

可调谐二极管激光吸收光谱技术的应用研究进展

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摘要 随着半导体激光器的发展,可调谐二极管激光吸收光谱(TDLAS)技术有了巨大的进步,应用领域迅速扩大。已经有超过 1000 种 TDLAS 仪器应用于连续排放监测以及工业过程控制等领域,每年全球出售的 TDLAS 气体检测仪器占据了红外气体传感检测仪器总数的 5%~10%。运用 TDLAS 技术,已经完成了几十种气体分子的高选择性、高灵敏度的连续在线测量,实现了不同领域气体浓度、温度、流速、压力等参数的高精度探测,为各领域的发展提供了重要的技术保障。本文综述了 TDLAS 技术气体检测的原理以及最近的应用研究进展,主要从大气环境监测、工业过程监测、深海溶解气体探测、人体呼吸气体测量、流场诊断以及液态水测量六个应用领域进行介绍。

关键词 可调谐二极管激光吸收光谱(TDLAS); 大气环境监测; 工业过程检测; 呼吸气检测; 流场诊断; 深海溶解气体探测; 液态水测量

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Research Progress on the Application of Tunable Diode Laser Absorption Spectroscopy

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Abstract With the development of semiconductor lasers, tunable diode laser absorption spectroscopy (TDLAS) technology has achieved great development and rapid expansion of application fields. There have been more than 1000 kinds of TDLAS instruments, which are applied to continuous emission monitoring and industrial process control fields. According to the statistics, 5%-10% of all infrared gas sensors based on TDLAS technology are sold in the world every year. Dozens of gases are measured on-line with high sensitivity and precision by the TDLAS technology, and gas parameters, including concentration, temperature, velocity and pressure, are also determined, which provide important technical support for the development of various fields. This article reviews the principle and recent research of TDLAS technology, with introduction from six application fields, such as atmospheric environmental monitoring, industrial process monitoring, deep sea dissolved gases detection, breath analysis, flow field diagnosis, and liquid water measurement.

Key words tunable diode laser absorption spectroscopy (TDLAS); atmospheric environmental monitoring; industrial process detection; breath analysis; flow field diagnosis; deep sea dissolved gases detection; liquid water measurement

OCIS codes 300.1030; 300.6260; 140.3600; 120.1740

1 引言

气体组分浓度与状态参数(温度、压力、流速

等)的准确测量在许多领域都具有非常重要的作用,例如,在大气环境监测领域,大气污染物浓度测量是空气质量评估^[1-3]、污染防治^[4]的首要基

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础;在工业过程控制中,中间产物排放的连续检测^[5]、气体泄漏检测^[6-7]对产品质量、环境保护及安全生产等都具有重要作用;在燃烧流场诊断中,对燃烧温度、产物浓度以及流速测量^[8-10],是提高燃烧效率以及评估发动机性能的重要手段;在风洞试验中^[11],流场参数的精确测量是保证风洞试验有效性不可或缺的手段;在深海探测中,对深海溶解气体及其同位素精确检测,是了解深海热液和冷泉系统的关键途径,也是了解深海极端环境的窗口^[12];人体呼吸气体检测,能实现对人体疾病的快速无损检查^[13];对液态水(例如水膜、油膜)的实时快速测量,是了解液膜形成过程及蒸发现象的有效方法^[14]。而传统气体测量方法存在着一些弊端,限制了其在实际气体测量中的应用,例如质谱法^[15]响应速度慢,仪器体积质量较大,价格较高,很难实现原位在线测量;气相色谱法^[16]无法实现原位在线测量;电化学传感^[17]通常含有有毒有害材料,而且重复性差。光谱学方法利用气体分子对光的吸收、发射及散射的原理工作,具有非接触、快速响应、良好选择性等优点,能较好满足不同环境条件下气体测量的要求。

针对气体检测的需要,国内外发展了多种基于光谱学的气体探测方法^[18]。主要有激光诱导荧光(LIF)^[19-20]、拉曼光谱法(Raman)^[21-22]、傅里叶变换红外光谱(FTIR)^[23-24]、非色散红外光谱(NDIR)^[25-26]、光声光谱(PAS)^[27-29]、差分吸收光谱(DOAS)^[30-32]、激光雷达(LIDAR)^[33]、腔增强吸收光谱(CEAS)^[34-35]、腔衰荡光谱(CRDS)^[36-37]以及可调谐二极管激光吸收光谱(TDLAS)^[38-40]。其中 TDLAS 技术采用可调谐二极管激光器,通过改变激光器输入电流或温度来调谐激光器输出波长,使其扫描气体分子单根或多根完整的吸收线,获得高分辨率的气体吸收光谱,对光谱进行分析获得气体参数信息。与其他气体检测方法对比,TDLAS 技术有如下特点:原位、连续、实时测量;环境适应性强(能适应高温高压、低温低压、高湿、高流速、腐蚀性环境);选择性强(测量目标气体光谱受到其他气体吸收光谱干扰小);灵敏度高(检测限可达到 10^{-9} 量级);可靠性高;成本低,使用过程没有消耗品;无需预处理,免标定测量;操作简单,数据处理简便快速;易于小型化,非常适合实际工程应用。

近年来,国内外的研究机构对 TDLAS 技术在气体传感探测方面进行了大量的理论及应用研

究。本文首先对 TDLAS 技术气体测量的原理及方法、各类激光器特性以及典型激光波长对应的气体检测限进行介绍,其次针对 TDLAS 技术在大气环境监测、工业过程监测、深海溶解气体探测、人体呼吸气体测量、流场诊断以及液态水测量六个应用领域的最新应用及存在的挑战进行综述,最后展望 TDLAS 技术在气体检测领域的发展与应用。

2 TDLAS 技术原理

2.1 红外波段气体分子吸收光谱

一般来说,红外光谱为分子的振动跃迁光谱^[41]。图 1 为根据 HITRAN 数据库^[42]模拟的部分气体分子在近红外和中红外波段的光谱带。

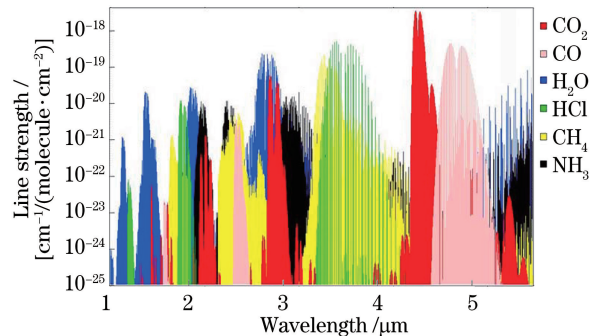


图 1 根据 HITRAN 数据库模拟部分气体的吸收线
Fig. 1 Absorption spectra of several gas molecules, data from spectroscopic database HITRAN

红外波段包含了大量气体分子基频、泛频及合频谱带,所以具有大量的跃迁吸收线。HITRAN^[42]、HITEMP^[43]及 GEISA^[44]光谱数据库较详细地列出了各吸收谱线的光谱参数。由于数据库中光谱参数部分是理论计算的结果,与实际环境情况存在一定的误差。所以,国内外研究者在实验室利用可控式实验仪器,模拟不同环境,对各种气体的光谱参数进行了实际测量。例如, Mondelain 等^[45]运用 TDLAS 技术,测量得到了 4 条 CH_4 气体 $\nu_2 + \nu_4$ 吸收谱线的线强、展宽系数、压窄系数和压力频移系数;王敏锐等^[46]利用 TDLAS 技术测量了二氧化碳和一氧化碳在 $1.5 \mu\text{m}$ 附近, $300 \sim 800 \text{ K}$ 温度范围的线强值,并用配分函数、振动跃迁矩平方实验值以及 Herman-Wallis 系数计算得到线强值,实验值、计算值及 HITRAN 数据库值对比,偏差小于 3%;Ding 等^[47]利用高灵敏的腔衰荡吸收光谱及傅里叶变换吸收光谱技术,测量了 CO_2 同位素的吸收线的位置,得到大量 HITRAN 数据库中没有列出

的吸收线; Pogány 等^[48-49]利用 TDLAS 技术, 测量了 CO₂ 在 2.7 μm 附近的吸收线线强以及 1.4~2.7 μm 波段 H₂O 吸收线的线强值; 聂伟等^[50-51]利用 TDLAS 技术测量了常温下 NH₃ 及低温 H₂O 吸收线的线强值及自展宽系数; 王贵师等^[52]测量了 1.65 μm 附近的乙烷分子吸收光谱线的中心位置及线强值, 这对于提高 TDLAS 气体探测精度具有重要的作用。

图 1 中所示的光谱线都有特定的线宽和线型。影响光谱展宽的因素很多, 主要有自然展宽、多普勒展宽和高斯展宽。不同的展宽机制, 可以用不同的线型模型 $\varphi(\nu)$ 对光谱进行描述。高温低压环境下, 分子运动的多普勒效应对光谱展宽起主导作用, 这种情况一般采用高斯线型对光谱进行描述; 低温高压环境下, 分子运动时的碰撞展宽效应对光谱展宽起主导作用, 这种情况一般采用洛伦兹线型对光谱进行描述^[53]; 对于一般环境, 需同时考虑洛伦兹展宽与高斯展宽的作用。当不考虑洛伦兹展宽与高斯展宽之间的相互作用时, 仅对两者作卷积处理, 会得到 Voigt 线型模型^[54-55]。当考虑洛伦兹展宽与高斯展宽之间的耦合作用时, 有两种不同的物理机制来描述该耦合作用: Dicke 效应和速度依赖效应^[56-57], 这时有软球碰撞假设的 Galatry 线型和硬球碰撞的 Rautian 线型、速度依赖 Voigt 线型、速度依赖 Galatry 线型和速度依赖 Rautian 线型^[58-60] 以及 The Hartman-Tran 线型^[61] 来对光谱轮廓进行描述。

2.2 激光器

激光器作为激光气体传感器的光源, 应该具备紧凑、稳定、寿命长以及输出功率高等特点; 同时, 由于 TDLAS 技术需要扫描气体的单根或多根完整的吸收线, 要求激光器线宽远小于吸收光谱线宽。在实际 TDLAS 气体检测应用中, 使用较多的激光器有分布反馈 (DFB) 二极管激光器、垂直腔表面发射激光器 (VCSELs)、外腔二极管激光器 (ECDL)、带间级联激光器 (ICL) 和量子级联激光器 (QCL)。一般采用蝶形、TO、C-mount 或高热负载 HHL (High Heat Load) 方式封装, 并且含有一个波长选择器件 (例如光栅) 使其发射出特定波长的光。近红外 DFB 激光器典型的输出功率在 10 mW 左右, 带宽 2 MHz 左右, 工作波长范围一般在 730~3000 nm^[62-64], 可在室温环境下工作, 无需制冷, 一般能带尾纤输出。近红外 ECDL 是通过腔外光栅运动来调谐激光器输出波长, 实现更宽范围的连续波长扫描 (例如 1490~1580 nm)^[65-66], 但其调制频

率不高, 偏振噪声大, 不适合气体的快速测量, 通常只适用于实验室。Sonnenfroh 等^[67]利用 ECDL 测量了 1.57 μm 附近的 CO 和 CO₂ 吸收光谱。VCSEL 是沿着激光器表面方向发射激光的, 所以 VCSEL 具有较小的发射角^[68]。Shau 和 Ortsiefer 等^[69-72]在 1.4~2.3 μm 波长范围运用 VCSEL 进行气体测量。与 DFB 相比, VCSEL 具有较宽的调谐范围 (约 5 nm), 较小的阈值电流, 电流调谐率 ($\Delta\lambda/\Delta I$) 远大于 DFB 激光器^[73]。QCL 是中红外波段的激光光源, 输出光功率通常大于 10 mW, 输出线宽约为 7 MHz, 光束发散角通常小于 6 mrad (发散全角), 工作波长一般在 4.5~17 μm^[74]。由图 1 可以看出, 一般中红外波段的吸收线强要大于近红外波段的吸收线强, 所以 QCL 非常适合用于痕量气体的探测。但 QCL 工作温度较低, 在室温环境使用时需要附加合适的制冷装置^[75] (例如热电制冷装置), 而且一般不带尾纤输出。目前 QCL 已广泛应用于痕量气体探测^[76-78]。ICL^[79-80]与 QCL 不同之处在于光子产生的机制是带间跃迁而非子带间跃迁, 这使得 ICL 工作波长更短, 填补了 ECDL 与 QCL 工作波长之间的空白, 当前, 商用 ICL 在常温下连续波工作时波长覆盖范围可达 3~6 μm。

激光器频率稳定是 TDLAS 气体传感器性能稳定的前提, 通常可以通过艾伦方差^[81]对激光器频率稳定性进行分析, 采用激光器温度补偿等方法^[82-83]对激光器的频移现象进行修正。由于单只激光器的调谐范围较小 (DFB: 1~2 nm, VCSEL: 5~10 nm), 为了满足多种气体探测的需要, 发展了波分复用技术、时分复用技术及频分复用技术等^[84-85]。但是在某些波段处, 一个激光器能同时覆盖多种气体的吸收线, 能实现多种气体同时测量^[86]。在实际测量中, 需根据实际环境状态 (温度、浓度、压力等), 选择合适的激光器进行测量, Zhou 等^[84, 87]详细介绍了吸收线选择要求及方法。

2.3 检测限

TDLAS 技术通过选用不同激光波长, 可以实现不同气体的检测。对于同一种气体测量, 选用不同波长能获得不同的检测极限, 假设最小的可探测吸光度为 10^{-5} , 带宽为 1 Hz, 有效吸收光程为 1 m, 各种气体探测的典型波长与浓度检测限如表 1 所示。

利用中红外调制光谱技术与长光程结合, 能使浓度检测限继续降低至 10^{-12} 量级^[89]。文献^[90-92]也给出了不同气体的检测限。

表 1 TDLAS 技术的典型浓度检测限^[88]

Table 1 Typical concentration detection limits in TDLAS technology^[88]

Molecule	NIR		MIR		Molecule	NIR		MIR	
	Wavelength /	Typical	Wavelength /	Typical		Wavelength /	Typical	Wavelength /	Typical
	nm	limits /10 ⁻⁶	nm	limits /10 ⁻⁹		nm	limits /10 ⁻⁶	nm	limits /10 ⁻⁹
H ₂ O	1390	0.06	5940	2	SO ₂	—	—	7280	14
CO ₂	1960	3	4230	0.13	CH ₄	1650	0.6	3260	1.7
CO	1570	30	4600	0.75	C ₂ H ₂	1520	0.08	7400	3.5
	2330	0.5	4872	0.005	HF	1310	0.01	—	—
NO	1800	60	5250	5.8	HCl	1790	0.15	3400	0.83
	2650	1	5331	0.14	HBr	1960	0.6	3820	7.2
NO ₂	680	0.34	6140	3	HI	1540	2.1	4391	1.6
N ₂ O	2260	1	4470	0.44	HCN	1540	0.29	6910	12
H ₂ S	1570	20	7328	0.008	H ₂ CO	1930	50	3550	8.4
O ₃	—	—	9500	11	PH ₃	2150	1	10100	6.2
NH ₃	1500	0.8	10300	0.8	O ₂	760	78	—	—

2.4 直接吸收光谱技术

直接吸收光谱技术是 TDLAS 中常用的一种方法,这种方法装置结构简单,信号处理相对简易,测量结果无需标定。

由 Beer-lambert 吸收定律,某条孤立吸收线的积分吸光度可表示为

$$A = \int_{-\infty}^{+\infty} \ln(I_0/I_t) d\nu = P \cdot x \cdot L \cdot S(T), \quad (1)$$

式中: I_0 和 I_t 分别为透射光强和出射光强; A 为积分吸光度; P 为气体总压; x 为目标气体分子的体积分数; L 为有效吸收光程; $S(T)$ 为温度 T 下的吸收线强值。获得高分辨率气体吸收光谱后,运用 Voigt 线型模型进行拟合处理,根据(1)式即可获得气体温度、浓度或压力等信息。温度测量一般有三种方法:多普勒展宽测温法、玻尔兹曼图法以及线强比值法。其中,线强比值法是利用同种气体两条吸收线的线强比为温度的单值函数来反演温度,很容易实现快速计算,是 TDLAS 技术温度测量中采用最多的方法^[93-96]。

浓度测量^[97-99]是通过拟合获得的积分吸光度值或吸收光谱峰值,结合已知的环境总压及有效吸收光程,根据(1)式计算出气体体积分数。流速测量^[100-101]是基于多普勒效应,当气体流速在激光传输方向有速度分量时,会造成气体分子吸收光子,探测器接收吸收峰频率与静态吸收频率会产生频移(多普勒频移),通过频移计算气体流速。

2.5 调制光谱技术

一般而言,由于激光器、探测器以及电子学等噪声的影响,直接吸收技术能探测的最小吸光度在

10^{-3} 量级,对于更小的吸光度探测(例如 10^{-4} 及更小),一般采用调制技术,包括波长调制光谱技术(WMS)^[102]和频率调制光谱技术(FMS)^[103]。与 WMS 和 FMS 不同的调制技术还有双频调制光谱技术^[104],差分检测技术^[105],自动平衡检测技术^[106]等。导数吸收光谱分析技术^[107-108]是利用电子学微分方法对硬件电路中的光谱信号进行微分处理,该方法能将某一痕量气体的光谱从较宽的干扰峰或者其他背景干扰中分离出来,并且能够分辨出吸光度随波长急剧上升所掩盖的弱吸收峰,但其对和吸收频率相近的噪声成分抑制能力较弱。

波长调制技术是将低频扫描锯齿波和高频调制正弦波同时加载至激光器上,被调制的激光光束被气体吸收后到达探测器,然后由锁相放大器解调出透过率各阶次谐波信号,根据二次谐波信号与气体体积分数成正比的关系实现气体体积分数的测量:

$$I_{2f} \propto I_0 \cdot S(T) \cdot P \cdot x \cdot L. \quad (2)$$

当 $S(T)$ 、 P 、 L 已知时,光强归一化后的二次谐波信号 I_{2f} 正比于气体的体积分数 x ,所以在测量时可以采用较为简单的反演方法:在 WMS 测量系统内引入参考光路,并在其中加入参考吸收池,通过在气体吸收池内充入已知浓度的待测气体,并对参考光路的 $2f$ 信号进行测量,从而得出待测光路中气体的体积分数^[109]。

对于那些不易标定的测试环境,需要研究 WMS 免标定测量方法。近几年发展的 WMS 免标定方法主要以 WMS- $2f/1f$ 模型为基础。选择合适的光强和调制频率模型,结合朗伯比尔定律模拟出调制吸收

信号,利用模拟的 $1f$ 归一化的 $2f$ 信号或者扣除背景后的信号拟合相应的测量信号,当调制参数不变时,可将积分吸光度 A 、吸收中心频率 ν_0 、吸收半宽 ν_L 或 ν_D 作为拟合参数,多次迭代之后得到最佳拟合值,从而得到吸收气体的吸收信息^[110-112]。

3 TDLAS 技术的应用研究进展

3.1 大气环境监测

近年来,国家非常重视全球环境和气候变化问题,我国在近 20 年来,气象灾害损失已达到 GDP 的 3%~6%,是世界上经济损失最严重的国家。同时,对大气环境进行监测,了解地球大气状态,为大气环境保护和污染修复提供数据参考,是我国履行国际公约不可回避的义务。

大气温室气体的测量,是研究其浓度变化及源和汇的基础。近地面的温室气体测量不仅需要测量其浓度水平,还需要了解浓度随时间的变化情况。为了更好地了解区域范围温室气体源和汇的分布,有必要研究温室气体在不同区域不同时间范围内的变化情况。对于大型的增汇复杂生态系统,下垫面的非均一性及天气过程的不可重复性,使得温室气体的分布存在较大的时空变异性,故需要分辨率高、监测尺度广、准确性高和可实现尺度转换的自动监

测技术。另外,在气候变化研究中需要的是年增长量的监测,而传统仪器设备只能实现浓度监测。

在大气灰霾方面,二次细颗粒物污染主要是由 NO、NO₂、NH₃、SO₂、VOC 这些前体物相互反应形成的。这些前体物的监测是研究 PM_{2.5} 形成与演化过程的关键^[2]。但这些污染气体,正常空气中体积分数较小(约 10⁻⁹)、变化范围大(10⁻⁹~10⁻⁶)、变化速度快,现有的监测仪器因灵敏度低、响应时间慢、动态范围小等缺点,不能进行准确的测量。

TDLAS 技术光谱分辨率非常高,检测灵敏度较高,非常适合大气环境气体实时连续在线监测。当前,包括中国科学院安徽光学精密机械研究所(以下简称中科院安光所)在内的多家国内外机构利用 TDLAS 技术实现了多种温室气体(例如 H₂O、CO₂、CH₄ 以及 N₂O 等)的天地一体高精度实时测量^[38-41,110,113],同时实现了 NO、NO₂、NH₃、SO₂ 以及 H₂S 等污染气体的测量^[31,36,85,99,114-115] 以及农业和森林等大尺度、大范围的气体监测,为大气气体立体监测提供了重要的技术保障。图 2 为中科院安光所利用 TDLAS-QCL 波长调制光谱技术,在 60 m 开放光路中,对大气中的 NO₂、NH₃ 和 NO 三种气体进行同时连续在线测量的结果^[115],响应时间在 1 s 左右,检测限小于 10⁻⁹。

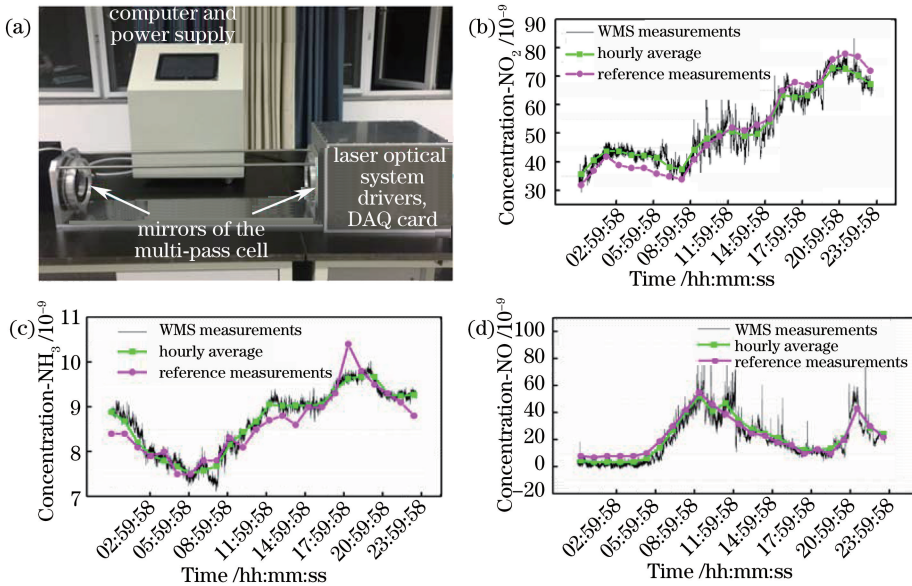


图 2 (a) 基于波长调制光谱技术进行大气气体探测的装置图及 (b) NO₂, (c) NH₃ 和 (d) NO 在线测量的结果^[115]

Fig. 2 (a) Device diagram for atmospheric gas sensing based on wavelength modulation spectroscopy technique and the results of continuous online monitoring of (b) NO₂, (c) NH₃ and (d) NO^[115]

TDLAS 技术为视线平均测量,它测量得到的是光路上的平均浓度。对于大范围的空气质量评估需要进行大范围的采样或移动测量,这增加了测量

过程的复杂性,另外,由于当前可调谐二极管激光器扫描范围具有一定的限制,对多种气体进行检测时需要多个激光器同时工作,这必然会导致仪器成本

较高。未来随着半导体激光器的发展,激光器调谐范围将进一步增加,TDLAS 测量系统的成本将随之降低,其在大气环境监测中的应用规模也将大大增加。

3.2 工业过程应用

在工业生产过程中,为了保证产品质量、生产安全以及工艺效率,需要对生产过程中的气体进行监测。钢铁制造业中,通过实时监测控制电弧炉 O_2 的注入量,以实现脱磷、脱碳、去除杂质及迅速均匀加热至出钢温度的目的^[116-118];火力发电厂中,为了节能减排以及提高发电效率,燃烧气体组分(CO_2 , CO , O_2 , SO_2 等)及温度的测量也非常重要^[119-120];石油化工产业对气体测量有巨大的需求,例如催化裂化过程中 O_2 、 CO_2 、 CO 的测量,合成氨中的 O_2 、 CO_2 、 CO 、 H_2S 、 SO_2 、 CH_4 、 NH_3 等的测量,尿素合成中 O_2 、 CO_2 、 NH_3 的测量以及硫磺回收中 O_2 、 H_2S 、 SO_2 等的测量^[121-122];半导体产业中,为保证精密产品的质量,对反应气体纯度要求极高,需要严格监测杂质气体的浓度^[123];安全生产领域,对氨气逃逸及天然气泄漏进行监测^[124-125],炸药存放过程中对三硝基甲苯等材料分解产生的 NO 和 NO_2 进行实时在线监测^[126]等,是保证安全生产的关键;人们生产生活环境中,尤其是工业园区的恶臭气体^[127](例如:氨、硫化氢、二硫化碳、甲硫醇、甲硫醚、二甲二硫、苯乙烯、三甲胺等)也需要实时准确地

进行监控。

针对工业过程 TDLAS 气体监测,已有大量的研究成果。Pisano 等^[128]利用 TDLAS 技术实现了柴油汽车痕量逃逸氨的测量,浙江大学王飞等^[129]测量了含有颗粒的氨气浓度,Schloser 和 Qu 等^[130-131]利用 TDLAS 技术测量了高温煤燃烧过程中的钾原子浓度,中国石油大学^[132]针对石油天然气开采现场可能泄露的甲烷和硫化氢气体,研制了开放光路下基于 TDLAS 技术的隧道及天然气开采现场甲烷及硫化氢气体复合一体检测装置,Jenkins 等^[133]运用 TDLAS 技术在燃煤电厂中进行了原位温度测量,Walter 等^[134]运用 TDLAS 技术对垃圾焚烧过程产生的气体进行测量,Ebert 等^[135]运用 TDLAS 技术对燃气电厂进行了温度及多组分气体浓度的测量,Hirmke 等^[136]运用 TDLAS 技术检测金刚石生长过程中产生的气体,Chou 等^[137]利用 TDLAS 技术测量了等离子体腐蚀炉中的 HBr ,中科院安光所^[138-143]利用 TDLAS 技术实现了天然气管道泄漏的定量遥测,氨逃逸的在线监测,工业过程产生的 H_2S , CH_4 , O_2 以及燃烧过程产生的 CO , CO_2 等的浓度测量,汽车尾气的路边监测,酒驾遥测等。图 3 是利用 TDLAS 技术与光闪烁互相关技术共同对工业气体排放总量进行测量的装置结构图及测量结果,结果表明该装置可实现工业气体排放管路中的氧气浓度及氧气流速的精确测量。

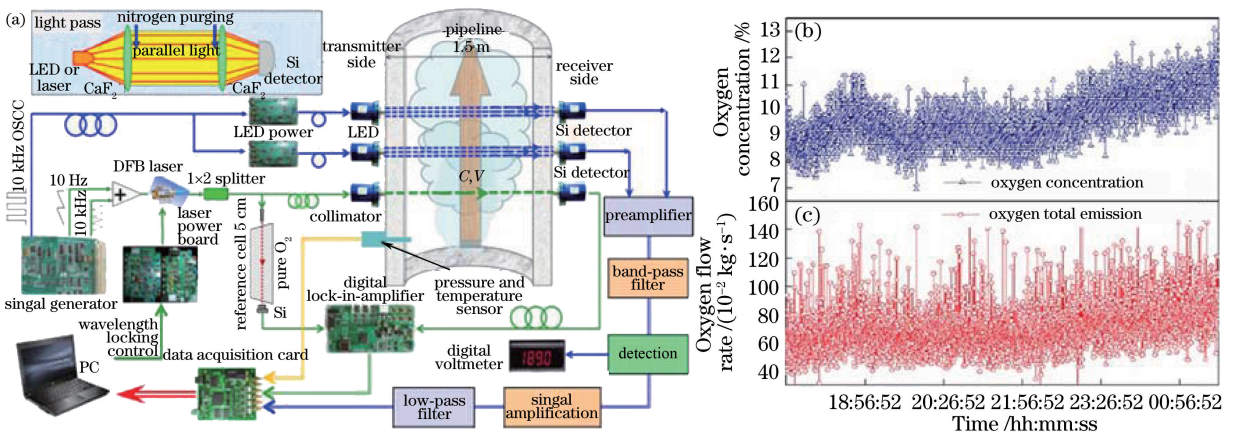


图 3 (a) TDLAS 技术与光闪烁互相关技术结合测量工业总排放装置示意图及(b)氧气浓度及(c)流速测量的结果^[141]

Fig. 3 (a) Schematic diagram of the online total emission measurement experimental setup and the continuous measurement results of (b) oxygen concentration and (c) oxygen flow rate^[141]

TDLAS 技术在工业应用过程中面临的问题主要体现在测量对象及测量环境越来越复杂,从层流到湍流、从清洁火焰到碳烟火焰(气态燃料到液体、固体燃料)、从常/低压强环境到高压强环境、从高

温/常温到极低温环境等;测量的气体组分越来越复杂,需要监测的气体的浓度越来越低。这就对 TDLAS 技术的环境适应性及系统工作的长期稳定性提出了更加严格的要求,同时也对不同气体的检

测限要求越来越低,这就需要更加先进的去噪技术及长光程技术。将来,随着 TDLAS 技术的进一步发展,及其与其他光谱学和非光谱学方法的交叉融合,其在工业领域中发挥的作用将越来越大,应用范围也必然会进一步扩大。

3.3 呼吸气诊断

呼吸气诊断是一种无创、精确且安全的疾病诊断或评估技术,是生物医学工程领域的一个热点发展方向^[144]。通过人体生理或病理状态时呼出气中特定成分的存在与否或含量多少来实现对特定疾病的诊断。现已知呼出气体中一些可被即

刻检测到的挥发性有机物(如烃类、二氧化碳、一氧化氮和一氧化碳等)和可在冷凝后检测到的非挥发性有机物(如 8-异前列腺,过氧化氢、亚硝酸盐和硝基酪氨酸等)是某些呼吸系统疾病的潜在生物标志物^[146]。表 2 是不同疾病对应的分子标志物及 TDLAS 测量的典型波长^[145-150],通过表 2 可以看到利用 TDLAS 技术进行呼吸气在线疾病诊断的巨大应用前景。TDLAS 技术对相关气体浓度进行测量,在分子水平上早期以较低成本发现病原体,且诊断过程无创,对医护人员及病人都非常安全。

表 2 生理症状与对应的气体分子标志物及 TDLAS 激光测量典型波长

Table 2 Physiological symptoms corresponding to their breath biomarker and typical laser wavelengths for TDLAS

Physiological symptom	Breath biomarker	Typical laser wavelength / μm	Detection limit / 10^{-9}	Normal concentration / 10^{-9}
Asthma, hypertension, rhinitis, various air way inflammations	Nitrogen monoxide (NO)	5.26	2	adult < 50 children < 35
Cystic fibrosis, liver failure, acute Rejection of transplanted lungs	Carbonyl sulfide (OCS)	3.3-5.5	0.5	3-30
vitamin E deficiency, chronic Respiratory diseases, cells oxidative stress, scleroderma	Ethane (C_2H_6)	2.6-4.0	0.1	~0.12
Helicobacter Pyroli, oral cavity disease	Ammonia (NH_3)	10-11	1	250-2900
Hyperbilirubina, oxidative stress, respiratory infections, asthma	Carbon monoxide (CO)	4.6-5	10	< 10000 (for smokers: < 20000)
Colonic fermentation, intestinal problems	Methane (CH_4)	3.3-3.5	500	3000-10000

人体的呼吸气中,氮气、氧气、二氧化碳以及氩气占 99%,其余 1%包含约 2000 种以上不同气体,体积分数在 10^{-12} 至 10^{-6} 间^[148,150-151]。目前已有应用 TDLAS 检测技术对部分疾病进行无创检测,并获得了较好的检测效果,例如斯坦福大学 Wang

等^[152]应用中红外吸收光谱技术结合法拉第旋光光谱实现人体呼吸气中浓度较低的 NO 及其同位素测量(装置与实验结果如图 4 所示)。

人体呼吸气温度与环境温度之间存在着差异,使得呼出气中的水汽很容易液化而对测量造成影

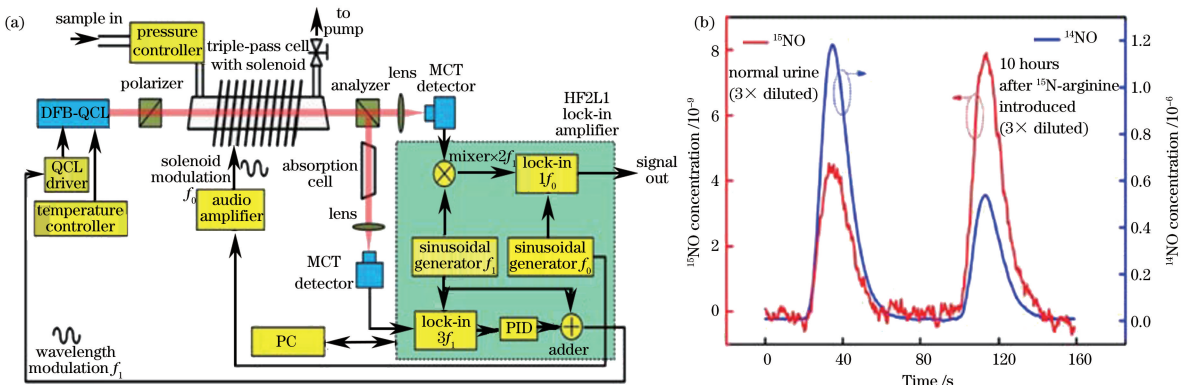


图 4 (a) TDLAS 技术病人呼吸气测量原理图及(b) ¹⁵NO, ¹⁴NO 测量结果^[152]

Fig. 4 (a) Schematic configuration of a TDLAS system and (b) measurement of ¹⁵NO and ¹⁴NO concentration^[152]

响,且不同气体的吸收干扰会影响测量精度,所以疾病与呼出气含量间的定量关系的普适性等是目前TDLAS呼吸气诊断中面临的问题。随着对人体呼吸气与相关疾病关系间的深入研究,以及具有更低检测限能力的TDLAS技术的发展,TDLAS技术呼吸检测未来发展的方向将是实现更多种呼吸气测量以及更多种疾病的无创诊断和评估,同时提高相关仪器的便携性、稳定性与安全性。

3.4 深海溶解气体探测

海洋是大气温室气体(例如甲烷和二氧化碳)的重要排放源,大气中甲烷的2%~4%来源于海洋^[153],因此对深海溶解气体进行的原位测量,对海洋生态系统、碳循环系统的研究以及海底能源的勘探等都具有重要意义^[154]。针对水下溶解气体的原位探测,国内外先后研制了水下质谱仪^[155-156]、半导体气敏传感器^[157]以及非分散红外吸收光谱技术(NDIR)。水下质谱仪无法满足水下长时间的实时准确探测需求;SnO₂半导体气敏传感器因气体在半导体表面发生的氧化还原反应其敏感元件阻值发生变化,所以其测量结果受含

氧量的影响较大,相关仪器的稳定性有待进一步强化;而NDIR技术因采用宽带光源,其抗干扰性和灵敏度会受到限制。

近年来,国内外科研机构将目标瞄向了高分辨的激光光谱探测方法。英国国家海洋中心Boulart^[158]认为光学技术是溶解气体的未来。哈佛大学的Wankel等^[159]利用离轴积分腔输出光谱分析仪(OA-ICOS)在美国蒙特雷湾区域实现了对3000 m海深的冷泉沉积物中CH₄碳同位素的丰度测量,但是测量CH₄浓度的下限只达5×10⁻⁴(如图5所示)。亥姆霍兹海洋研究中心的Arévalo-martínez等^[160]利用离轴积分腔输出光谱分析仪(OA-ICOS)与NDIR测量了深海及大气中的N₂O,CO,CO₂。Gonzalez-Valencia等^[161]利用离轴积分腔输出光谱分析仪(OA-ICOS)测量了溶解气体中的CH₄和CO₂。中国海洋大学利用激光腔衰荡光谱对溶解气体进行了可行性实验研究,取得了一定的研究进展^[162]。法国国家科研中心(CNRS)开发了光学反馈-腔增强吸收光谱技术(OA-CEAS),首次测量了南极冰芯中的CH₄浓度^[163]。

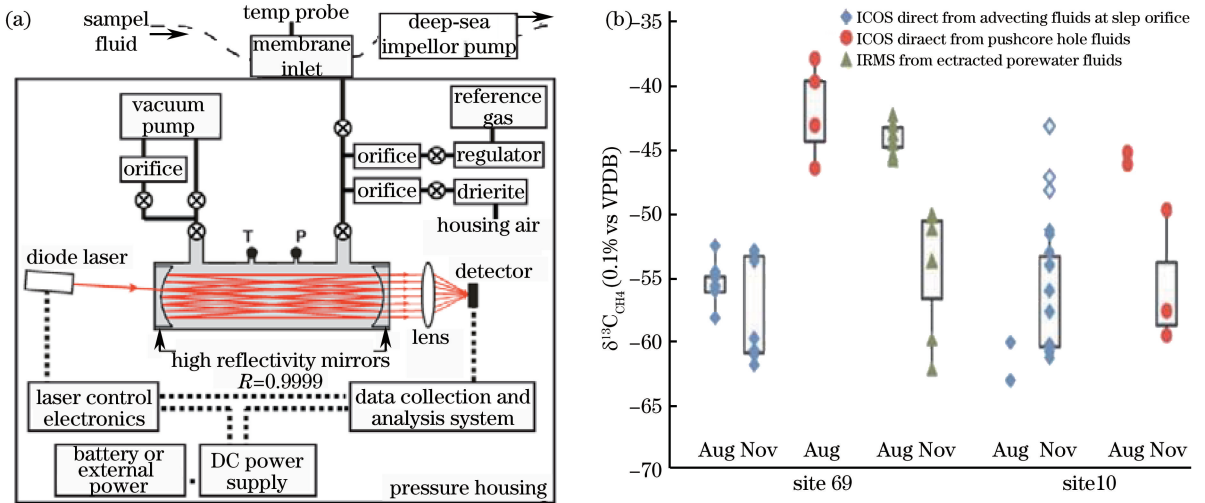


图5 (a)离轴积分腔输出光谱分析仪实验装置图及(b)甲烷稳定同位素测量的结果^[159]

Fig. 5 (a) Schematic of instrument layout and methane carbon stable isotopic composition ($\delta^{13}C_{CH_4}$) measured via the *in situ* ICOS analyzer and (b) a conventional isotope ratio mass spectrometry (IRMS)^[159]

在深海海水溶解气体检测时,对TDLAS技术的耐压能力要求较高,同时要保证海水取样及水汽分离技术的精度。因此,深海溶解气体及其同位素检测中,需要使用气体检测范围宽的TDLAS技术、功率较高的激光器以及成熟的水汽分离技术。

3.5 流场诊断

随着国防事业和航天航空技术的不断发展,航空发动机燃烧流场诊断、性能评估以及风洞流场测

量受到越来越多的关注。传统的流场诊断设备如压力传感器、侵入式探针、热电偶等存在干扰待测流场、响应速度慢、灵敏度低等缺点。此外,很多探测设备无法满足高超音速飞行器在高温、高速等恶劣环境下的工作需求。TDLAS以H₂O、CO₂、CO、O₂等气体组分为探针,可以有效实现发动机燃烧流场以及风洞流场中温度、压力、流速和气体浓度等参数的非侵入式、快速、实时在线测量,为超燃冲压发动

机的气动研究、关键部件实验、地基性能评估、推力计算以及天地一致性验证提供有力的技术支持^[9,11]。

TDLAS 流场诊断在测量维度上分为一维诊断和二维诊断,一维诊断是基于视线平均的测量,测量光路上流场参数(温度、浓度等)的平均值^[8,9,95-98]。这种测量方法装置结构简单,数据处理算法简便,但是只能反映流场状态的视线平均值。二维诊断是随着断层扫描(CT)技术以及扫描系统和图像处理技术的进步而发展起来的,当前断层扫描技术已被广泛应用于流体力学及燃烧诊断领域^[10]。对流场温度及浓度等信息的二维分布进行扫描测量,根据扫描形式可分为移动旋转方式^[164]和空间固定方式^[165]。流场二维诊断较一维测量数据处理算法更复杂,主要有代数迭代(ART)算法^[166-167]、滤波反投影(FBP)算法^[168]、卷积反投影算法^[169]、Abel 变换、最大邻近近似估算法^[170]、超光谱重建法^[171]、虚拟光线方法^[172]等。

美国 Stanford 大学最早在 20 世纪 70 年代开展了激波管流场激光吸收光谱测量研究,先后在实验室开展了激波管中氧气的速度、温度、压力和质量流

量的测量研究,为动力学研究和碳氢燃料分解速率的探测奠定了基础^[173-174]。同时,该小组在实验室和全尺寸发动机的地面测试中都开展了将 TDLAS 技术用于脉冲爆震发动机(PDE)的研究,证明了 TDLAS 技术能成功被应用于恶劣和动态环境中。国内如中科院安光所、中国科学院力学研究所、西北核工业研究所、西北大学、装备指挥学院等单位都开展了燃烧流场 TDLAS 测量,并在地面台架实验研究中进行了应用。目前已经完成了汽化炉^[175]、喷气发动机燃烧室羽流^[176]、激波管^[177]、航空发动机进气道/燃烧室^[178]、超燃冲压发动机隔离段/燃烧室^[179]、高超声速燃烧加热风洞等燃烧设备的温度、组分浓度和速度的测量。图 6 是中科院安光所自主设计的高超声速燃烧加热风洞来流测量系统,采用 TDLAS 技术,以 H₂O 分子为探针,对 6.5 Ma 风洞来流进行现场测量,获得了 0.2 ms 时间分辨高超声速燃烧加热风洞开车过程中来流的流速、温度及 H₂O 分子数浓度,同时检测到了约 60 ms 的波动,与风洞补氧波动对应^[180]。图 7 是 TDLAS 层析成像技术对平焰炉燃烧中水汽的二维温度和浓度重建的结果^[181]。

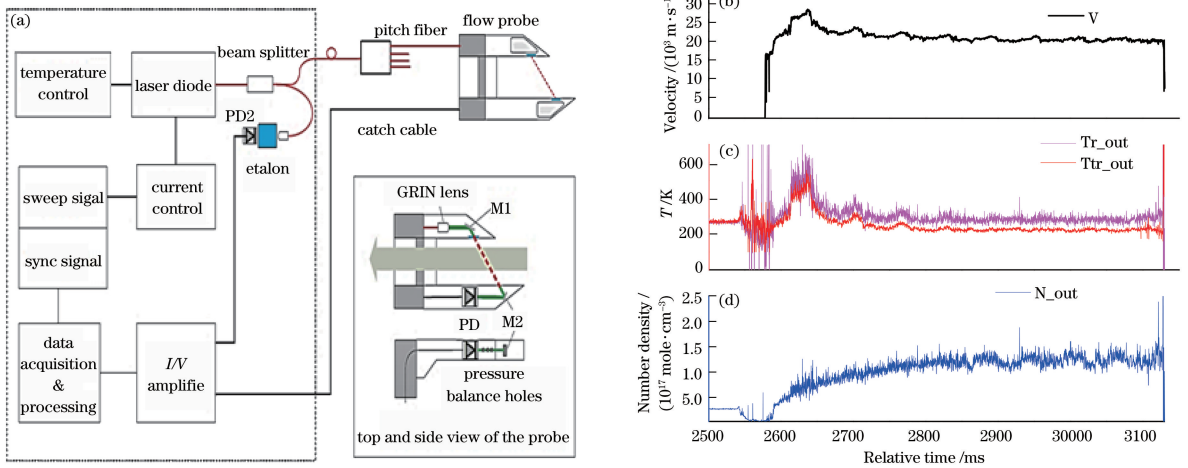


图 6 (a)高超声速燃烧加热风洞来流测量装置^[180]及(b)~(d)测量结果

Fig. 6 (a) Measuring device and (b)-(d) results of hypersonic combustion heating wind tunnel^[180]

当前,TDLAS 技术在燃烧诊断领域已经有了较为成熟的研究结果,但是由于我国在航空航天的迅速发展,对流场测量的需求越来越苛刻,如:从一维测量需求转向高维测量需求,从低重复频率测量需求转向高重复频率测量需求,集成的测量装置转向智能、小型的需求等。这些需求的提升使得 TDLAS 技术需要采用更加先进的测量策略(例如,采用高速采集测量分析超快过程),同时发展更加高

效、智能的算法程序以用于多维重建等。

3.6 液态水测量

对液膜厚度进行定量分析,不仅可以设计和优化工业过程,保证工业过程的安全,也能为仿真模拟提供确切可信的数据,还可以对蒸发现象进行研究,因此液膜的测量广泛地应用于各领域中。例如 Darke 等^[182]针对液体燃料油膜可能导致的碳氢化合物沉积及污染物排放量增加,对直喷发动机活塞

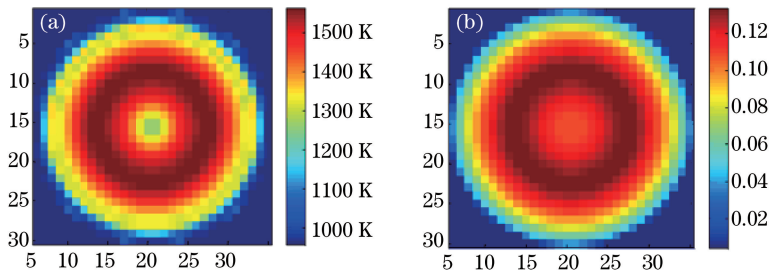


图 7 重建结果。(a)温度二维分布结果;(b)水汽浓度(体积分数)分布的结果^[181]

Fig. 7 Reconstructed distribution results. (a) Temperature; (b) water vapour concentration (volume fraction) ^[181]

表面油膜进行了测量;Hentschel 等^[183]利用激光诱导荧光技术对汽油机进油管道壁面油膜厚度进行了测量;Mawhinney 等^[184-188]利用 TDLAS 技术测量了不同溶液中水膜的厚度。

液态水与气态水不同,液态水由于范德瓦尔斯氢桥键的结合,阻碍了水分子的转动,在近红外光谱范围表现为 O—H 的伸缩振动,又由于 H 原子相对 O 原子较轻,其振动幅度比较大,加上诸多吸收峰的迭加,使得液态水吸收为宽带吸收,而且光谱位置会随着温度的升高而向短波方向移动^[189],Maréchal^[190]详细介绍了液态水在整个红外波段的吸收特性(如图 8 所示)。Hale 等^[191]综述了 0.2~200 μm 范围液态水的吸收光谱,Kou 等^[192]较详细地介绍了 0.65~2.5 μm 范围液态水的吸收光谱。

对于图 8 所示的宽带吸收光谱,由于 TDLAS 技术无法实现某条吸收线的完整扫描,通常采用波长固定 TDLAS 技术:选择多个波长,通过固定激光器温度和电流使其分别发射固定的激光波长,根据所选的不同波长在液态水中的透射系数之比为温度、溶液溶度以及液膜厚度的函数的特性,结合简单的数据处理(对数比等),得到液膜厚度、温度及溶液浓度等信息^[185-189]。

利用光谱学的方法对液态水进行测量,具有高精度、高灵敏度及无干扰等优点。Mouza 等^[193]利用 635 nm 的激光器测量了低至 1 mm 的掺杂亚甲蓝的水膜厚度;Porter 等^[194]发明了一种双波长中红外激光吸收测量技术用于同时测量气态燃料的摩尔分数和油膜厚度;Yang 等^[185-187]采用的 TDLAS 技术,研制了基于波长在 1.4 μm 附近多个 DFB 二极管激光器的 TDLAS 系统,同时测量得到了普通液态水膜厚度、衰减系数、液态水温度及蒸发过程气态水温度。

图 9 所示的是 Yang 等利用 4 个近红外 DFB 激光器的 TDLAS 系统,同时测量液膜厚度(三角形)、蒸发的气相温度(方块)及液态水温度(圆圈),并与热电偶测量结果(空心方块)对比,得到较一致的结

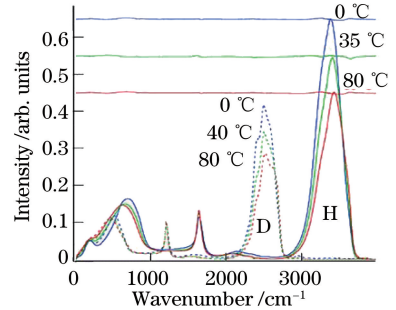


图 8 普通液态水(实线,H 区域)和重水(虚线,D 区域)在三个不同温度下的吸收光谱^[190]

Fig. 8 Absorption spectra of ordinary water (full lines, H area) and heavy water (dotted line, D area) at three selected temperatures^[190]

果。在后面的研究工作中,他们又实现了对尿素水溶液的液膜厚度及尿素浓度的测量,且对气流道中液膜动态厚度进行实施监测。Pan 等^[188]利用 4 个 DFB 激光器,实现了 NaCl 水溶液的液膜厚度、浓度和温度的同时测量。以上研究工作证明了 TDLAS 技术在液态水测量方面具有响应快、灵敏度高、结构紧凑和操作相对简便等优点。

4 结 论

本文综述了 TDLAS 技术的应用研究现状,首先介绍了 TDLAS 技术气体检测的特点及原理,然后介绍了 TDLAS 在大气环境监测、工业过程监测、深海溶解气体测量、人体呼吸气体测量、流场诊断以及液态水测量中的应用背景以及研究现状。TDLAS 技术在各领域气体检测中具备非接触测量、时间响应速度快、高精度、免标定、易于小型化等优势,其技术应用领域不断扩大。

TDLAS 技术经过 40 多年的发展,已经成为了一种比较成熟的光谱检测技术。在检测原理发展成熟的基础上,相应的硬件(例如可调谐二极管激光器、探测器等)的发展,使得激光检测波长范围不断扩大,测量气体种类不断增多;多次发射池技术的不

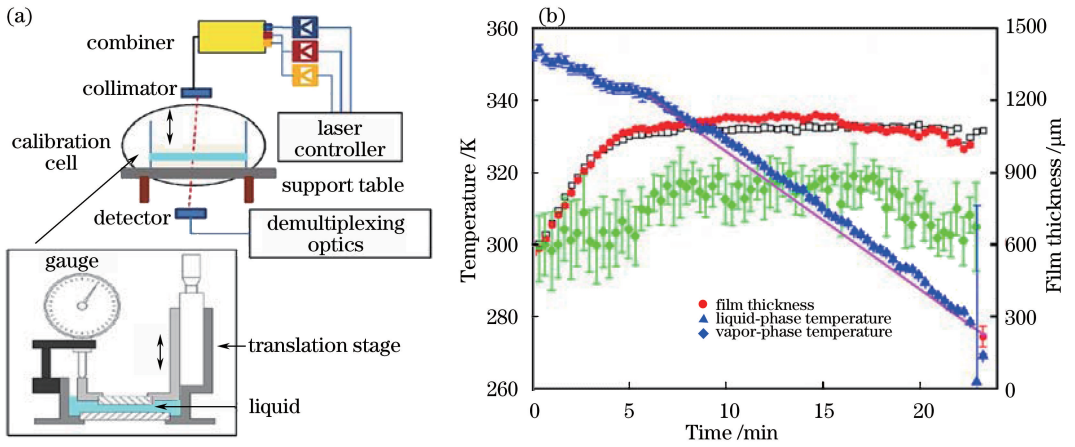


图 9 (a) TDLAS 液态水挥发过程温度及膜厚度测量装置及(b)结果^[186]

Fig. 9 (a) Experimental setup and time-resolved measurement of film thickness and (b) temperature during film evaporation by TDLAS^[186]

断优化,使得 TDLAS 气体检测浓度极限不断降低;光纤技术、电子学技术及光机结构设计技术的不断发展,使得 TDLAS 测量仪器趋近于小型化及具备长期稳定性,极大地提高了工程化应用的便利性。但是,TDLAS 技术在各领域的应用中仍然面临着一些问题及挑战:首先表现为测量需求越来越苛刻,如从一维测量需求到高维测量需求、从低重复频率测量需求到高重复频率、集成的测量装置转向智能、小型的需求等;其次是测量对象越来越复杂,如从层流到湍流、从清洁火焰到碳烟火焰(气态燃料到液体、固体燃料)、从常/低压强环境到高压强环境、从高温/常温到极低温环境、从地面到深海环境等;最后是测量的气体组分越来越复杂,气体的浓度越来越低。所以,TDLAS 技术未来的发展主要将朝着以下方向发展:环境适应性更强,测量的光学结构、电子学系统长期稳定性更高,算法更加高效成熟,仪器更加小型智能、检测限更低以及测量参数逐渐增多以满足不同应用领域的需求等。最终,TDLAS 技术将在工业、生态、国防、健康等领域发挥越来越大的作用。

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