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.

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 ~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 ~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 ~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 ~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 (**Hi**gh Resolution **Tran**smission) 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]:

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

where α_ν is the spectral absorbance, k_ν [cm^{-1}] is the spectral absorption coefficient, L [cm] is the absorption pathlength, n [molecule/cm^3] is the number density of the absorbing species, σ_ν [cm^2/molecule] is the absorption cross section, S [cm^{-2}/atm] is the absorption linestrength of an individual transition line, φ_ν [cm] is the frequency-dependent lineshape function, P [atm] is the total gas pressure, and χ_i is the mole fraction of the absorbing species i. The subscript ν denotes the spectral dependence of the parameter on the light frequency ν.

Different forms express the gradual expansions of the total absorbance α_ν. The first three forms are applicable to absorption spectroscopic measurements in general. When knowing the absorption cross section σ_ν, 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 μm) 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 CO_2, CH_4, O_3, *etc*., is of great concern to those who study climate change. Moreover, Detection of some other atmospheric constituents (NH_3, 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 [31]: Continuous monitoring of some iconic gases, e.g. O2, CH_4, C_2H_4, 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 [32]: 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 [33]: 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 [34][35]: 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 [17][36]: 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.

References

1. Du, Z.H.; Zhang, S.; Li, J.Y.; Gao, N.; Tong, K.B. Mid-Infrared Tunable Laser-Based Broadband Fingerprint Absorption Spectroscopy for Trace Gas Sensing: A Review. Appl Sci-Basel 2019, 9, 338. doi:10.3390/app9020338.
2. Wang, F.; Jia, S.; Wang, Y.; Tang, Z.J.A.S. Recent developments in modulation spectroscopy for methane detection based on tunable diode laser. Appl Sci (Basel) 2019, 9, 2816. doi:10.3390/app9142816
3. Morville, J.; Kassi, S.; Chenevier, M.; Romanini, D. Fast, low-noise, mode-by-mode, cavity-enhanced absorption spectroscopy by diode-laser self-locking. Applied Physics B 2005, 80, 1027-1038. doi:10.1007/s00340-005-1828-z.
4. Zybin, A.; Kuritsyn, Y.A.; Mironenko, V.R.; Niemax, K. Cavity enhanced wavelength modulation spectrometry for application in chemical analysis. Applied Physics B: Lasers and Optics 2004, 78, 103-109. doi:10.1007/s00340-003-1342-0.

5. Foltynowicz, A.; Schmidt, F.M.; Ma, W.; Axner, O. Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy: Current status and future potential. Appl. Phys. B-Lasers Opt 2008, 92, 313. doi:10.1007/s00340-008-3126-z.
6. Weiguang, M.; Yueting, Z.; Zhao Gang; Jia Mengyuan; Liu Jianxin; Guo Songjie; Dong Lei; Zhang Lei; Yin Wangbao; Xiao Liantuan, et al. Review on Noise Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy. Chinese Journal of Lasers 2018, 45, 0911007. doi:10.3788/CJL201845.0911007.
7. Gordon, I.E.; Rothman, L.S.; Hill, C.; Kochanov, R.V.; Tan, Y.; Bernath, P.F.; Birk, M.; Boudon, V.; Campargue, A.; Chance, K.V., et al. The HITRAN2016 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer 2017, 203, 3-69. doi:10.1016/j.jqsrt.2017.06.038.
8. Sharpe, S.W.; Johnson, T.J.; Sams, R.L.; Chu, P.M.; Rhoderick, G.C.; Johnson, P.A. Gas-phase databases for quantitative infrared spectroscopy. Appl Spectrosc 2004, 58, 1452-1461. doi:10.1366/0003702042641281.
9. Guan, H.; Wang, X.; Han, R.; Yuan, L.; Meng, S.; Wang, S.; Du, Z.J.J.o.Q.S.; Transfer, R. High-resolution and-precision spectra of acetonitrile at the ν5-band for laser remote sensing. 2020, 255, 107254. doi:10.1016/j.jqsrt.2020.107254
10. Wang, Z.; Wang, R.; Li, J.; Yan, Y.; Du, Z. Ultrahigh resolution spectroscopy for dimethyl sulfide at the ν1- and ν8-bands by a distributed feedback interband cascade laser. Journal of Quantitative Spectroscopy and Radiative Transfer 2020, 246. doi:10.1016/j.jqsrt.2020.106930.
11. Du, Z.; Li, J.; Gao, H.; Luo, G.; Cao, X.; Ma, Y. Ultrahigh-resolution spectroscopy for methyl mercaptan at the ν 2 -band by a distributed feedback interband cascade laser. Journal of Quantitative Spectroscopy and Radiative Transfer 2017, 196, 123-129. doi:10.1016/j.jqsrt.2017.03.027.
12. Xiong, B.; Du, Z.; Li, J. Modulation index optimization for optical fringe suppression in wavelength modulation spectroscopy. Rev Sci Instrum 2015, 86, 113104. doi:10.1063/1.4935920.
13. Du, Z.H.; Yan, Y.; Li, J.Y.; Zhang, S.; Yang, X.T.; Xiao, Y.H. In situ, multiparameter optical sensor for monitoring the selective catalytic reduction process of diesel engines. Sensor Actuat B-Chem 2018, 267, 255-264. doi:10.1016/j.snb.2018.04.035.
14. Du, Z.H.; Li, J.Y.; Cao, X.H.; Gao, H.; Ma, Y.W. High-sensitive carbon disulfide sensor using wavelength modulation spectroscopy in the mid-infrared fingerprint region. Sensors and Actuators B-Chemical 2017, 247, 384-391. doi:10.1016/j.snb.2017.03.040.
15. Du, Z.H.; Wan, J.X.; Li, J.Y.; Luo, G.; Gao, H.; Ma, Y.W. Detection of Atmospheric Methyl Mercaptan Using Wavelength Modulation Spectroscopy with Multicomponent Spectral Fitting. Sensors-Basel 2017, 17. doi:ARTN 37910.3390/s17020379.

16. Tian, X.L.; Li, J.Y.; Du, Z.H.; Wan, J.X.; Fan, H.Q.; Li, H.L. Simultaneous Inversion of Methyl Thiol, Methane and Water Vapor Concentration from Wavelength Modulation Spectroscopy Using Neural Network. Proc Spie 2019, 11337. doi:Unsp 113370210.1117/12.2538008.

17. Li, J.; Yu, Z.; Du, Z.; Ji, Y.; Liu, C. Standoff Chemical Detection Using Laser Absorption Spectroscopy: A Review. Remote Sens. 2020, 12. doi:10.3390/rs12172771.

18. Downs, C.; Vandervelde, E.T. Progress in Infrared Photodetectors Since 2000. Sensors 2013, 13. doi:10.3390/s130405054.

19. Shen, C.; Zhang, Y.; Ni, J. Compact cylindrical multipass cell for laser absorption spectroscopy. Chin. Opt. Lett. 2013, 11, 091201. doi:10.3788/COL201311.091201.

20. Mohamed, T.; Zhu, F.; Chen, S.; Strohaber, J.; Kolomenskii, A.A.; Bengali, A.A.; Schuessler, H.A. Multipass cell based on confocal mirrors for sensitive broadband laser spectroscopy in the near infrared. Appl. Opt. 2013, 52, 7145-7151. doi:10.1364/AO.52.007145.

21. Liu, K.; Wang, L.; Tan, T.; Wang, G.; Zhang, W.; Chen, W.; Gao, X. Highly sensitive detection of methane by near-infrared laser absorption spectroscopy using a compact dense-pattern multipass cell. Sens. Actuator B-Chem 2015, 220, 1000-1005. doi:10.1016/j.snb.2015.05.136.

22. Ofner, J.; Kruger, H.U.; Zetzsch, C. Circular multireflection cell for optical spectroscopy. Appl. Optics 2010, 49, 5001-5004. doi:10.1364/Ao.49.005001.

23. Mangold, M.; Tuzson, B.; Hundt, M.; Jagerska, J.; Looser, H.; Emmenegger, L. Circular paraboloid reflection cell for laser spectroscopic trace gas analysis. Journal of the Optical Society of America a-Optics Image Science and Vision 2016, 33, 913-919. doi:10.1364/Josaa.33.000913.

24. Graf, M.; Emmenegger, L.; Tuzson, B. Compact, circular, and optically stable multipass cell for mobile laser absorption spectroscopy. Optics Letters 2018, 43, 2434-2437. doi:10.1364/Ol.43.002434.

25. Li, J.; Luo, G.; Du, Z.; Ma, Y. Hollow waveguide enhanced dimethyl sulfide sensor based on a 3.3 μm interband cascade laser. Sensors and Actuators B: Chemical 2018, 255, 3550-3557. doi:10.1016/j.snb.2017.09.190.

26. Tutuncu, E.; Naegele, M.; Fuchs, P.; Fischer, M.; Mizaikoff, B. iHWG-ICL: Methane Sensing with Substrate-Integrated Hollow Waveguides Directly Coupled to Interband Cascade Lasers. Acs Sensors 2016, 1, 847-851. doi:10.1021/acssensors.6b00238.

27. Gayraud, N.; Kornaszewski, L.W.; Stone, J.M.; Knight, J.C.; Reid, D.T.; Hand, D.P.; MacPherson, W.N. Mid-infrared gas sensing using a photonic bandgap fiber. Appl. Optics 2008, 47, 1269-1277. doi:10.1364/Ao.47.001269.

28. Jouy, P.; Mangold, M.; Tuzson, B.; Emmenegger, L.; Chang, Y.C.; Hvozdara, L.; Herzig, H.P.; Wagli, P.; Homsy, A.; de Rooij, N.F., et al. Mid-infrared spectroscopy for gases and liquids based

on quantum cascade technologies. Analyst 2014, 139, 2039-2046. doi:10.1039/c3an01462b.

29. Pacheco-Londono, L.C.; Warren, E.; Galan-Freyle, N.J.; Villarreal-Gonzalez, R.; Aparicio-Bolano, J.A.; Ospina-Castro, M.L.; Shih, W.C.; Hernandez-Rivera, S.P. Mid-Infrared Laser Spectroscopy Detection and Quantification of Explosives in Soils Using Multivariate Analysis and Artificial Intelligence. Appl. Sci.-Basel 2020, 10, 19. doi:10.3390/app10124178.
30. Röpcke, J.; Davies, P.B.; Hamann, S.; Hannemann, M.; Lang, N.; Van Helden, J.-P.H. Applying quantum cascade laser spectroscopy in plasma diagnostics. Photonics 2016, 3, 45. doi:10.3390/photonics3030045
31. Lackner, M. Tunable diode laser absorption spectroscopy (TDLAS) in the process industries–a review. Rev. Chem. Eng 2007, 23, 65-147. doi:10.1515/REVCE.2007.23.2.65.
32. Li, J.Y.; Zhang, C.G.; Wei, Y.Y.; Du, Z.H.; Sun, F.S.; Ji, Y.; Yang, X.T.; Liu, C. In situ, portable and robust laser sensor for simultaneous measurement of ammonia, water vapor and temperature in denitrification processes of coal fired power plants. Sensor Actuat B-Chem 2020, 305, 127533. doi:10.1016/j.snb.2019.127533.
33. Henderson, B.; Khodabakhsh, A.; Metsala, M.; Ventrillard, I.; Schmidt, F.M.; Romanini, D.; Ritchie, G.A.D.; Hekkert, S.T.; Briot, R.; Risby, T., et al. Laser spectroscopy for breath analysis: towards clinical implementation. Applied Physics B-Lasers and Optics 2018, 124.
34. Goldenstein, C.S.; Spearrin, R.M.; Jeffries, J.B.; Hanson, R.K. Infrared laser-absorption sensing for combustion gases. Progress in Energy and Combustion Science 2017, 60, 132-176.
35. Liu, C.; Xu, L.J. Laser absorption spectroscopy for combustion diagnosis in reactive flows: A review. Applied Spectroscopy Reviews 2019, 54, 1-44. doi:10.1080/05704928.2018.1448854.
36. MacLeod, N.A.; Weidmann, D. High sensitivity stand-off detection and quantification of chemical mixtures using an active coherent laser spectrometer (ACLaS). In Proceedings of Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) Sensing XVII, Baltimore, MD, 2016 Apr 18-20; p. 98240B.