}_3$ ,  $\text{NO}$  ...) is necessary for environmental assessment and protection. Concentrations of the trace gases in the atmosphere are measured e.g. with laser radar (LiDAR) methods in the context of atmospheric environmental monitoring. Similarly, pollutants can be detected in water, and concentrations of medically active substances can be measured.

**Industrial process measurement and control** <sup>[31]</sup>: Continuous monitoring of some iconic gases, e.g. O<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, HCl, HF, etc., are usually required in the production process. LAS is one of the most promising techniques currently for the detection of industrial process gases, benefiting from its non-contact, high sensitivity, fast response and robustness.

**In-situ monitoring of pollution emissions** <sup>[32]</sup>: LAS based sensors have been proved to be robust when working in the harsh environment. Very typical applications also involve detection of exhaust emissions from coal-fired power plants, metal smelter, pharmaceutical factory, etc.

**Biology and medicine** <sup>[33]</sup>: For example, detection and analysis of volatile compounds in exhaled breath represents an attractive tool for monitoring the metabolic status of a patient and disease diagnosis, since it is non-invasive and fast. LAS has become a powerful tool to measure concentrations of various substances in human breath, which helps people retrieve vital information on medical conditions.

**Combustion diagnosis** <sup>[34][35]</sup>: Line-of-sight LAS has been validated to quantitatively measure the path-averaged temperature, species concentrations, pressure and velocity in the combustion fields with sufficiently high temporal resolution. Spatially resolved 1D and 2D distributions of the parameters in the reacting flows are enabled by the combination of LAS and hard-field tomography.

**Security applications** <sup>[17][36]</sup>: The detection objects often include explosives, drugs, chemical warfare agents and toxic gases. This is very meaningful for national for early-warning in national defense and counter-terrorism.

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