

引用格式: WANG Chenglong, XIE Jiabao, ZHUANG Ruobin, et al. Highly Sensitive Carbon Dioxide Gas Sensor Based on 2 μm Laser Diode and Herriott Multi-pass Absorption Cell (Invited)[J]. Acta Photonica Sinica, 2023, 52(10):1052406
王成龙, 谢嘉保, 庄若彬, 等. 基于 2 μm 激光二极管和 Herriott 多光程吸收池的高灵敏二氧化碳气体传感器(特邀)[J]. 光子学报, 2023, 52(10):1052406

基于 2 μm 激光二极管和 Herriott 多光程吸收池的高灵敏二氧化碳气体传感器(特邀)

王成龙¹, 谢嘉保¹, 庄若彬¹, 林灏杨¹, 林乐晴¹, 崔茹悦², 武红鹏²,
郑华丹¹, 董磊²

(1 暨南大学 理工学院 光电工程系, 广州 510632)

(2 山西大学 量子光学与光量子器件国家重点实验室, 太原 030006)

摘要: 为了提高二氧化碳气体检测系统的测量空间分辨率并减小系统体积, 设计了一种基于 2 μm 激光二极管和 Herriott 多光程吸收池的高灵敏二氧化碳气体传感器。设计并加工了有效光程为 2.6 m 的 Herriott 池来进行光路折叠。使用中心波长为 2 μm 的激光二极管, 覆盖二氧化碳分子在 4 989.9 cm^{-1} 处的较强吸收线。采用波长调制技术减小系统的噪声。此外, 为系统加载 Kalman 滤波技术来进一步提高探测灵敏度。实验结果表明, 采用该传感器, 系统的探测极限在 1 s 的积分时间下可达到 0.18×10^{-6} , 而经过自编程实时 Kalman 滤波后探测极限可达到 0.13×10^{-6} , 提高了 27%。采用该传感器对室内二氧化碳浓度进行长达 8 h 的连续监测, 并在暨南大学理工学院楼顶进行了 24 h 的二氧化碳浓度监测, 证明了仪器的稳定性。

关键词: 光谱学; 可调谐二极管激光吸收光谱技术; 多光程池; Herriott 池; 二氧化碳传感器

中图分类号: O433

文献标识码: A

doi: 10.3788/gzxb20235210.1052406

0 引言

二氧化碳(CO_2)浓度的测量在工业生产控制、医学诊断^[1-3]、大气污染检测等领域有着极其重要的意义。随着“双碳”目标被提出,《中共中央、国务院关于完整准确全面贯彻新发展理念做好碳达峰碳中和工作的意见》中明确指出,到 2025 年,单位国内生产总值二氧化碳排放比 2020 年下降 18%;到 2030 年,单位国内生产总值二氧化碳排放比 2005 年下降 65% 以上^[4]。要达到碳达峰和碳中和目标,精准地测量二氧化碳浓度十分重要。

二氧化碳的测量手段主要分为天基和地基测量。天基的二氧化碳测量主要依靠星载的二氧化碳高光谱载荷。我国首颗 CO_2 观测科学实验卫星 TANSAT 于 2016 年末发射,并且于 2022 年 10 月首次利用中国碳卫星进行观测量识别和计算城市碳排放^[5]。天基的二氧化碳测量手段主要是宏观层面度量,可以测量整个国家或者整个城市的二氧化碳分布,多用于大气和环境监测场合。地基的二样化碳测量手段主要面向局部二氧化碳浓度度量,主要依靠质谱、色谱、电化学和光学原理。质谱和色谱方法测量精度高,但是响应速

基金项目: 国家自然科学基金(Nos. 62375111, 62005105, 12174156, 12174155, 62105125, 62075088, 62175137), 国家重点研发计划(Nos. 2021YFB2800801, 2019YFE0118200), 广东省自然科学基金(Nos. 2020B1515020024, 2019A1515011380), 广东省重点领域研发计划(No. 2019B010138004), 广东高校优秀青年创新人才培养计划项目(No. 2018KQNCX009), 广州市科技项目(No. 202102020445), 中国航空研究院项目(No. 201808W4001), 广州市产业领军人才项目(No. CXLJTD-201607), 中央高校基本科研专项资金(Nos. 21619402, 11618413), 应用光学国家重点实验室基金(No. SKLAO-201914), 广东省科技创新战略专项资金(No. pdjh2023a0052)

第一作者: 王成龙, wangchenglong@stu2021.jnu.edu.cn

通讯作者: 郑华丹, zhenghuadan@jnu.edu.cn

收稿日期: 2023-06-09; 录用日期: 2023-08-31

<http://www.photon.ac.cn>

度相对较慢,仪器价格相对较高,不利于大面积分布组网^[6-7]。电化学传感器体积小、性价比高,一般用在灵敏度和选择性要求不高的场合。光学的测量方法,尤其是基于激光光谱的测量方法,具有灵敏度高、选择性好且能实时在线快速监测等特点,常被用于大气环境监测、工业过程控制、农业畜牧业监测、医学呼气诊断和新能源等^[8-9]。

激光光谱测量方法又分为光腔衰荡光谱(Cavity Ring-Down Spectroscopy, CRDS)^[10]、光声光谱^[11-19](Photoacoustic Spectroscopy, PAS)和可调谐二极管激光吸收光谱技术(Tunable Diode Laser Absorption Spectroscopy, TDLAS)^[20]。这些技术中,TDLAS技术因为灵敏度高、结构相对简单、鲁棒性好,在各个领域被广泛应用。

根据检测气体的方式不同,可以将TDLAS分为3类:直接吸收光谱(Direct Absorption Spectroscopy, DAS)、波长调制光谱(Wavelength Modulation Spectroscopy, WMS)以及频率调制光谱(Frequency Modulation Spectroscopy, FMS)。直接吸收光谱是一种最简单的气体检测方式,通过对基线拟合得到透射光谱,更适合光强衰减明显的系统。但是反演出的浓度容易受到散射以及激光器光强变化的影响。波长调制光谱最大的优点是能够利用锁相放大器对输入信号中处于参考频率的二次谐波或者是高次谐波进行检测,从而获得一个基本无背景的信号^[21]。波长调制光谱的精度比直接吸收光谱高一到两个数量级。是一种通过减小噪声增加信噪比的手段,适用于测量痕量气体。波长调制光谱噪声主要来源于 $1/f$ 噪声。频率调制光谱使用比波长调制光谱更高的调制频率,使得系统的主要噪声来自于散粒噪声,有更好的探测灵敏度^[22]。

2022年,陈剑虹采用1 578.67 nm分布式反馈(Distributed Feedback, DFB)激光器作为光源,使用10.1 m Herriott多光程池折叠光路,加载小波去噪提高系统的信噪比。经过Allan分析在1 s积分时间下获得系统测量二氧化碳的探测极限为960 ppm($1 \text{ ppm} \times 10^{-6}$)。在90 s的积分时间下探测极限达83 ppm^[23]。2022年,赵成龙使用波长为2 004 nm激光器与设计的300 mm的Herriott型多通池构成TDLAS二氧化碳检测系统,经过Allan计算出在101.6 s的积分时间下可以获得系统测量二氧化碳的探测极限为15.12 ppm^[24]。2022年,冯仕凌使用波长为1 578 nm的激光器作为光源,结合长度为10 m的White型吸收池折叠光路,加入小波变换为系统去噪,得到系统测量二氧化碳的探测极限为7 ppm^[25]。2022年,刘锬利用双平凸反射镜构成抗环境腐蚀膜层且长度为6.8 m的Herriott型多通池,使用2 004 nm激光器在0.1 s的积分时间下获得系统测量二氧化碳的探测极限为0.68 ppm^[26]。2023年,李恒宽选择中心波长为2 008 nm的激光器作为光源,自主研发长达40 m的柱面镜多通池折叠光路。在72 s的积分时间下获得系统测量二氧化碳的探测极限为7.2 ppm。加载卡尔曼-小波分析滤波后,在61 s的积分时间下获得的探测极限提升为5.5 ppm^[27]。2023年KONG Rong使用2 004 nm的激光器作为光源,使用双通道多光程池中长达2.1 m的线性单元折叠光路,在271 s的积分时间下获得系统测量二氧化碳的探测极限为437.8 ppb($1 \text{ ppb} \times 10^{-9}$)^[28]。

本文设计了一种基于Herriott多光程吸收池的二氧化碳TDLAS传感器。该多光程池采用两面1英寸(25.4 mm)的凹面反射镜和笼式镜架结构。该多光程池可以在54 mm几何长度内,通过多次反射实现2.6 m的长吸收路径。采用波长为2 μm 的蝶形分布反馈式(DFB)可调谐激光二极管作为光源来探测二氧化碳,结合自行编写的Kalman滤波算法进一步提高探测信噪比。

1 实验部分

1.1 CO₂吸收线的选择与激光器定标

当激光束穿过气体介质时,激光器发出强度为 I_0 的入射光,光强由于气体的吸收而呈指数衰减。探测器上接收到的激光光强 I_t 可以用朗伯-比尔定律来描述^[29],即

$$I_t = I_0 \cdot \exp[-P \cdot S(T) \cdot \phi(\nu) \cdot X \cdot L] \quad (1)$$

式中, P 是气体压力, $S(T)$ 是气体温度 T 下的分子跃迁线强度, $\phi(\nu)$ 是不同激光频率 $\nu(\text{cm}^{-1})$ 的线型函数, X 是吸收物质的浓度, L 是吸收路径长度。选择较强的目标吸收线和设计较长的吸收路径都可以提高探测灵敏度。

如图1,通过查询HITRAN数据库^[30],二氧化碳分子在4 900~6 400 cm^{-1} 范围内具有多根较强的吸收线。实验初始,使用布鲁克傅里叶红外光谱仪(VERTEX 70)对2 μm DFB激光器进行定标。如图2,傅里叶

红外光谱仪的扫描精度设置为 0.25 cm^{-1} 。当激光芯片温度控制在 $15\sim 35 \text{ }^\circ\text{C}$ 时,通过调谐激光器的注入电流,其波长调谐范围可以达到 $4986\sim 4994 \text{ cm}^{-1}$,能够覆盖 CO_2 分子的多根吸收线。为了尽可能避免空气中 H_2O 分子的吸收串扰,查询激光器调谐范围内的 CO_2 与 H_2O 吸收线线强。如图3所示,在波数为 4989.9 cm^{-1} 时, H_2O 对 CO_2 的测量干扰较小。本实验选择波数为 4989.9 cm^{-1} 的吸收线,其强度为 $1.319 \times 10^{-21} \text{ cm/molecule}$ 。

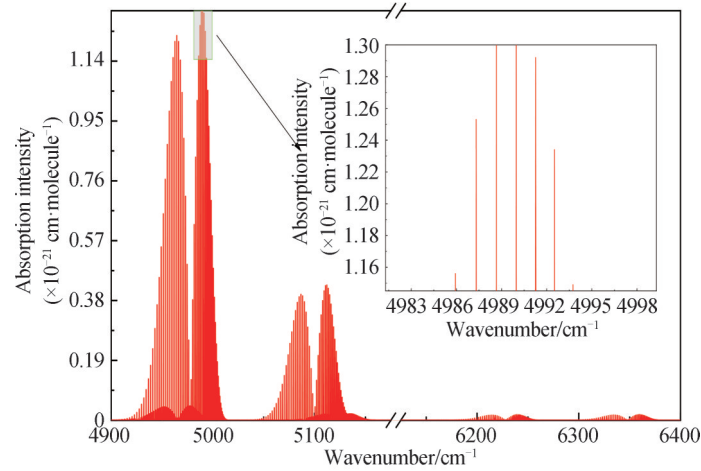


图1 HITRAN数据库查询的 CO_2 分子吸收线
Fig.1 Absorption line of CO_2 from HITRAN database

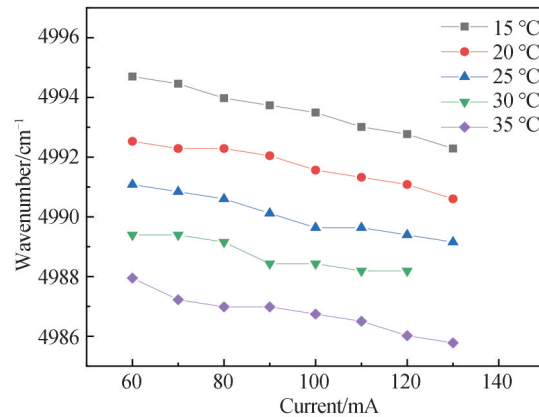


图2 DFB激光器输出波长与芯片温度、注入电流的关系
Fig. 2 DFB laser emission wavelength as the function of diode temperature and injection current

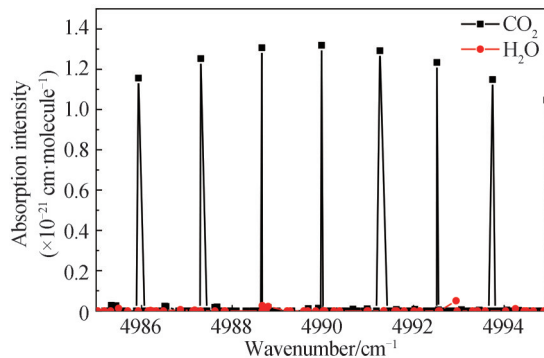


图3 DFB激光器调谐范围内的 CO_2 和 H_2O 吸收线
Fig. 3 The absorption line of CO_2 and H_2O within the tuning range of the used DFB laser

1.2 Herriott池的仿真与设计

使用矩阵光学对Herriott池进行推导^[31],将一束光的镜面反射、空间传输用矩阵表示为

$$\mathbf{r} = (x, S_x, y, S_y)^T \quad (2)$$

式中, r 是光束的向量表达, x 、 y 、 S_x 、 S_y 分别是光线的发射点与斜率。

自由空间的传输矩阵为

$$T(l) = \begin{bmatrix} T_x(l) & 0 \\ 0 & T_y(l) \end{bmatrix} \quad (3)$$

式中, $T_x(l)$ 和 $T_y(l)$ 分别 x 、 y 方向上的自由空间传输矩阵, 其表达式为

$$T_x(l) = T_y(l) = \begin{bmatrix} 1 & l \\ 0 & 1 \end{bmatrix} \quad (4)$$

式中, l 是两个透镜中心间距。

反射镜的反射矩阵为

$$T(R) = \begin{bmatrix} T_x(R) & 0 \\ 0 & T_y(R) \end{bmatrix} \quad (5)$$

式中, $T_x(R)$ 和 $T_y(R)$ 分别 x 、 y 方向上的反射矩阵, 其表达式为

$$T_x(R) = T_y(R) = \begin{bmatrix} 1 & 0 \\ -2/R & 1 \end{bmatrix} \quad (6)$$

式中, R 为透镜的曲率半径。经过 N 次往返后可以得到光斑的分布为

$$x_N = U \sin(N\Phi + \alpha) \quad (7)$$

$$y_N = V \sin(N\Phi + \beta) \quad (8)$$

式中, U 、 V 分别是 x 、 y 方向上的光斑分布的边界, α 、 β 为是 x 、 y 方向上的初始相位。当两者的相位差为 $\pi/2$, 且 $U = V$ 时, 光斑会分布在一个圆上。当初始光线的入射位置选定为 $(0, V)$ 时, 初始光线的入射角度为

$$S_{x0} = U/lP \quad (9)$$

$$S_{y0} = -V(P - W)/lP \quad (10)$$

式中,

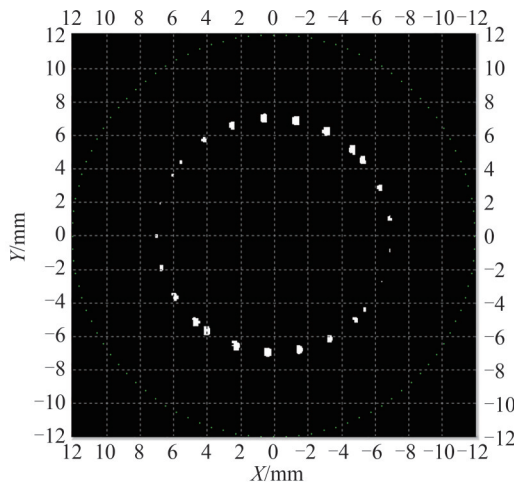
$$P = g_2 / \sqrt{g_1 g_2 (1 - g_1 g_2)} \quad (11)$$

$$W = g_1 g_2 / \sqrt{g_1 g_2 (1 - g_1 g_2)} \quad (12)$$

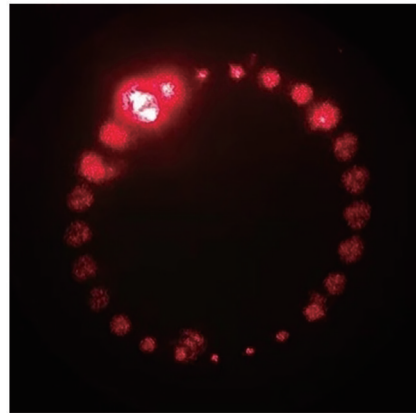
式中, g_1 和 g_2 是谐振腔的两个反射镜的几何参数 g 参数, 定义为

$$g_1 = g_2 = 1 - l/R \quad (13)$$

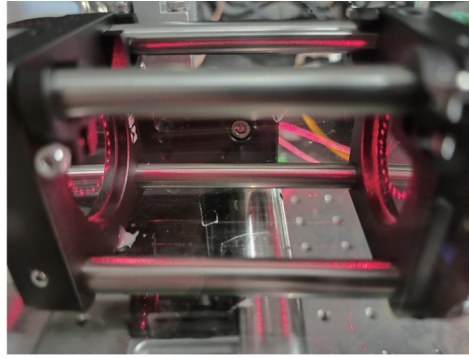
因此, 设计了一款两个凹面镜间距 $l = 54$ mm 的 Herriott 多光程池。两个凹面镜的直径为 25.4 mm, 焦距为 100 mm, 表面为银膜。通过机械加工的方法进行开孔, 入射孔与出射孔分别位于两个镜面之上。设置光线的入射高度为 7 mm。根据式(9)、(10)计算入射光线的初始倾斜角度为 $S_{x0} = 0.0886$ rad, $S_{y0} = -0.0350$ rad。通过 TracePro 仿真验证, 得到光斑分布如图 4(a)。单面凹面反射镜的光斑数为 25 个, 一共反射次数为



(a) The spot distribution by TracePro simulation



(b) The spot distribution of a physical Herriott cell



(c) Herriott multi-pass cell physical object

图4 Herriott多光程池的仿真及实物

Fig. 4 Simulation and physical implementation of Herriott multi-pass cell

50次,得到多光程池的有效光程为2.6 m。实验中,使用笼式结构将两个凹面镜保持在固定位置,并通过调整光纤的入射角度得到Herriott多光程池实物。使用可见光显现光斑分布位置,得到如图4(b)所示的镜面图案。图4(c)展示了Herriott多光程池的整体样貌。

1.3 实验装置

图5展示的是基于 $2\ \mu\text{m}$ 激光二极管和Herriott多光程吸收池的高灵敏二氧化碳气体传感器系统。实验中采取的调制技术为二次谐波调制技术。通过电脑控制自制的激光驱动器^[32]。为了扫过特定的吸收波长,需要使用斜坡信号扫描激光器的注入电流。通过叠加一个正弦信号完成激光器的波长调制工作。输出的激光通过一个光纤准直器注入到Herriott多光程吸收池内。Herriott多光程吸收池的工作半径为7 mm,高为54 mm,体积为8.312 mL,有效光程为2.6 m。通过多光程池的出射激光经过一个焦距 $f=5\ \text{mm}$ 的凸透镜汇聚到光电探测器的探测面上。光电探测器将得到的光强信号转化为电信号传输至锁相放大器(SR830 DSP)。设置锁相放大器的积分时间为1 s,滤波器为12 dB/oct。锁相放大器对输入信号中处于参考频率的二次谐波信号进行检测与解调。最后通过电脑读取解调信号并反演浓度。整个实验采用由Labview编写的程序控制。实验中采用高纯氮气(纯度为99.999%)与浓度为0.05%的 CO_2 (载气为氮气)经过流量控制器混合出需要的浓度梯度。

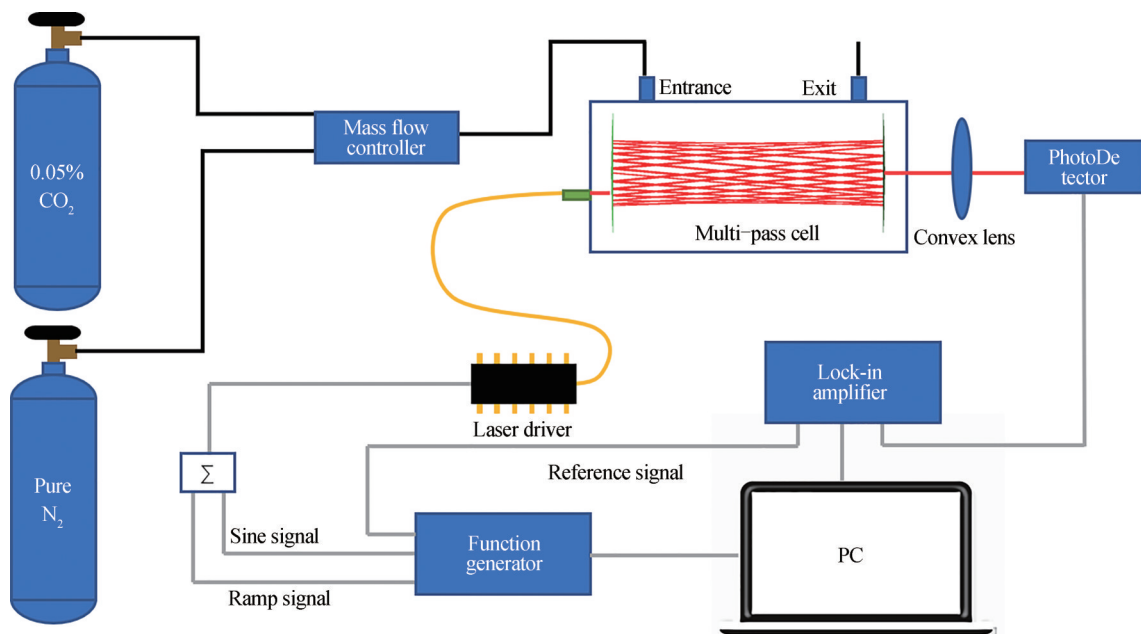


图5 实验装置原理

Fig. 5 Experimental setup diagram

2 系统性能测试

设置激光器的工作温度为 $17.3\text{ }^{\circ}\text{C}$, 斜坡信号的扫描范围为 $109.4\sim 132.4\text{ mA}$, 步长为 0.1 mA 。正弦信号的调制深度为 10 mA , 频率为 32 kHz 。通过流量控制器完成指定浓度二氧化碳—氮气混合气的配气, 固定混合气流速为 200 sccm 。待气体浓度稳定后, 通过读取二次谐波的吸收峰确定整个系统测量到的浓度。如图 6 所示, 分别在 CO_2 浓度为 500 ppm 、 400 ppm 、 300 ppm 、 200 ppm 和 100 ppm 的条件下, 测量得到的二次谐波信号。对不同浓度下每组实验测量 5 次取平均值, 获得不同浓度与信号大小的线性关系, 如图 7 所示。线性拟合决定系数 R^2 为 0.999 , 表明 TDLAS 二次谐波信号幅值与待测 CO_2 气体浓度之间有着良好的线性关系。在 500 ppm 条件下测量出的信号为 19.1 mV 。将波长锁定在吸收线上, 充入纯氮气测量获得噪声信号。60 个采样点下得到噪声的标准差 1σ 为 $6.86\times 10^{-6}\text{ V}$ 。计算得到的信噪比 $\text{SNR}=2784.2$, 相应的探测极限为 0.18 ppm 。利用自行编写的程序, 对获得的信号进行在线 Kalman 滤波。如图 8, 在预测方差为 9.7 , 过程方差为 3 时, 滤波效果显著。经过 Kalman 滤波程序后, 在 500 ppm 条件下测量出的信号为 18.8 mV , 噪声的标准差 1σ 改善为 $5.07\times 10^{-6}\text{ V}$ 。滤波后的探测信噪比提高至 3708.1 , 探测极限提高至 0.13 ppm , 探测性能提高了 27% 。

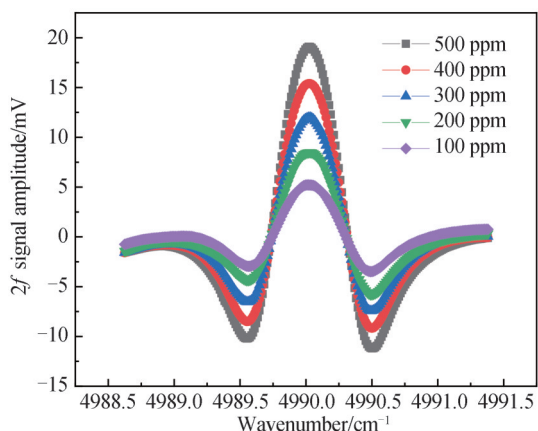


图 6 二次谐波信号与 CO_2 浓度之间的关系
Fig. 6 $2f$ signal amplitude as the function of CO_2 concentration

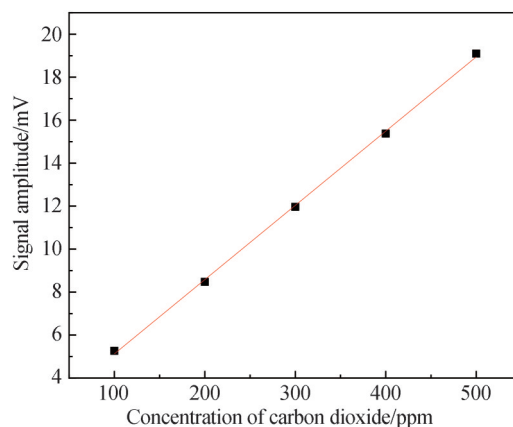


图 7 TDLAS 信号幅值与 CO_2 浓度之间的关系
Fig. 7 Relationship between TDLAS signal amplitude and CO_2 concentration

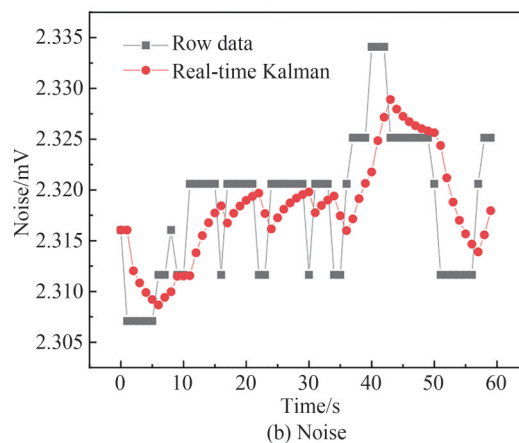
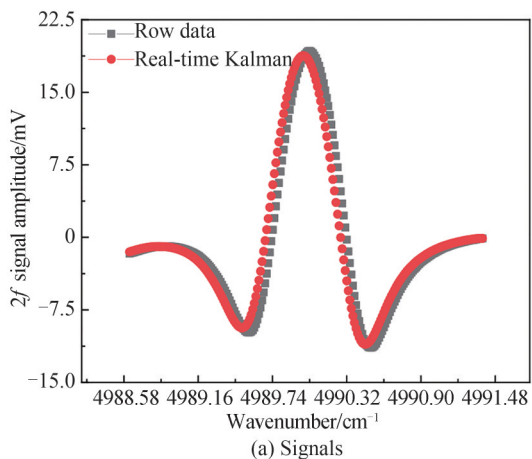


图 8 原始和实时 Kalman 处理后的信号与噪声
Fig. 8 Raw and real-time Kalman processed signals and noise

3 实测

3.1 室内 CO_2 浓度监测

二氧化碳浓度是一个室内宜居性的重要指标。在高浓度二氧化碳环境中, 人的决策能力会显著下

降^[33],明显降低人类健康和幸福感,并会使人感到疲惫和注意力不集中^[34]。为了评估实验室内二氧化碳浓度变化,对暨南大学实验室的二氧化碳含量进行时长为8 h的连续监测,结果如图9所示。

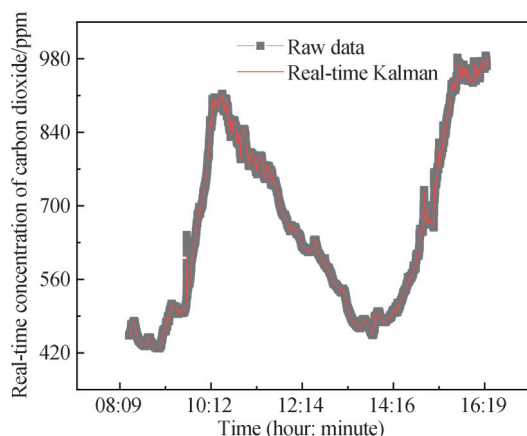


图9 实验室内8 h连续监测 CO_2 浓度随时间变化

Fig. 9 8 h continuous monitoring of CO_2 concentration over time in the laboratory

由于实验室是一个封闭的环境,其二氧化碳浓度变化主要受人员活动的影响。在9:00以前,实验室人员较少,二氧化碳浓度为429 ppm。随着被测实验室内实验人员的增多,二氧化碳浓度显著上升,其峰值达到913 ppm。午休期间,由于实验人员较少,二氧化碳浓度回落至454 ppm。

3.2 室外 CO_2 浓度监测

人类活动以及植物的光合作用对环境中的二氧化碳含量会产生显著影响。为了连续监测暨南大学理工楼顶附近的二氧化碳浓度,采用基于 $2\ \mu\text{m}$ 激光二极管和Herriott多光程吸收池的高灵敏二氧化碳气体传感器进行24 h的实时监测。结果如图10所示,空气中二氧化碳浓度在8点40分达到最大值450 ppm,而在14点28分达到最小值395 ppm。据考察,暨南大学理工学院蒙民伟楼地处较为复杂的地理位置,位于广州东部出口的主干道黄埔大道附近,有着较大的车流量且经常拥堵;同时,在楼的东南方向,存在地铁站的施工、建造;正西方是车流量复杂的华南快速路。因此,在白天和夜晚,二氧化碳传感器测量得到的结果显示二氧化碳浓度并不是一个相对平滑的数据。在多重因素的相互作用之下,二氧化碳的浓度随人类活动及周围植物的作用有较大的变化。

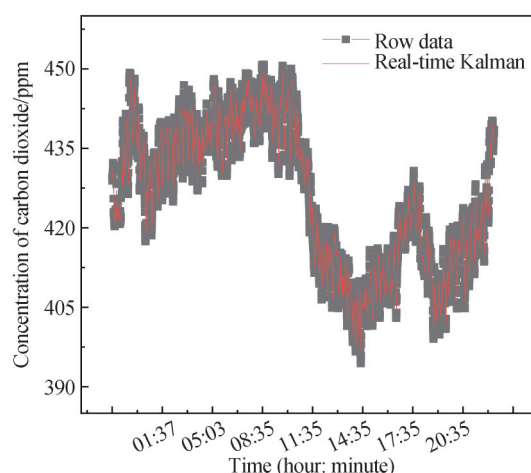


图10 暨南大学理工楼楼顶24 h连续监测 CO_2 浓度随时间变化

Fig. 10 24 h continuous monitoring of CO_2 on the roof of the Jinan University Science and Engineering Building

4 结论

本文设计了一种基于 $2\ \mu\text{m}$ 激光二极管和Herriott多光程吸收池的高灵敏二氧化碳气体传感器,该传感

器的核心器件是由两个中心相距 54 mm 的凹面镜构成 Herriott 池,有效光程为 2.6 m。使用 2 μm DFB 中红外激光器对不同浓度的二氧化碳进行测量,拟合的决定系数为 0.999,表明二氧化碳浓度和信号之间有着很好的线性关系。选择目标吸收线为 4 989.9 cm^{-1} ,当调制深度为 10 mA,积分时间为 1 s 时,系统的探测极限达到 0.18 ppm。系统实时 Kalman 滤波得到探测极限为 0.13 ppm,提高了 27 %。最后采用传感器分别进行了室内 8 h 和室外 24 h 的二氧化碳浓度连续监测,结果表明系统有较强的稳定性、鲁棒性和可靠性。

基于光谱吸收的高灵敏度二氧化碳传感器有着响应速度快、可以实时测量、系统鲁棒性强等优点。通过增加一个 Herriott 多光程吸收池进行光路的折叠,明显减少整个系统的体积,实现了小型化,这利于实现室内宜居性的检测要求。同时多光程可以有效提高空间分辨率,便于提高车载巡航、无人机巡航中空间测量的分辨率。

参考文献

- [1] GRAHAM D Y, KLEIN P D. Accurate diagnosis of Helicobacter pylori: 13C-urea breath test [J]. *Gastroenterology Clinics of North America*, 2000, 29(4): 885-893.
- [2] WANG Wenting, ZHOU Wenzhao, WANG Sheng, et al. Accuracy of breath test for diabetes mellitus diagnosis: a systematic review and meta-analysis [J]. *BMJ Open Diabetes Research and Care*, 2021, 9(1): e002174.
- [3] DELLERT S F, NOWICKI M J, FARRELL M K, et al. The 13C-xylose breath test for the diagnosis of small bowel bacterial overgrowth in children [J]. *Journal of Pediatric Gastroenterology and Nutrition*, 1997, 25(2): 153-158.
- [4] CHEN Qiong, ZHANG Hongyu, LAU Y Y, et al. Climate change, carbon peaks, and carbon neutralization: a bibliometric study from 2006 to 2023 [J]. *Sustainability*, 2023, 15(7): 5723.
- [5] YANG Dongxu, HAKKARAINEN J, LIU Yi, et al. Detection of anthropogenic CO₂ emission signatures with TanSat CO₂ and with Copernicus Sentinel-5 Precursor (S5P) NO₂ measurements: first results [J]. *Advances in Atmospheric Sciences*, 2023, 40(1): 1-5.
- [6] FISHER R, LOWRY D, WILKIN O, et al. High-precision, automated stable isotope analysis of atmospheric methane and carbon dioxide using continuous-flow isotope-ratio mass spectrometry [J]. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry*, 2006, 20(2): 200-208.
- [7] WANG Ming, ZENG Limin, LU Sihua, et al. Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds [J]. *Analytical Methods*, 2014, 6(23): 9424-9434.
- [8] MA Yufei, LIANG Tiantian, QIAO Shunda, et al. Highly sensitive and fast hydrogen detection based on light-induced thermoelastic spectroscopy [J]. *Ultrafast Science*, 2023, 3: 0024.
- [9] ZHANG Zhihao, ZHANG Fangbo, XU Bo, et al. High-sensitivity gas detection with air-lasing-assisted coherent raman spectroscopy [J]. *Ultrafast Science*, 2022: 9761458.
- [10] HU Mai, CHEN Bing, YAO Lu, et al. A fiber-integrated CRDS sensor for in-situ measurement of dissolved carbon dioxide in seawater [J]. *Sensors*, 2021, 21(19): 6436.
- [11] MA Yufei, HE Ying, YU Xin, et al. HCl ppb-level detection based on QEPAS sensor using a low resonance frequency quartz tuning fork [J]. *Sensors and Actuators B: Chemical*, 2016, 233: 388-393.
- [12] GONG Zhenfeng, CHEN Ke, CHEN Yewei, et al. Integration of T-type half-open photoacoustic cell and fiber-optic acoustic sensor for trace gas detection [J]. *Optics Express*, 2019, 27(13): 18222-18231.
- [13] ZHENG Chuantao, HU Lien, ZHENG Kaiyuan, et al. Quartz-enhanced photoacoustics and photothermal spectroscopy for gas sensing and application [C]. *2021 IEEE 6th Optoelectronics Global Conference (OGC)*, IEEE, 2021: 87-90.
- [14] CHEN Ke, WANG Nan, GUO Min, et al. Detection of SF₆ gas decomposition component H₂S based on fiber-optic photoacoustic sensing [J]. *Sensors and Actuators B: Chemical*, 2023, 378: 133174.
- [15] WANG Qiang, WANG Zhen, REN Wei. Wavelength-stabilization-based photoacoustic spectroscopy for methane detection [J]. *Measurement Science and Technology*, 2017, 28(6): 065102.
- [16] YIN Xukun, SU Yongliang, XI Teli, et al. Research progress on photoacoustic SF₆ decomposition gas sensor in gas-insulated switchgear [J]. *Journal of Applied Physics*, 2022, 131(13): 130701.
- [17] HUANG Ruobin, LIN Leqing, WANG Chenglong, et al. Quartz-enhanced photoacoustic spectroscopy-conductance spectroscopy for gas mixture analysis [J]. *Analytical Chemistry*, 2023, 95: 9575-9580.
- [18] LIN Haoyang, ZHENG Huadan, MONTANO B A Z, et al. Ppb-level gas detection using on-beam quartz-enhanced photoacoustic spectroscopy based on a 28 kHz tuning fork [J]. *Photoacoustics*, 2022, 25: 100321.
- [19] LIN Leqing, LIN Haoyang, WANG Chenglong, et al. Highly-sensitive H₂O sensor exploiting a 1.39 μm near-infrared distributed-feedback laser diode [J]. *Journal of Russian Laser Research*, 2022, 43: 590-594.
- [20] CUI Ruyue, DONG Lei, WU Hongpeng, et al. Three-dimensional printed miniature fiber-coupled multipass cells with

- dense spot patterns for ppb-level methane detection using a near-IR diode laser[J]. *Analytical Chemistry*, 2020, 92(19): 13034-13041.
- [21] LINS B, ZINN P, ENGELBRECHT R, et al. Simulation-based comparison of noise effects in wavelength modulation spectroscopy and direct absorption TDLAS[J]. *Applied Physics B*, 2010, 100: 367-376.
- [22] WANG Fei, JIA Shuhai, WANG Yonglin, et al. Recent developments in modulation spectroscopy for methane detection based on tunable diode laser[J]. *Applied Sciences*, 2019, 9(14): 2816.
- [23] CHEN Jianhong, SUN Chaoyue, LIN Zhiqiang, et al. Research on CO₂ concentration detection method based on TDLAS technology[J]. *Journal of Electronic Measurement and Instrumentation*, 2022, 36(6): 229-235.
陈剑虹, 孙超越, 林志强, 等. 基于TDLAS技术的CO₂浓度检测方法研究[J]. *电子测量与仪器学报*, 2022, 36(6): 229-235.
- [24] ZHAO Chenglong, HUANG Danfei, LIU Zhiying, et al. Measurement of trace CO₂ concentration with open-path TDLAS-WMS technology[J]. *Acta Photonica Sinica*, 2022, 21(2): 0230001.
赵成龙, 黄丹飞, 刘智颖, 等. 开放型TDLAS-WMS技术CO₂痕量气体检测[J]. *光子学报*, 2022, 51(2): 0230001.
- [25] FENG Shiling, CUI Qi, GUO Xinqian, et al. Optical fringes removal in TDLAS based on wavelet denoising[J]. *Journal of Atmospheric and Environmental Optics*, 2022, 17(3): 328-335.
冯仕凌, 崔琪, 郭心骞, 等. 小波降噪对TDLAS干涉抑制的研究[J]. *大气与环境光学学报*, 2022, 17(3): 328-335.
- [26] GU Mingsi, CHEN Jiajin, MEI Jiaoxu, et al. Open-path anti-pollution multi-pass cell-based TDLAS sensor for the online measurement of atmospheric H₂O and CO₂ fluxes[J]. *Optics Express*, 2022, 30(24): 43961-43972.
- [27] LI Hengkuan, PU Heng, WANG Peng, et al. Development of high precision CO₂ detection system based on near infrared absorption spectroscopy[J]. *Infrared and Laser Engineering*, 2023, 52(3): 115-121.
李恒宽, 朴亨, 王鹏, 等. 基于近红外吸收光谱技术的高精度CO₂检测系统的研制[J]. *红外与激光工程*, 2023, 52(3): 115-121.
- [28] KONG Rong, MA Ningyi, LIU Peng, et al. Dual trace gas detection using a compact two-channel multipass cell with dense and line spot patterns[J]. *Heliyon*, 2023, 9(2): e13677.
- [29] LIU Chang, XU Lijun, CAO Zhang. Measurement of nonuniform temperature and concentration distributions by combining line-of-sight tunable diode laser absorption spectroscopy with regularization methods [J]. *Applied Optics*, 2013, 52(20): 4827-4842.
- [30] HITRAN online [EB/OL]. [2021-03-10]. <https://hitran.org>.
- [31] XIN Jianguo, DUNCAN A, HALL D R. Analysis of hyperboloidal ray envelopes in Herriott cells and their use in laser resonators[J]. *Applied Optics*, 1989, 28(21): 4576-4584.
- [32] LIN Haoyang, HUANG Zhao, LIU Yihua, et al. Ultra-compact QEPAS acoustic detection module with acoustic wave confinement[J]. *Infrared Physics & Technology*, 2020, 106: 103278.
- [33] SATISH U, MENDELL M J, SHEKHAR K, et al. Is CO₂ an indoor pollutant? Direct effects of low-to-moderate CO₂ concentrations on human decision-making performance[J]. *Environmental Health Perspectives*, 2012, 120(12): 1671-1677.
- [34] KAJTÁR L, HERCZEG L. Influence of carbon-dioxide concentration on human well-being and intensity of mental work [J]. *Quarterly Journal of the Hungarian Meteorological Service*, 2012, 116(2): 145-169.

Highly Sensitive Carbon Dioxide Gas Sensor Based on 2 μm Laser Diode and Herriott Multi-pass Absorption Cell (Invited)

WANG Chenglong¹, XIE Jiabao¹, ZHUANG Ruobin¹, LIN Haoyang¹, LIN Leqing¹,
CUI Ruyue², WU Hongpeng², ZHENG Huadan¹, DONG Lei²

(1 Department of Optoelectronic Engineering, College of Science and Technology, Jinan University,
Guangzhou 510632, China)

(2 State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy,
Shanxi University, Taiyuan 030006, China)

Abstract: The measurement of carbon dioxide plays a very important role in breath diagnostics, monitoring industrial safety, monitoring greenhouse gases, observing industrial chemical reactions, measuring combustion completeness, and avoiding fires. Tunable Diode Laser Absorption Spectroscopy (TDLAS) technology has the advantages of high selectivity, high sensitivity, and strong anti-interference ability. The

TDLAS systems with a multi-pass cell increase the minimum detection limit by increasing the length of the absorption path. Increasing the absorption path has strict requirements on the divergence characteristics of the laser, and requires enough space. By designing the multi-pass absorption cell, the requirements on optical beam quality can be reduced. The volume of the system can be compressed, and the spatial resolution of the measurement can be improved. In this paper, a highly-sensitive carbon dioxide gas sensor based on a 2 μm laser diode and a Herriott multi-pass absorption cell is designed. The basic parameters of the Herriott multi-pass absorption cell are calculated by paraxial approximation. The solution includes the incident position and the incident angle of the incident light, and the distance between the two spherical concave mirrors. According to the simulation results, a Herriott type multi-path absorption cell is fabricated. The multi-pass cell can fold the optical path with an optical path length of 2.6 m within a length of 54 mm. The minimum detection limit of the system is related to the absorption line intensity of the selected absorption peak. In order to reduce the cost of the system, a distributed feedback laser diode with a center wavelength of 2.004 μm is used to cover the strong absorption line of carbon dioxide molecules at 4 989.9 cm^{-1} . The second harmonic signal with zero background noise at the detection frequency can be detected by $2f$ -wavelength modulation spectroscopy technology. This technique effectively reduces the noise of the system. The signal measured by the system has white noise, and the method of signal averaging requires a long measurement time. A self-programming real-time Kalman filtering technology on the software level helps to improve the anti-interference ability of the system. Interference by background white noise and abrupt changes to the signal can be avoided. The experimental results show that with the developed TDLAS sensor, the minimum detection limit for carbon dioxide can reach 0.18×10^{-6} with an integration time of 1 s. After the self-programmed real-time Kalman filter, the minimum detection limit can be further improved to 0.13×10^{-6} , resulting in an increase of $\sim 30\%$. The TDLAS sensor was used to continuously monitor the indoor carbon dioxide concentration for 8 h. An outdoor 24 h continuous monitoring for carbon dioxide concentration on the building roof of Jinan University. This work demonstrates the stability and robustness of the developed TDLAS sensor. The sensor can respond in real time to changes of carbon dioxide concentration in the ambient air. The real-time Kalman filter carried by the system has better stability, which can effectively improve the minimum detection limit of the system.

The optical multi-pass can be accurately designed by the method of paraxial and non-paraxial approximation. In the next work, a dense multi-pass absorption cell can be designed to fold longer optical paths between the same two mirror. However, the light spot of the dense multi-pass absorption cell will become irregular with the increase of the number of reflections. In this case, the incident hole and exit hole of the cell need to be manufactured with higher precision. If the multi-passed light cannot pass through the exit hole completely, the interference of the absorption cell will increase resulting in a decrease in signal to noise ratio. The Herriott multi-path absorption cell can avoid this problem very well.

Key words: Spectroscopy; Tunable diode laser absorption spectroscopy; Multipass-cell; Herriott cell; Carbon dioxide sensor

OCIS Codes: 300.6360; 280.1120; 300.6390

Foundation item: National Natural Science Foundation of China (Nos. 62375111, 62005105, 12174156, 12174155, 62105125, 62075088, 62175137), National Key Research and Development Program of China (Nos. 2021YFB2800801, 2019YFE0118200), Natural Science Foundation of Guangdong Province (Nos. 2020B1515020024, 2019A1515011380), Key-Area Research and Development Program of Guangdong Province (No. 2019B010138004), Foundation for Distinguished Young Talents in Higher Education of Guangdong (No. 2018KQNCX009), the Science and Technology Projects of Guangzhou (No. 202102020445), Aeronautical Science Foundation of China (No. 201808W4001), Project of Guangzhou Industry Leading Talents (No. CXLJTD-201607), the Fundamental Research Funds for the Central Universities (Nos. 21619402, 11618413), Fund of State Key Laboratory of Applied Optics (No. SKLAO-201914), Special Funds for the Cultivation of Guangdong College Students' Scientific and Technological Innovation (No. pdjh2023a0052)