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可调谐二极管激光吸收光谱氟化氢检测

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摘　要：研究分布式反馈激光器的温度电流调谐特性及氟化氢气体在近红外波段的吸收线分布特征. 利用归一化洛伦兹函数实现 Voigt 线型快速近似计算，并分析气体吸光度曲线的 Voigt 线型拟合以及波长扫描气体浓度反演算法. 选择 1.28 μm 附近氟化氢气体单根吸收线作为目标吸收线设计可调谐二极管激光吸收光谱系统，对已知标准浓度氟化氢气体配置的不同浓度气体进行测量. 系统的检测限达到 1.12 ppm-m，且具有较高的测量准确度和长期稳定性，满足氟化氢气体实时在线监测的需要.

关键词：氟化氢；TDLAS；Voigt 线型；DFB 激光器；气体测量；在线监测；吸收
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Laser Absorption Spectroscopy for Detection of Hydrogen Fluoride Using Tunable Diode Laser

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Abstract: Temperature and current tuning characteristics of distributed feedback laser and absorption lines distribution of HF gas in near infrared was investigated, generalized Lorentz functions was used to realize rapid approximate calculation of Voigt function. The Voigt profile fitting of absorbance and the inversion of gas concentration for wavelength scanning technology. A tunable diode laser absorption spectroscopy system for HF gas concentration measurement was designed, using one absorption line of HF gas near 1.28 μm as the target absorption line, using known standard concentration HF gas for preparation of different concentration HF gas to measurement. The detection limit is 1.12 ppm-m. The system has high measurement accuracy and long-term operate stability, satisfies the needs of HF gas real-time online monitoring.

Key words: Hydrogen fluoride; Tunable diode laser absorption spectroscopy; Voigt profile; Distributed feedback laser; Gas measurement; Online monitoring; Absorption
OCIS Codes: 280.3420;300.1030;300.6260

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0 Introduction

Hydrogen fluoride (HF) is a highly toxic and corrosive gas[1], its release should be tightly regulated; HF gas is also an important industrial chemical, because it has the ability of dissolving oxide, plays an important role in the purification of aluminum and uranium, real-time monitoring HF gas can improve the productivity of aluminum and uranium and optimize the production process; HF gas does not react in the stratosphere and is absent in other parts of the atmosphere, so it is a good tracer molecule for atmospheric spectroscopy[1], Therefore, accurately, sensitive and rapid monitoring HF gas is very meaningful for environmental protection, industrial production, atmospheric spectral research.

In recent years, kinds of gas detection method have emerged, in which Tunable Diode Laser Absorption Spectroscopy (TDLAS) is a non-intrusive, highly sensitive, highly selective and fast time response trace gas detection technique[4-5]. TDLAS technique couple with diode laser is suitable for gas measurement. Even though the application of TDLAS for gas monitoring mainly concentrated on the measurements of H_2O[2], CO_2[4], H_2S[10], CH_4[3] etc, there is some research focus on HF gas[10][11].

In this paper, we focus on the generalized Lorentz functions for realizing rapid approximate calculation of Voigt function, and Voigt profile fitting for absorbance curve using the nonlinear least squares method. We study the inversion of gas concentration for wavelength scanning technology, and present a system for HF gas measurement based on the TDLAS technology, using 1.28 μm DFB laser as light source.

1 Fundamental Spectroscopy

According to the Beer-Lambert law[3,6], when near-IR laser radiation with incident intensity I_0 at frequency v passes through a uniform gas medium , since the gas absorption, light intensity will attenuate, the transmitted light intensity I_t is

$$I_t = I_0 \exp(-k_v L) \tag{1}$$

where k_v (cm^{-1}) is the spectral absorption coefficient, L(cm) is the length of absorbing species.

For an isolated transition of a single gas

$$k_v = S(T)\varphi(v)PxL \tag{2}$$

where $S(T)$ ($cm^{-2}\,atm^{-1}$) is the line strength of the transition at temperature T(K), $\varphi(v)$(cm) is the line-shape function, P is the total pressure of gas mixture and x is the mole fraction of the absorbing species.

In practice, absorbance is often used to describe the absorption characteristics of the target gas, absorbance α_v can be expressed as

$$\alpha_v = \ln\left(\frac{I_0}{I_t}\right) = k_v L = S(T)\varphi(v)PxL \tag{3}$$

Since the line-shape function $\varphi(v)$ is normalized so that $\int \varphi(v)\,dv \equiv 1$. The line-shape function $\varphi(v)$ is usually approximated using a Voigt profile. Integrating absorbance through the frequency domain to obtain the integral area, namely the integrated absorbance (cm^{-1})

$$A = \int a_v\,dv = S(T)PxL \tag{4}$$

According to Eq. (3) and Eq. (4), the peak of absorbance $A(v_0)$ can be expressed as

$$A(v_0) = S(T)PxL\varphi(v_0) \tag{5}$$

where v_0 (cm^{-1}) is the spectral center frequency.

In the condition of known temperature, pressure and optical path length, using Eq. 4 and Eq. 5, we can get the gas concentration

$$x = \frac{A}{S(T)PL} \tag{6}$$

$$x = \frac{A(v_0)}{S(T)PL\varphi(v_0)} \tag{7}$$

The selection of optimum absorption lines is the first step in design a TDLAS system. Based on HITRAN database to find suitable lines. Fig. 1 is the absorption lines of HF gas within $\Delta v = 2$ overtone based on HITRAN 2008 database. As shown in Fig. 1, the absorption line at 1 278.1 nm (7 823.821 2 cm^{-1}) has the maximum absorption linestrength (1.907 09 cm^{-2} atm^{-1}) in the 1.2～1.3 μm region, so we choose this line as the target absorption line to probe HF gas.

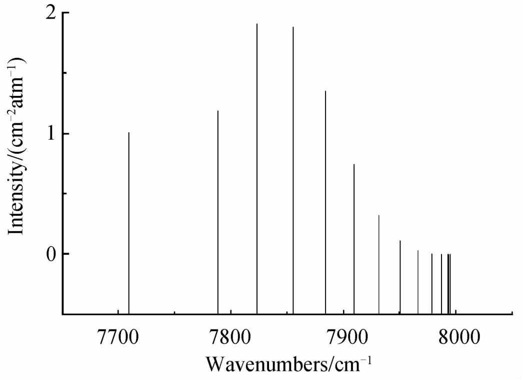


Fig. 1 The absorption lines of HF gas at temperature 296 K in the 1.2～1.3 μm region based on HITRAN 2008 database

2 DFB laser tuning characteristics research

We adopt optical fiber coupled distributed feedback (DFB) semiconductor laser as light source. DFB laser has tunable properties, by changing laser working temperature and driving current can change the output laser wavelength.

Fig. 2 is the tuning characteristics of the DFB laser. The laser temperature tuning characteristics is about 0.09 nm/℃; the laser current tuning characteristic is about 0.005 nm/mA.

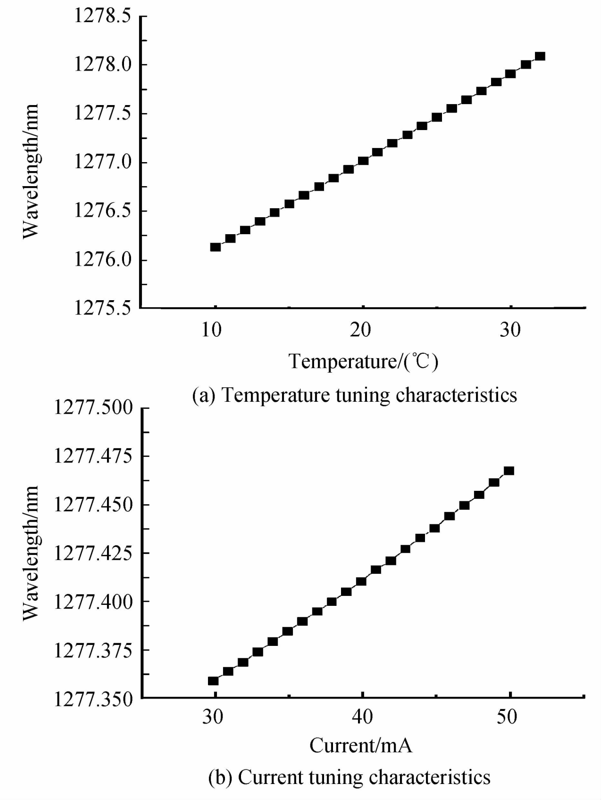


Fig. 2 Tuning characteristics of the DFB laser

As shown in Fig. 2, the DFB laser output wavelength changes linearly with the temperature and the driving current, which the DFB laser is suitable for TDLAS system as the light source.

3 Gas concentration inversion

For the gas concentration inversion, the incident intensity baseline is fitted. Signal detected from the photodiode is cumulative averaged for several times to eliminate the random error. We obtain the transmission light intensity I_t, the no absorption part of I_t is used to gain the incident intensity I_0 by nonlinear polynomial fitting[7]. The selection of no absorption part is related to the absorption line width, for the Voigt profile, the absorption will fall to 1% beyond 4 times line width distance from the center of the absorption frequency, so we choose this range as the baseline fitting range.

The ratios of I_0 and I_t are used to eliminate the noise of the laser output power, which are the primary noise for a TDLAS system. The noise may be caused by the fluctuation of injection current, temperature change of operation environment and mechanical vibration. Noise of photodetector, which is related to the signal bandwidth, can be weakened by using a low pass filter to reduce the signal bandwidth.

We use the Eq. (3) to extract the absorbance curve, owing to temperature change and system noise, absorbance curve may distort, non-linear line-shape fitting is needed to smooth absorbance curve for processing. Voigt profile is the convolution of Gaussian profile and Lorentz profile, the traditional calculation method of Voigt function is time-consuming and difficult to achieve real-time online processing. We adopt generalized Lorentz functions[8-9] to realize rapid approximate calculation of Voigt function, and use the nonlinear least squares method to accomplish Voigt profile fitting of absorbance curve.

a) Voigt profile function model

Voigt line-shape can be expressed as

$$\varphi_V(v)=\frac{\gamma_L}{\gamma_G}\alpha_L\ \sqrt{\pi\ln 2}\,V(X,Y) \tag{8}$$

where α_L is amplitude of Lorentz profile, γ_L (cm^{-1}) is the Full Width at Half Maximum (FWHM) of Lorentz profile, γ_G (cm^{-1}) is the FWHM of Gaussian profile, $V(X,Y)$ is the Voigt function.

With four generalized Lorentz functions, the Voigt function is expressed as

$$V(X,Y)=\sum_{i=1}^{4}\frac{C_i(Y-A_i)+D_i(X-B_i)}{(Y-A_i)^2+(X-B_i)^2} \tag{9}$$

$$X=\frac{2\sqrt{\ln 2}(v-v_0)}{\gamma_G}$$
$$Y=\sqrt{\ln 2}\frac{\gamma_L}{\gamma_G} \tag{10}$$

where A_i, B_i, C_i, D_i are constants, the values of the constants used to generate the Voigt approximation are given in Table 1. Considering the detected spectrum signal may have the presence of direct current background, we add a dc offset y_0 for Eq. (8), so the Voigt profile can be expressed as a function model

Table 1 Constants used to generate the numerical approximation to the Voigt function[8-9]

i	A_i	B_i	C_i	D_i
1	−1.215 0	1.235 9	−0.308 5	0.021 0
2	−1.350 9	0.378 6	0.590 6	−1.185 8
3	−1.215 0	−1.235 9	−0.308 5	−0.021 0
4	−1.350 9	−0.378 6	0.590 6	1.185 8

$$\varphi_V(v)=y_0+\frac{\gamma_L}{\gamma_G}\alpha_L\ \sqrt{\pi\ln 2}\cdot\sum_{i=1}^{4}\frac{C_i(Y-A_i)+D_i(X-B_i)}{(Y-A_i)^2+(X-B_i)^2} \tag{11}$$

where the dc offset y_0, spectral line center v_0, amplitude of Lorentz profile α_L, FWHM of Lorentz profile γ_L and FWHM of Gaussian profile γ_G are the parameters of model.

b) Nonlinear fitting of Voigt profile

For Voigt profile fitting, iteration is the only way to determine the best parameters. Levenberg-Marquardt (L-M) [7] method is very effective in practice, which has become a standard nonlinear least squares method.

The convergence results and iteration times of L-M method depend on fitting parameters initial values, the selection of initial parameters values is as follows:

I) For dc offset y_0, the initial value is the minimum of absorbance curve or zero;

II) For spectral line center v_0, the initial value is the frequency corresponding the peak of absorbance curve;

III) For amplitude of Lorentz profile α_L, the initial value is the peak absorbance curve;

IV) For FWHM of Lorentz profile γ_L, the initial value is 0.85 times the FWHM of absorbance curve;

V) For FWHM of Gaussian profile γ_G, the initial value is 0.85 times the FWHM of absorbance curve or the fixed value calculated by $\gamma_G=7.1632\times10^{-7}v_0\sqrt{T/M}$.

After the initial values selection of the fitting parameters, we bring Voigt profile function expression and the partial derivatives of fitting parameters into the L-M algorithm to carry out nonlinear fit. With the Voigt profile fitting, we obtain absorbance peak and the integral area. The gas concentration can be obtained by bringing the line strength, pressure, optical path length into the Eq. (6) and Eq. (7).

4 The experimental results and analysis

Fig. 3 is the schematic diagram of the experimental system. The laser current and temperature controller control the DFB laser output. The laser beam was divided into three beams by a beam splitter, the first beam was directed into a wavemeter for wavelength measuring; the second beam was directed through a sample gas cell onto a photodetector for HF gas probing; the third beam was directed through a reference gas cell onto a photodetector for the laser output wavelength lock-in. The photodetector signals were transferred to a computer for data processing. We adjusted the laser driving current to 50 mA, operating temperature to 28.45℃, and then the laser output wavelength was stable at 1 278.1 nm near one HF gas absorption line. The laser wavelength was tuned over the desired absorption line by a linear ramp of current of 100 Hz from a function generator.

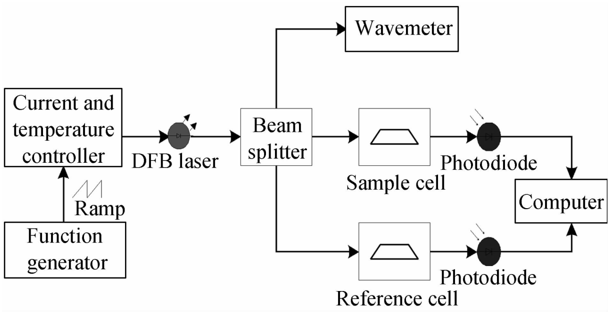
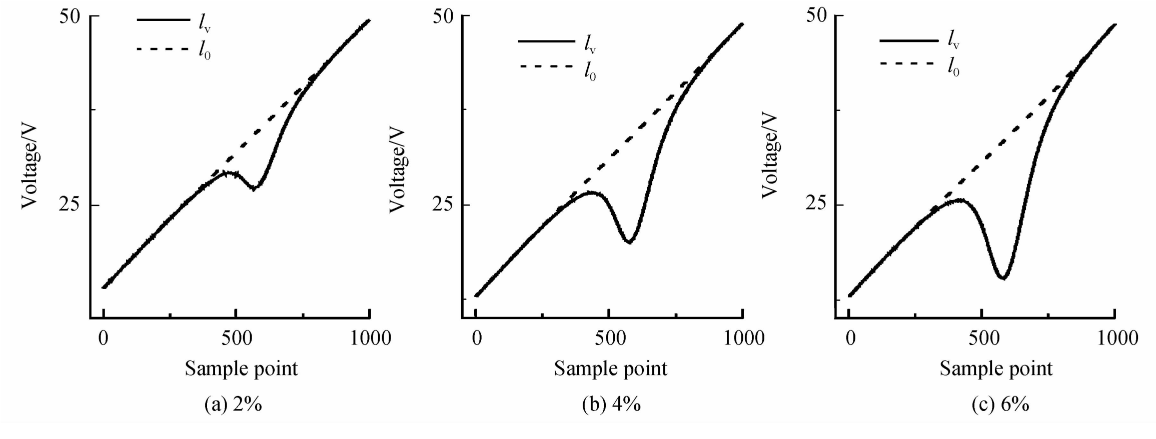


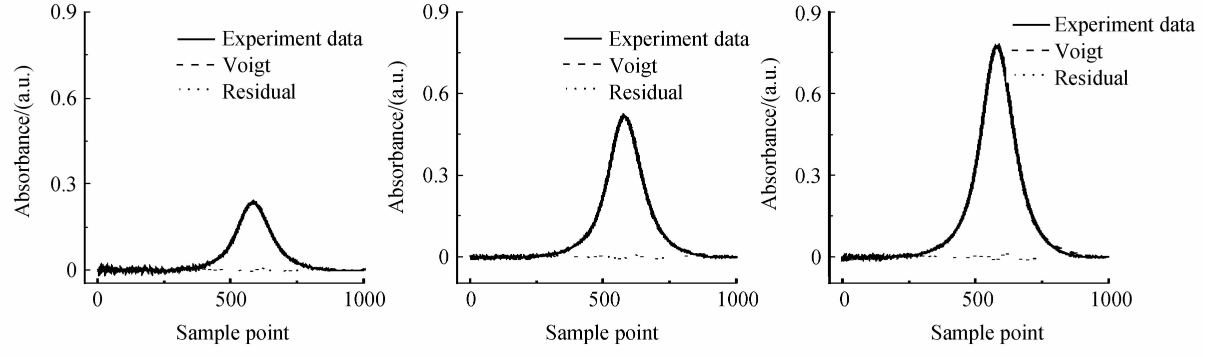
Fig. 3 The schematic diagram of the experimental system

We measured 2%, 4%, 6% HF gas with the TDLAS system, respectively. The photodiode signals were accumulated averaged 20 times to obtain the absorption spectrum as shown in Fig. 4. Fig. 5 shows the absorbance curve, the absorbance curve of Voigt profile fitting and the fitting residual of two curves, respectively. The Signal Noise Ratio(SNR) are 31.75, 52.50, 58.09, respectively. SNR increased as the concentration increased. The fitting residuals maximums (absolute value) are 0.713%, 0.974%, 1.318%, all of them are within ±1.5%, indicating that the proposed Voigt profile fitting method is effective and suitable for absorbance curve fitting. The corresponding linear relationship between the absorbance peak, the integral area and the concentration are shown in Fig. 6, the fitting coefficients are 0.998 5, 0.996 2, respectively, indicating that the absorbance peak, the integral area have a good linear relationship with different concentration. We can use the proposed concentration inversion method for HF gas concentration measurement.



(a) 2% (b) 4% (c) 6%

Fig. 4 The absorption spectrum of HF gas

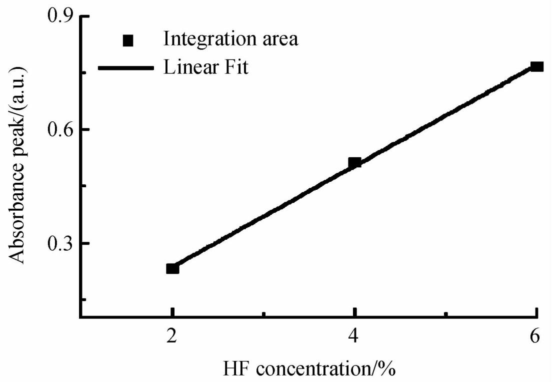


(a) 2%

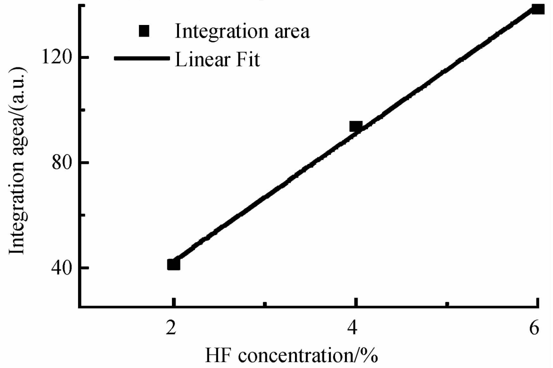
(b) 4%

(c) 6%

Fig. 5 The absorbance curve of HF gas



(a) Absorbance peak with HF concertrations



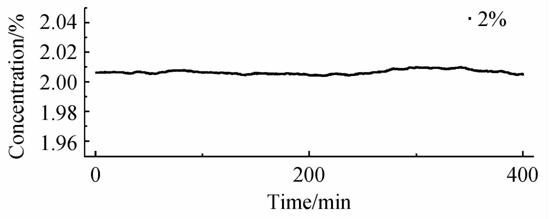
(b) Integral area with HF concertrations

Fig. 6 The corresponding relationship between the absorbance peak, the integral area and different gas concentrations

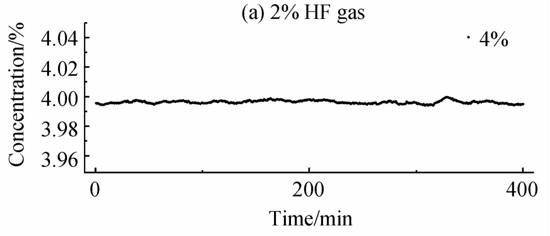
We evaluated the performance of the system shown in Fig. 3 by using the relative error, detection limit and repeatability.

Fig. 7 is the measurement results of 2%, 4% HF gas, respectively, measurement interval is 1 min, measurement time lasted for 400 minutes. We adopted the integral area for concentration measurement.

The test results are shown in Table 2. For concentration of 2%, the accuracy is 0.325%, while the relative error is 0.094% for concentration of 4%. As the concentration increased, the relative error becomes lower, and the trend is consistent with SNR. We adopted 3 times the standard deviation of the measurement results to calculate the detection limit. The detection limit is related to the optical path length, the detection limit are 1.12, 2.21 ppm-m, respectively. With a longer optical path length, the detection limit can be improved. The maximum relative error was introduced to characterize the repeatability, the repeatability were 0.485%, 0.232%, respectively.



(a) 2% HF gas



(b) 4% HF gas

Fig. 7 Measurement of the system

Table 2 Results of performance test

Concentration/(%)	Relative error/(%)	Detection limit/(ppm-m)	Repeatability/(%)
2	0.325	1.12	0.485
4	0.094	2.21	0.232

The experimental results show that system have high measurement accuracy, good stability, consistent repeatability, which can meet application requirements of HF gas real-time online monitoring.

5 Conclusion

We use generalized Lorentz function for Voigt function analytical approximation, and use L-M method to conduct Voigt profile fitting of absorbance. The experimental results show that peak and integral area of absorbance have a good linear relationship with gas concentration. The system detection limit is 1.12 ppm-m, measurement accuracy is 0.325%, and repeatability is 0.485%. The system has high measurement accuracy and long-term operate stability, which satisfies the need of HF gas real-time online monitoring.

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