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灵敏的基于分布反馈式半导体激光波长调制光声光谱

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摘 要：利用室温下单模运行的近红外半导体二极管激光，报导了波长调制共振光声光谱结合二次谐波探测技术．实验系统应用到乙炔探测，在1个标准大气压和3毫瓦平均光功率以及3毫秒锁相积分时间条件下其探测灵敏度可达10ppm(体积比)，归一化到激光功率和系统带宽最小可探测吸收为 4.0×10^{-8} Wcm^{-1}/Hz，并且实验中发现系统最佳压力响应值在 2.66×10^{4} Pa 附近．本实验装置可有效的消除光声光谱系统中常见的窗片和光声腔壁吸收入射光而引起的背景噪声．此外，相对于其他方法我们描述的基于半导体激光共振光声光谱具有很大的优点，为进一步发展便利、实用、便携式环境监测仪器奠定了坚实的基础．

关键词：光声光谱；波长调制；近红外二极管激光器；乙炔

中图分类号：O65 **文献标识码**：A

Sensitive wavelength-modulated photoacoustic spectroscopy with DFB diode laser

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Abstract: A new approach to wavelength-modulation resonant photoacoustic spectroscopy is reported with 2nd harmonic detection, which incorporates room-temperature single mode distributed feedback (DFB) diode laser in the near-infrared. We demonstrate the technique with acetylene detection, yielding a sensitivity limit is about 10 ppm v of acetylene at atmospheric pressure with 3ms time constant and 3 mW average optical power, which corresponds to the minimum detectable absorption coefficient normalized by laser power and bandwidth is 4.0×10^{-8} Wcm^{-1}/Hz. Moreover, the optimal pressure condition of buffer gas (N_2) has been found to be near 2.4×10^{4} Pa for our photoacoustic system. The present system can effectively eliminate the background signal generated by absorption of the cell windows and by the walls of the sample chamber whose spatial and temporal character are clearly distinct from the resonant wave. We believe that the resonant PA system based on diode laser described here offers substantial advantages over other methods and appears promising as a basis for developing convenient, robust, portable instruments for environmental monitoring and process control.

Key words: photoacoustic spectroscopy, wavelength modulation, NIR-diode laser, acetylene

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1 Introduction

Diode laser based photoacoustic spectroscopy (PAS) is the most powerful spectroscopic techniques in trace gas analysis owing to its high sensitivity, selectivity, broad dynamic range, and comparatively simple experimental set up[1]. As a zero background (baseline) technique (since absence of target molecules should not generate any signal), it has become an important tool in atmosphere pollution monitoring, industrial process control, medical diagnostics and combustion diagnostics. However, the sensitivity of this technique is power dependent (since the magnitude of the PA signal scales with the incident light power) thus it has been almost dominated by CO and CO_2 gas lasers for several tens years[2-4], because of their high output power from several watt to several hundreds watt (intracavity arrangement)[5], and their line tenability to strong fundamental vibrational transitions, these lasers seem to be ideal light sources to push the sensitivity of photoacoustic trace gas detection, but these line-tunable gas lasers are relatively large, complex, expensive. Presently, the main mission will focus on the development of compact on-line trace gas sensors for the detection, quantification, and monitoring of all kinds of trace gas species in ambient air. As we all know it is difficult to fulfill this mission for laser mass spectrometry (LMS), laser induced flourescence (LIF) and cavity ring-down spectroscopy (CRDS) although they also have high sensitivity[6-9]. In recent years continuously tunable diode lasers have been combined with photoacoustic spectroscopy. The diode lasers have the advantages of small size, reliability, long lifetime and low costs. This technique has the potential for compact size, ruggedness, simple optical alignment, and relatively low-cost although with relatively low-power. A special advantage of diode lasers is their electronic modulation feature, where both intensity and wavelength modulation can be achieved.

It is well known, often the noises and background PA signals limited the sensitivity of the PA detection system. In addition to the intrinsic noise of the microphone, preamplifier noise, gas flow noise, and electronic and external acoustic noise from the environment, the background signal generated by the windows and the wall absorbed the incident light may play an important role. Since these noise sources have nearly a characteristic $1/f$ frequency dependence, low modulation frequencies should be avoided in PA trace gas detection. In order to minimize the noise, modulation frequencies in the 1～4 kHz frequency region are usually recommended. On the other hand, noise and background levels of the PA detection system could be decreased by proper PA cell design (longitudinal, azimuthal, radial, or Helmholtz resonances, even resonant cells designed for multipass or intracavity operation.) and sophisticated methods of data collection and processing. Moreover, the sensitivity of the PA detection can be further increased by employing a microphone array instead of one single microphone device. This configuration has been demonstrated as enhancing the detection sensitivity considerably. In wavelength modulation spectroscopy the laser frequency is modulated with f, but the PA signals are analyzed at the frequency $2f$. This can reduce the effect of these background signals on the detection sensitivity[10-12].

In this work we have developed a photoacoustic spectrometer, which is based on room-temperature single mode distributed feedback (DFB) diode laser near 1511 nm. Our experiments were performed on the R25 rotational line of the C_2H_2 vibrational transition, which was selected for the experiment on the basis of laser availability.

2 Experimental set-up

The experimental arrangement is presented schematically in Fig.1. Briefly, the diode laser is operated in wavelength modulation or frequency modulation (WM or FM) mode, whereby it is scanned with a combination of sawtooth and sinusoidal signal waveform. The sawtooth signal shape induces the laser to scan slowly in wavelength across the absorption peak of the target molecule, and the sinusoidal

waveform dithers the laser's wavelength at half the resonant frequency of the photoacoustic cell's second longitudinal mode at $f=2.1$ kHz. The amplitude of the WM signal was another parameter that was optimized in the framework of photoacoustic detection. The main challenge is to optimize the signal amplitude by proper adjustment of these operational parameters.

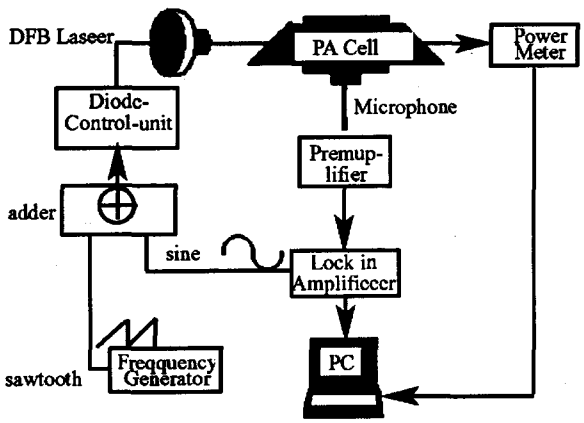

Fig. 1 Schematic diagram of the experimental set-up used in our experiments.

Generally a coupling between wavelength or frequency modulation and amplitude modulation of the laser's output power can be observed with semiconductor diode lasers. The degree of coupling of both modulations depends on the laser operating point and structure, and manifests itself as the so called residual amplitude modulation. Both wavelength and power changes will influence the PA signal, however, the two effects can not be separated in the lock-in output signal synchronously, which is the main disadvantage in our PA detection system.

3 Results and discussion

The frequency response of the PA cell has been investigated around 2.1 kHz at room temperature and atmospheric pressure, as shown in Fig.1. Circles are experimental points and the curve is the result of a fit by a Lorentzian distribution, from the figure we can obtain the quality factor $Q=22$ with a FWHM of 0.095 kHz. The FWHM refers to the width of the resonance profile at half the intensity, and is measured between the points where the amplitude of the resonance profile is at 1/2 the peak value[13].

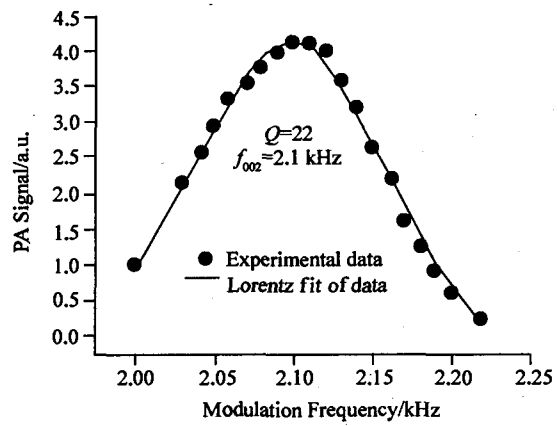

Fig.2 Second longitudinal acoustic resonance of our PA cell at 2.1 kHz. Circles are experimental points and the curve is the result of a fit by a Lorentzian distribution. The quality factor $Q=22$.

The PA signal is directly proportional to the PA cell's quality factor Q and the molecular absorption and also depends on the vibrational-translational relaxation rate of the target transition[14]. Therefore the optimum operating pressure has to be determined for each gas and even for each selected transition. The quality factor Q decreases with pressure approximately as a power function, so three kinds of mixtures of C_2H_2 with N_2 were prepared (1:9, 1:19, 1:99 v/v). The dependences of the PA signal on the overall pressure in the photoacoustic cell were measured for these mixtures at a resonance frequency of 2.1 kHz and represented in Fig.2 as a function of the PA cell total pressure. The R25 rotational line of the C_2H_2 molecule was selected as a model. It is apparent from the Fig.2 that, the higher the acetylene content in the mixture, the higher the PA signal intensity, and we also draw a conclusion that the optimum pressure condition is near 2.66×10^4 Pa, which may be corresponding to optimal response of microphone. This phenomenon can also be explained as: the higher the buffer pressure, more favorable the collosional relaxation before the optimum pressure, once over this high-point, the decrease of C_2H_2 relative molecule number density and pressure broadening are dominant.

Although it is necessary to find the optimum

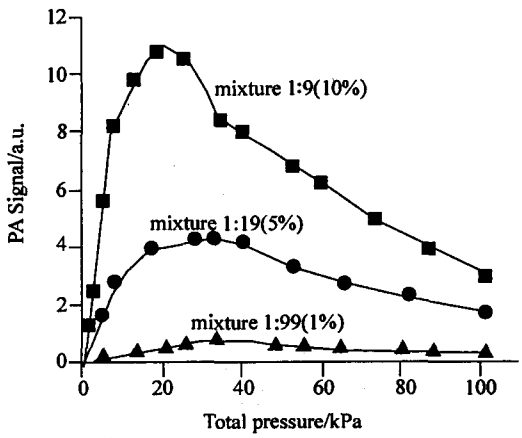

Fig. 3 Dependence of the PA signal on the total gas pressure buffered with N_2 in the PA cell for the R25 rotational line of C_2H_2(1513.19 nm).

total pressure for laboratory measurements. the practical applications are usually at atmospheric pressure, such as monitoring of industrial environment. As we all know at atmospheric pressure, pressure broadening seriously limits the sensitivity. Fig.3 gives an example of the measured PA spectrum and the result of fitting, the calculated signal to noise ratio (SNR) is approximately 100, this SNR indicates that the noise-limited minimal detection limit for this sensor is about 10 parts in 10^6 by volume (ppm v) of acetylene at atmospheric pressure (for SNR = 1) with 3ms time constant and 3 mW average optical power, corresponding to the minimum detectable absorption coefficient normalized by power and bandwidth is 4.0×10^{-8} Wcm^{-1}/Hz. Although the designed system described here were demonstrated with acetylene detection, in principle they are applicable to any gas species whose spectra (by selecting appropriate molecule absorption line) overlap with the wavelengths of diode lasers. The current performance of our PA sensing system is satisfying from comparative results for a low-power near-IR diode laser. However, the sensitivity needs to be further improved for practical applications and other needs. The noises in our system are mainly electrical noise, such as circuit noise and intrinsic noises of the microphone and preamplifier. So, if we can eliminate these noises furthermore, the sensitivity will be achieved in the range of sub-ppm even ppb. These works are in progress, and we consider it is very potential to achieve higher detection sensitivity for our PA system simultaneity.

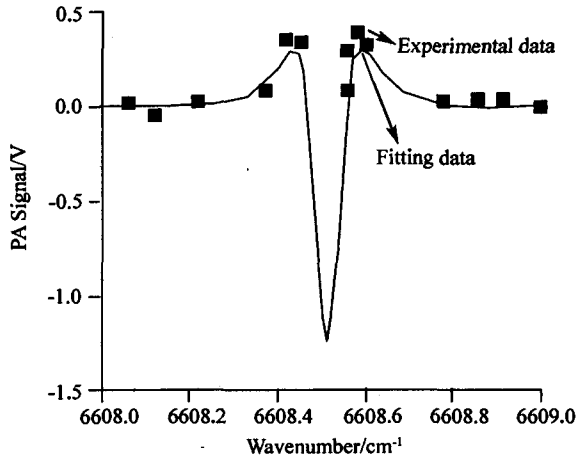

Fig. 4 PA spectrum obtained with WM modulation of 1‰ C_2H_2 buffered with N_2 at atmospheric pressure, modulation frequency 1.05 kHz---sensitivity 500 μv---time constant 3ms---2f detection. The dashed curve and solid curve are the results of experiment and fitting, respectively.

4 Conclusion

The present system can effectively eliminate the background signal generated by absorption of the cell windows and by the walls of the sample chamber whose spatial and temporal character are clearly distinct from the resonant wave. We believe that the resonant PA system based on diode laser described here offers substantial advantages over other methods.

Although we demonstrate the technique with acetylene detection, and achieve a detection limit is about 10 ppm v of acetylene at atmospheric pressure, which corresponds to the minimum detectable absorption coefficient normalized by power and bandwidth is 4.0×10^{-8} Wcm^{-1}/Hz. We believe the scheme described here can also be used for other gases by using a different diode laser and choosing optimal absorption lines of other molecules. Our systems still contain expensive and voluminous equipments, which were used for this test; but a special circuitry may replace the lock-in amplifier and preamplifier for amplifying and processing. With these modifications the apparatus could be made more portable and of

low cost. The flexibility and compact size of single mode distributed feedback (DFB) diode laser can lead to convenient, robust, portable tool for environmental monitoring and process control.

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