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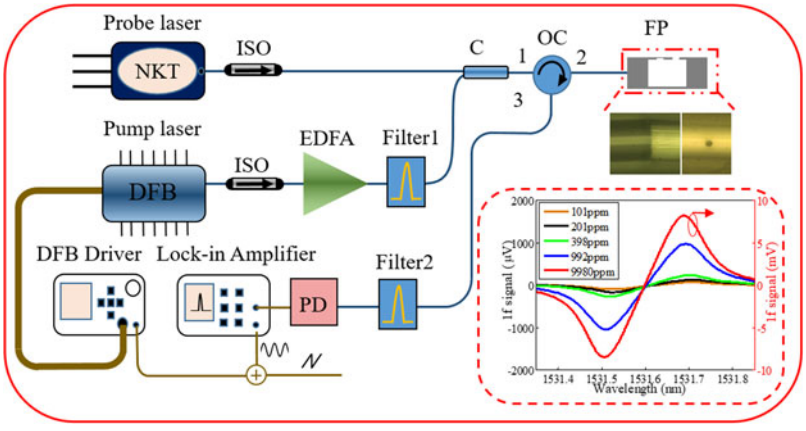

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Abstract: Photothermal interferometry (PTI) incorporated with wavelength modulation spectroscopy is a typical ultrasensitive spectroscopic technique for trace gas detection. In this paper, to our best knowledge, we demonstrate that the first harmonic signal is the best choice for a PTI spectroscopy gas sensing system for the first time. Both the theoretical and experimental results confirm that the first harmonics signal has the largest peak-to-peak amplitude in all harmonic signals. The noise measurement indicates that the all harmonic signals nearly have the same noise level. The detection limit in terms of noise equivalent concentration is improved by 30%, from 114 to 78 ppb (9×10^{-8} cm^{-1} in absorption coefficient) by use of the first harmonic signal instead of the second harmonic signal.

Index Terms: Optical fiber sensors, photothermal effects, gases, spectroscopy, interference.

1. Introduction

Tunable diode laser absorption spectroscopy (TDLAS) has been widely used for trace gas detection due to its unique selectivity and high sensitivity, and quick response [1], [2]. In TDLAS, laser wavelength is slowly swept over a certain 'fringe-print' absorption line of molecules, and it is simultaneously modulated by a high frequency signal of kHz. The interaction of the modulated laser with the absorption line leads to the generation of signals at different harmonics of the modulation frequency. Theoretically, the first harmonic (1f) signal has the biggest signal amplitude in all harmonic signals, but large background noise is simultaneously created by the extra intensity modulation accompanied with wavelength modulation [3], [4]. Furthermore, the noise leaked from the amplitude modulation has the same frequency with the 1f absorption signal, and hence it is hard to be removed from the absorption signal by using the lock-in amplifier. Therefore, the 1f signal is not suitable for trace gas detection in the TDLAS technology. In contrast, the second harmonic (2f) component is generally lower than the 1f signal, but the residual amplitude modulation signal created at 1f is strongly suppressed at 2f. To balance the signal amplitude and the intensity

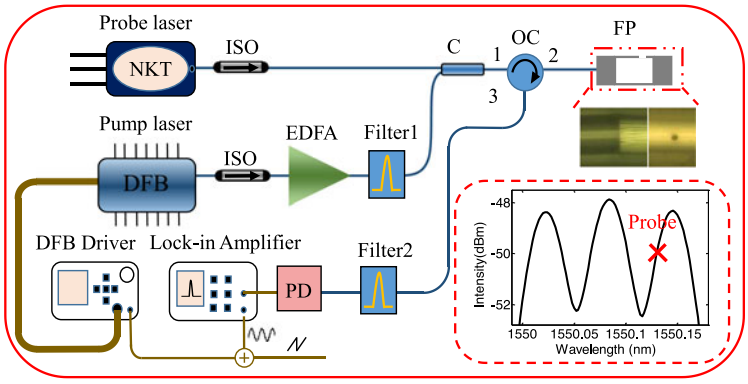

Fig. 1. Experimental setup for gas detection with PTI system. DFB, a distributed feedback laser as pump laser; OC, optical circulator; C, coupler; ISO, isolator; NKT, a tunable laser as probe light; EDFA, erbium-doped fiber amplifier; Inset: Microscopy image of the splicing point and the side drilled micro hole in the FP cavity, the reflection spectrum of the FP cavity.

modulation noise and obtain a good signal-noise-ratio (SNR), 2f signal is usually used to get the lowest noise equivalent concentration (NEC) in the TDLAS [1], [2], [5].

Instead of direct measurement of absorption spectral attenuation in TDLAS, photothermal interferometry (PTI) spectroscopy [6] is an indirect method for trace gas detection by using a pump-probe configuration, in which an optical interferometry is employed to probe the absorption-induced phase change via the photothermal effect [7]. Recently, W. Jin demonstrated a series of all-fiber PTI systems based on the gas-filled hollow-core photonic bandgap fibers (HC-PBFs) [8]. HC-PBFs are therefore selected as the gas cell because HC-PBFs could offer much better light confinement and long light-matter interaction length at long length with nearly 100% light- matter overlap. With a 10 m long HC-PBF gas cell, detection of acetylene gas down to 2 ppb was realized by using an optical fiber Mach–Zehnder interferometer. Compact PTI spectroscopy was demonstrated by use of a Fabry-Perot (FP) cavity in 2-cm long HC-PBF, and the minimum detection limit in terms of NEC is 117 ppb by using 77 s averaging time [9]. Sagnac-loop configuration with 1.1 m long HC-PBF was also reported to realize a NEC of 18 ppb with 145 s integration time [10], [11]. In all reported PTI spectroscopies, the 2f signal was took to estimate the gas concentration as done in in TDLAS, although the PTI spectroscopy detects the absorption-induced phase jitter instead of the absorption-induced spectral attenuation in the TDLAS.

In this letter, we demonstrated the feasibility of using the 1f signal for gas sensing in the PTI spectroscopy by characterizing the first-four harmonic signals. Compared with the 2f component, the 1f component nearly has the same noise level but provides a much larger amplitude, meaning that the detection limit in terms of NEC can further go down by using the 1f signal to estimate the phase modulation instead of the 2f signal. Experimental results indicated that the NEC was improved from 114 ppb to 78 ppb by changing the 2f signal to 1f signal.

2. Experimental Setup and Theoretical Analyzation

Fig. 1 shows the experimental schematic of the PTI gas sensor. Here, a FP cavity is constructed as the gas cell by splicing a 1.77 cm long HC-PBF (NKT HC-1550-02) with two sections of single mode fibers (Corning SMF-28e) [12], [13]. To make gas rapidly diffuse into the whole FP cavity, 6 micro-holes were side drilled into the hollow core of the HC-PBF by use of femtosecond laser micromachining. Then the FP cavity was put into a 20 cm $\times$ 15 cm $\times$ 15 cm gas chamber. We selected a distributed feedback (DFB) (NTT NLK1C5GAAA) semiconductor laser as the pump laser, and the center wavelength of DFB laser was tuned to the absorption line of acetylene at 1531.59 nm, the P(11) line of acetylene [14]. A 0.01 Hz sawtooth wave was set to sweep the center wavelength of the pump laser across the absorption line, and a 5 kHz sinusoidal wave was superimposed on

the slow sweep signal to modulate the laser wavelength [15]. The amplitude of wavelength modulation was set at 350 mV to maximize the harmonic signal. The DFB laser output can be easily amplified by the erbium-doped fiber amplifier to get different pump laser power, and filter 1 is used to minimize the amplified spontaneous emission noise. NTK narrow-linewidth laser (NKT BASIK E15) was selected as the probe laser, and its wavelength was tuned to the steepest point in the reflection spectrum of FP cavity (Inset of Fig. 1), i.e., 1550.13 nm. Filter2 is used to remove the remnant of the pump light and allow the probe light pass through. The probe laser power reached the PD (photoelectric detector) is about 100 μW. The electric signal will be demodulated by a lock-in amplifier (UHFLI Lock-in Amplifier 600 MHz).

In PTI spectroscopy, pump laser is injected into gas cell with wavelength modulated. The absorption of molecules will cause gas local heating along optical path. Accompanied by the jitter of temperature, pressure and density for local heating, the refractive index of the gas will be modulated. Because probe light has the same optical path as pump laser in the gas cell, the phase of probe laser will follow the tiny refractive variations and be modulated. The phase change of probe laser could be recovered accurately by use a sensitive interferometry. In detail, the phase change is converted into the intensity variation of the probe laser. To perform sensitive phase demodulation, the probe light needs to operate around a quadrature point of the interference spectrum, as shown the inset of Fig. 1. Hence, we can measure the photothermal effect in gas cell just by monitor the reflected probe light from the FPI in our experiment.

When a modulated pump and a probe beam propagate along the same path, the induced phase modulation in the probe beam due to pump absorption may be expressed as [8]:

$$\Delta\phi = k^* \bar{P}_{\text{pump}} \alpha_0 L \, g\left(\lambda_{\text{pump}}\right) C \tag{1}$$

where $\bar{P}_{\text{pump}}$ is average pump power over optical length L. k^* is a coefficient proportion to the mode field area of the pump laser. C is the gas concentration and $\alpha_0 = 1.154\,\text{cm}^{-1}$ is the peak absorption coefficient for a relative concentration of 100% at 1 atm pressure and 296 K (acetylene molecular line strength at P(11) is $1.17 \times 10^{-20}\,\text{cm}^{-1}/(\text{molec}\cdot\text{cm}^{-2})$ and air-broadened Lorentz halfwidth is 0.0796 $\text{cm}^{-1}\cdot\text{atm}^{-1}$ [14]). g(λ) is the peak normalized absorption line-shape and. $\lambda_{\text{pump}}(t) = \lambda_c + m\cos\omega t$, presents the pump laser is modulated by sine wave where λ_c is the center wavelength of DFB laser and m is the depth of wavelength modulation. It is found that the phase modulation $\Delta\phi$ is proportional to gas concentration, pump power, and the action length of pump laser with the gas.

To get the best sensitivity in system, probe laser is tuned at the at the quadrature point of the interferometer. In low gas concentration situation, the $\Delta\phi$ is small and the change of interference intensity of probe laser can be described:

$$\Delta I = I_{\text{probe}} \cos\left(\frac{\pi}{2} + \Delta\phi\right) \approx I_{\text{probe}} \Delta\phi = \eta \cdot g(\lambda_c + m\cos\omega t) \tag{2}$$

where I_{probe} is the probe laser intensity and $\eta = I_{\text{probe}} k^* \overline{P}_{\text{pump}} \alpha_0 LC$ is a constant coefficient for system with a given gas concentration. Equation (2) is very similar with the mathematic model of TDLAS without taking account of the extra intensity modulation. The absorption line-shape is Lorentz line at 1atm pressure and 296 K. And analytical solution of Fourier series for Lorentz line has been analyzed by Arndt [16]. The Fourier series of (2) can be described:

$$S_n = \eta \cdot \frac{1}{2}\frac{1}{m^n}\varepsilon_n i^n \frac{\left[\sqrt{(1-ix)^2+m^2} - (1-ix)\right]^n}{\sqrt{(1-ix)^2+m^2}} + c.c. \tag{3}$$

where the x is normalized frequency deviation, n is the order of the harmonic signals, $\varepsilon_o = 1$, $\varepsilon_n = 2$ ($n = 1, 2, 3\ldots$), and c.c. is the complex conjugate. Fig. 2(a) shows the numerical simulation of the first-four harmonic signals in (3). It is clearly found that the amplitude of the harmonic signal falls off rapidly with the increase of the order, and the1f signal has much larger amplitude than other harmonic signals. In TDLAS method, 1f signal cannot be used for gas detection because it contains

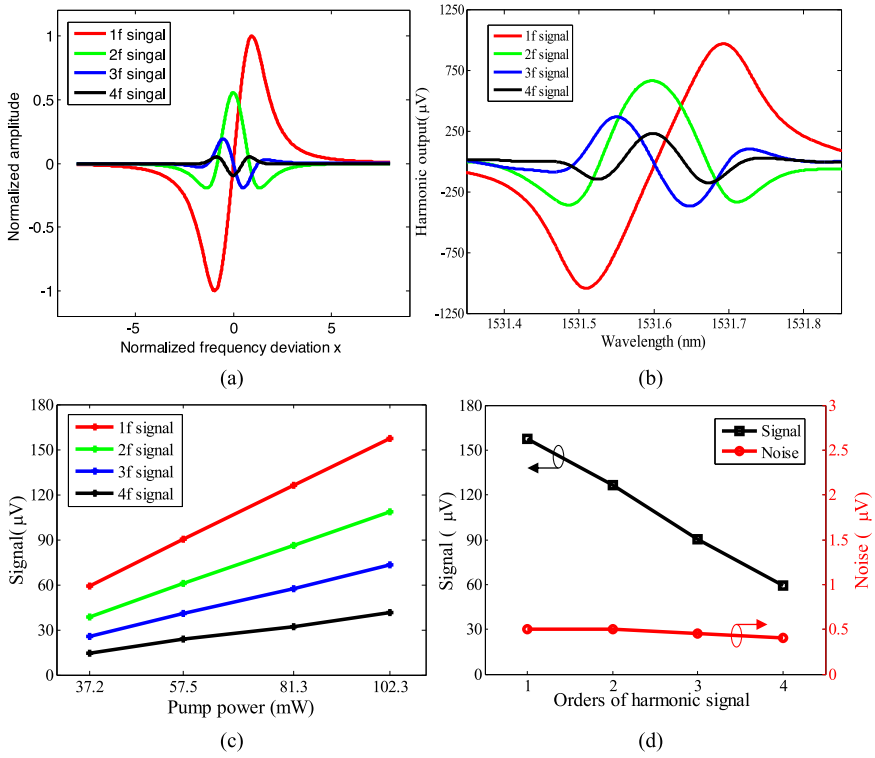

Fig. 2. Characterization of the first-four harmonic signals. (a) Numerical simulation for normalized harmonic signal with different order. (b) Experimental measurement of Harmonic signal output with different order when pump power is 102.3 mW and the concentration is 992 ppm. (c) Peak-to-peak amplitude of harmonica signals as function of the pump power with acetylene concentration of 100 ppm. (d) Peak-to-peak amplitude and s.d. of the noise over 100 s when the pump wavelength was tuned away from the absorption peak to 1531.27nm and the acetylene concentration is 100 ppm. The time constant of the lock-in amplifier is 1s with a filter slope of 18 dB/Oct.

the first order noise from extra intensity modulation accompanied with wavelength modulation. However, PTI spectroscopy detects phase jitter of probe laser caused by photothermal effect, rather than the intensity attenuation by characteristic absorption. There are hardly any noise from extra intensity modulation in the first order harmonic signal of probe laser. Therefore, the 1f signal will be the best choice, in theoretical, to get a highest signal amplitude and low noise in the PTI spectroscopy.

3. Experimental Results

Firstly, we experimentally compared the first four harmonic signals to demonstrate that the 1f has the highest peak-to-peak amplitude. Fig. 2(b) shows the experimental measurements of the first four harmonic signals when pump power is 102.3 mW and the gas concentration is 992 ppm. The amplitude of harmonic signal falls off with the increase of the orders, which agrees well with the theoretical predict and the numerical simulation in Fig. 2(a). Fig. 2(c) shows the peak-to-peak amplitude of harmonic signals when the pump power was increased from 37.2 to 102.3 mW. It is obviously found that the signal amplitude increases approximately linearly with pump power, which agree well with (1). More important, the 1f signal has the largest peak-to-peak amplitude than other harmonic signals at all pump powers.

In PTI gas sensing system, the probe laser is set at a constant power without any modulation, which means the PTI sensing system does not directly contain the noise from intensity modulation. To demonstrate this point, we calculated the standard deviation (s.d.) of the noise over a duration of

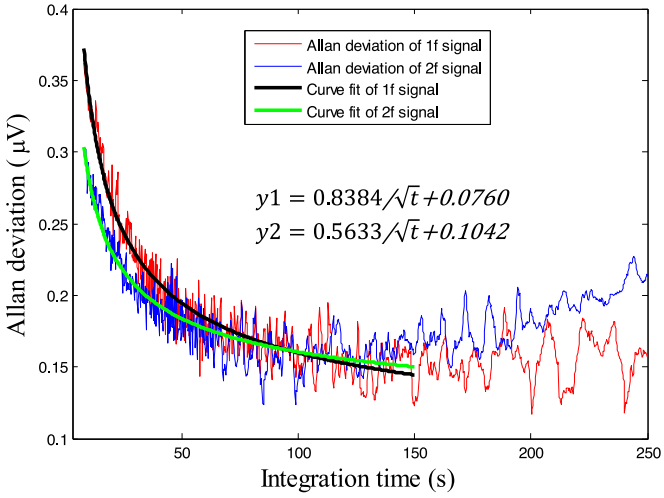

Fig. 3. Allan deviation analysis of 1f and 2f signals over one hour when the wavelength of pump laser is tuned away from absorption line to 1531.27 nm and the acetylene concentration is 100 ppm. The ripple curves are the Allan deviation calculation, and the smooth curves are the fitting result with function of $y = A/\sqrt{t} + B$. The time constant of the lock-in amplifier is 1 s with a filter slope of 18 dB/Oct.

100 seconds under 102.3 mW pump power when the wavelength of pump laser is tuned away from the absorption line to 1531.27 nm and the acetylene concentration is 100 ppm. Fig. 2(d) shows the calculated s.d. of the noise and the measured peak-to-peak amplitudes for the first-four harmonic signals. The peak to peak amplitudes of the 1f- 4f signals are 157.54, 108.12, 73.29 and 41.19 μV, the s.d. of the noise is 0.505, 0.5, 0.45 and 0.4 μV, and the calculated NECs of the four harmonic signals are 321, 460, 619, and 986 ppb (3.71×10^{-7} cm^{-1}, 5.31×10^{-7} cm^{-1}, 7.15×10^{-7} cm^{-1} and 1.137×10^{-6} cm^{-1} in noise equivalent absorption coefficient (NEA)), respectively. Comparing the four harmonic signals, it is found that the 1f signal holds the largest peak-to-peak amplitude and its noise level is not much larger than those of the higher order signals, hence the 1f harmonic signal give the lowest NEC. Furthermore, the lower orders signal means the lower bandwidth requirement of the lock-in amplifier. It is useful to decrease the cost of all system and further increase sensitivity in PTI spectroscopy by using the 1f signal.

To future demonstrate the noise characteristics of the harmonic signals and obtain the detection limit, we conducted an Allan deviation analysis [17], [18] over one hour when the wavelength of pump laser is tuned away from absorption line to 1531.27 nm. Fig. 3 shows the calculated Allan deviations of the 1f and 2f signals. With the increase of integration time, the Allan deviations of both 1f and 2f signal decrease rapidly and get very close when the integration time exceed 60 s. The Allan deviation analysis also convinces that the 1f signal has almost same noise limit with 2f signal. The relationship between the Allan deviation and the integration time follows the function $y = A/\sqrt{t} + B$, which indicates that the white noise dominates for a short integration time of below $\sim$150 seconds. For the 1f and 2f signals, the Allan deviations reach to the minimum values of 0.1228 and 0.1238 μV, when the averaging time is 149.75 and 85 s, respectively. Correspondingly, the detection limits in terms of NEC are 78 and 114 ppb (9×10^{-8} cm^{-1} and 1.32×10^{-7} cm^{-1} in NEA) for the 1f and 2f signals. This result of 2f signal is nearly the same as the previous reported result of PTI system with 2-cm long HC-PBF [9]. And the detection limit is improved by 32% when using the 1f signal for trace gas detection instead of the 2f signal.

In the FP system, the optical length is 3.54 cm which is twice of the length HC-PBF. The phase change at 10% acetylene concentration is calculated to be 0.251 rad by (1). It is satisfied the linear approximation used in (2) by assumption phase $\Delta\phi \leq 0.1\pi$. The dynamic range of the HC-PBF-based PTI spectroscopy with 1f signal was tested with acetylene concentration from $\sim$100 to 101000 ppm when the pump power is 102.3 mW. In this experiment, different gas samples

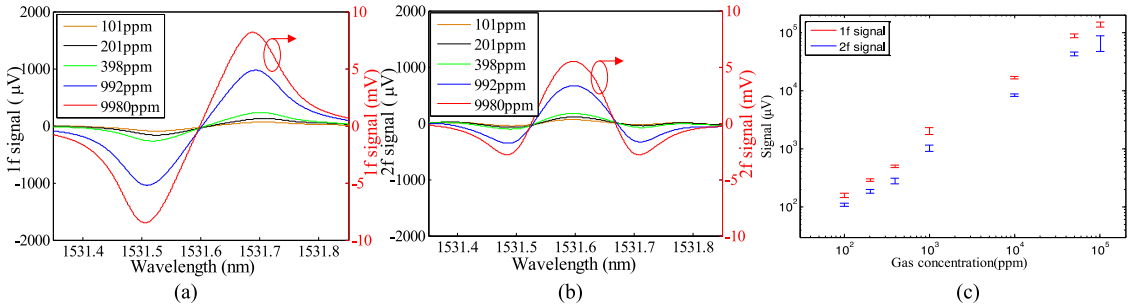

Fig. 4. 1f signal as function of gas concentration. (a) The 1f signal output for different acetylene concentration. (b) The 2f signal output for different acetylene concentration. (c) The peak-to-peak signal amplitude of 1f and 2f signal for different acetylene concentration. Error bar in the vertical axis shows the s.d. from 5 measurements and the magnitudes of the error bars are scaled by 10-fold for clarity reason. The time constant of the lock-in amplifier is 1 s with a filter slope of 18 dB/Oct.

are injected in sequence by the ranking of concentration. The lower concentration sample could be tested priority to reduce the effect of residual gas. Fig. 4(a) and (b) show the 1f and 2f harmonic lock-in output with different acetylene concentration. As shown in Fig. 4(c), with the gas concentration increasing, the peak to peak amplitude of the 1f and 2f signal increased in direct proportion to gas concentration. This comparison enforces that the improvement of the single amplitude is around 30% in our measurement range. Considering the lower detection limit in terms of NEC (78 ppb), the dynamic range by use of 1f signal is determined to be six orders of magnitude (1.29×10^6). Such result indicates that the 1f signal can achieve the same dynamic range as the 2f signal [8].

4. Conclusion

In conclusion, we characterized the harmonic signals of PTI spectroscopy and demonstrated the feasibility of using the 1f signal for gas sensing. In the side of the signal amplitude, both theoretical and experimental results show that the 1f harmonic signal has the largest peak-to-peak amplitude than other harmonic signals. In the side of the noise analyzation, both standard deviation and Allan deviation of the noise indicate that the 1f harmonic signal has the almost the same noise level with the 2f signal. Therefore, 1f signal gives the highest SNR and lowest NEC in the all harmonic signals, and it is the best choice to measure gas concentration in PTI spectroscopy system.

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