Behaviors of harmonic signals in wavelength-modulated spectroscopy under high absorption strength

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Behaviors of harmonic signals in wavelength modulation spectroscopy (WMS) for gas detection with Lorentzian line under high absorption strength are investigated. Approximate analytic expressions of the second, fourth, and sixth harmonics on the strength are presented in concise forms. Simulations show that the expressions are in agreement with the Fourier expansion by numerical integration. It is expected theoretically and experimentally in a WMS system for methane detection that there are not only a maximum, but also a null point in the harmonics versus strength relations, which should be of practical importance in methane sensing applications.

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Gas absorption detection is still an attractive topic in recent years because explosions in coal mines occur from time to time, especially in developing countries. Moreover, natural gas with methane as its main composition is now regarded as one of the most important energy sources so that its detection and measurement are of practical interest.

Wavelength modulation spectroscopy (WMS) has been developed and applied for long time, especially by using tunable diode lasers (TDLs), which is a powerful method for gas sensing. Reid performed the first TDL WMS experiment[1]. His analysis was based on Fourier analysis of a Lorentzian line profile under small absorption approximation, developed by Arndt[2] and Wahlquist[3]. Reference [4] analyzed WMS characteristics related to modulation frequency and modulation index; Ref. [5] discussed issues related to phase shift of the laser source.

Principle of the method is based on the Beer's law. At low absorption its exponential function can be approximated to be a linear one. However, at high absorption strength, with higher gas concentration or longer propagation distance, the linear approximation becomes invalid. Although the WMS is originally supposed to detect weak absorptions, but on some occasions, when big dynamic range of measurement is important, for distinguishing small changes from high background of absorption, WMS is still desirable for getting high resolution. There are always requirements in practice for detecting both low and high gas concentrations, such as in methane outburst in coal mines, in natural gas industries and for gas pipe lines. It is obviously necessary to understand the characteristics of WMS in high absorption.

Uehara[6] reported the dependence of harmonic signals on sample gas parameters, presented harmonic signal formulas in an infinite series for both of Lorentzian and Gaussian absorption lines, which is not so easy to be used directly. His simulation showed that variation of the second and fourth harmonic signals with the absorption strength is not a monotonic function, but a curve with a maximum value, and in the fourth harmonic simulation there are nulls under higher absorption. Iseki[7] calculated the ratio of second and first harmonic signals, which is for cases of not only wavelength modulation but also its intensity modulated[8].

This paper investigates behaviors of the harmonic signals at high absorption, gives simpler and more concise approximate expressions of some low even-order harmonic signals varying with the absorption strength for Lorentzian line. Calculated results by using the expressions are presented to be compared with the numerical simulation. It is shown that there are not only a maximum in even-order harmonics versus absorption strength, but also a null at certain position. Experimental results of harmonic signals varying with gas concentration are given in good agreement with the theoretical analysis.

The ability of direct current (DC) modulation of laser diode (LD) facilitates realization of WMS. If LD is modulated by a sinusoidal wave and a direct bias, its wavelength and output power are respectively modulated as $\lambda = \lambda_{\rm L} + \Delta\lambda \cos\omega t$ and $I = I_0(1 + a\cos\omega t)$, where ω is angular frequency of modulation, $\Delta\lambda$ is wavelength modulation depth, and a is relative amplitude modulation depth. Compared with the absorption coefficient $\alpha = \alpha_0/[1 + (\lambda - \lambda_0)^2/\delta\lambda^2]$, the line width of distribute feedback (DFB) laser is much smaller and can be neglected. Here a Lorentzian line is taken into consideration in the usual application case of pressure and temperature. Then the transmitted intensity can be expressed as

$$I_{\rm out} = I_0(1 + a\cos\omega t)\exp\frac{-x}{1 + (\mu + M\cos\omega t)^2}, \qquad (1)$$

where $\mu = (\lambda_{\rm L} - \lambda_0)/\delta\lambda$, $M = \Delta\lambda\lambda/\delta\lambda$, and $x = \alpha_0 CL$, and with gas concentration C (percentage) and light propagation distance L. The fractional term in the above expression can be expanded as a Fourier series[2],

$$\frac{x}{1 + (\mu + M\cos\omega t)^2} = x\sum_{n=0}^{\infty} S_n \cos n\omega t.$$

Its coefficients can be deduced as

$$S_n = \left\{ \frac{j^n[(1+j\mu) - \sqrt{(1+j\mu)^2 + M^2}]^n}{M^n\sqrt{(1+j\mu)^2+M^2}} + c.c. \right\} \times \left(1 - \frac{1}{2}\delta_{n0}\right),$$

where δ_{n0} is the Kronecker delta function; they can be simplified in case of $\mu = 0$ to be $S_{2n} = \frac{2}{\sqrt{1+M^2}}(jR)^{2n}$, with $R = \frac{\sqrt{1+M^2}-1}{M}$, and $S_{2n+1} = 0$. Thus the output can be rewritten as

$$I_{\text{out}} = I_0[1 + a\cos(\omega t)]\exp(-xS_0) \times \sum_{k=0}^{\infty} \frac{(-x)^k}{k!}(\sum_{n=1}^{\infty} S_{2n}\cos 2n\omega t)^k = \sum_{n=0}^{\infty} I_{\text{out}}^{[n]}(x, M)\cos n\omega t. \quad (2)$$

It is noticed that the odd-order harmonic signals are function of intensity modulation, while the even-order harmonics has no dependence on it. We will pay attention first to the even-order harmonics, which is usually used as a main parameter indicating gas concentration. In case of laser wavelength fixed to the center of absorption line, i.e. $\mu = 0$, some useful properties of the coefficients can be deduced as

$$S_{2(i+k)} = S_{2i}S_{2k}\sqrt{1+M^2}/2, \qquad (i, k \geq 1), \quad (3a)$$

$$S_{2(i-k)} = 2S_{2i}/S_{2k}\sqrt{1+M^2}, \qquad (i - k \geq 1), \quad (3b)$$

$$\sum_{i=1}^{\infty} S_{2i}^2 = \frac{4R^4}{(1+M^2)(1-R^4)}. \quad (3c)$$

By using these relations, products of the cosine functions can be reduced one term by one term. Nevertheless, exact analytic expressions are not available. To show a basic behavior qualitatively, harmonic signals can be expressed approximately by cutting the infinite series in Eq. (2) to terms of square of x as

$$I_{\text{out}}^{2n} \approx I_0 \exp(-S_0 x) \cdot (-S_{2n})(x - q_{2n}x^2), \quad (4)$$

where $q_2 = \frac{R^4}{\sqrt{1+M^2}(1-R^4)}$, $q_4 = \frac{1+R^4}{2\sqrt{1+M^2}(1-R^4)}$, and $q_6 = \frac{1}{\sqrt{1+M^2}(1-R^4)}$ for the first three terms as examples. Equation (4) describes the harmonics as a product of a descending exponential function and an ascending power function of absorption strength x, thereby it is understandable mathematically that there is a maximum as reported by Ref. [5]. The maximum can be obtained by differentiating Eq. (4) and setting it to zero, as follows,

$$x_{1,2} = \frac{1}{2q_{2n}S_0}[(S_0 + 2q_{2n}) \pm \sqrt{S_0^2 + 4q_{2n}^2}\ ]. \quad (5)$$

Furthermore, Eq. (4) tells another property, that is, a null occurs at points of $x = 1/q_{2n}$. To show the characteristics, numerical simulations are shown in the following.

Figure 1 shows the second harmonic signal versus absorption strength x with three modulation indices as parameters, where the symbols are calculated data by using Eq. (4) and the solid lines are given by numerical integration of Fourier expansion. It is seen that the maximal position shifts with the increase of the modulation index M, and agreement of the formula with the simulation becomes better for low absorption strength and modulation index. Figure 2 is for fourth harmonic, where the negative amplitude means a phase shift between the harmonic and the wavelength modulation. It is worth to notice that there appears null amplitude at certain absorption strength, over the null position the harmonic phase changes. The sixth harmonic has a similar behavior.

It is noticed distinctly that there are not only a maximum but also a null point in the curves of harmonic versus x, especially in Fig. 2. At two sides of the null point, the amplitudes of harmonics appear with opposite signs, that means a 180° discontinuity in phase. Theoretical analysis indicates that there is similar behavior in sixth harmonic, merely at different positions, which will be shown below together with the experimental data. For the second harmonic, nulls occur at pretty higher absorption strengths, which are usually with no practical interest. Qualitatively the maximum and null positions are in agreement of Eq. (4). To understand the phenomena physically, we should take a factor into consideration, that is, in the Lorentzian line the second derivatives take opposite signs at the peak and at the two wings near the bottom, respectively, which give opposite contributions to the harmonics. Firstly the peak contribution plays larger role, and weakened at higher absorption, and may

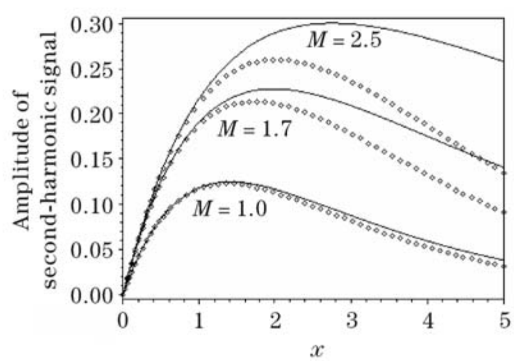

Fig. 1. Dependence of the second harmonic signal on absorption strength x and modulation index M.

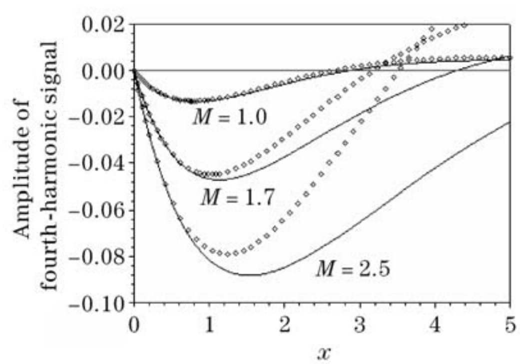

Fig. 2. Dependence of the fourth harmonic signal on x and M.

extinguish with each other in a certain case. By using Eq. (4), the behavior can be understood clearer than by using an infinite series as given in Ref. [6].

The behavior of maximal harmonic signal, rather than monotonic behavior, means that one amplitude datum may correlate with two gas concentrations. It is of practical importance, since which may lead to an error reading when measuring and sensing gas concentration by the harmonic amplitudes.

Figure 3 shows the experimental setup. A DFB laser in 1.65-μm range was used as the source, and modulated directly by driven current. Modulation index of the lasing wavelength and light intensity could be adjusted by the modulated current. A double-modulation technique of 4-kHz sinusoidal and 3-Hz triangular wave simultaneously was used to meet the requirement of alignment of wavelength with the absorption line, and the temperature of DFB LD was controlled with the precision of 0.1 K. The gas cell was made up of a sealed cylinder vessel and a pair of collimators with the effective length of 60 cm. Gas flow with changeable concentration was realized by mixing methane and nitrogen and calibrated by mass flow meter. The measurements were carried out under room temperature (RT) and normal pressure. Output signals were detected by an InGaAs PIN and an amplifier, and picked by a data acquisition device with the sampling rate of 100 kHz. Harmonic components were acquired by fast Fourier transform (FFT) of Labview program.

The $R(5)$ line of methane located at 1647.8 nm in $2\nu_3$ band was measured for 2% concentration, as shown in Fig. 4. The peak wavelength is coincident with the data reported by Refs. [9] and [10]. The absorption line profile matches Lorentzian function, and the full-width at half-maximum (FWHM) is 0.051 nm. The peak absorption coefficient of $\alpha_0 = 0.27$ cm^{-1} is measured, and the absorption across section of $R(5)$ line can then be obtained to be $\sigma = 1.1 \times 10^{-20}$ cm^2/molecule.

The harmonic signals varying with the methane concentration were measured in the range of 0% – 32%,

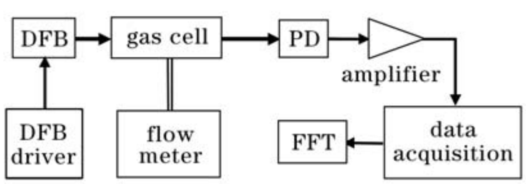

Fig. 3. Experimental setup.

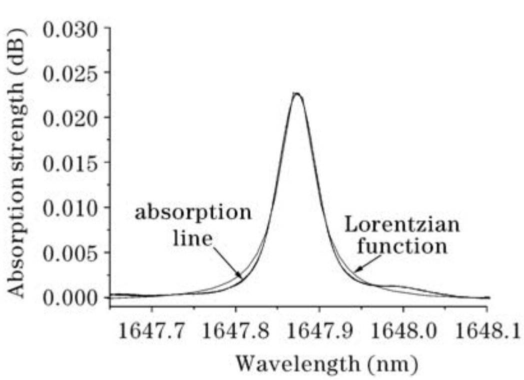

Fig. 4. Absorption spectrum of methane.

corresponding to $x = 0$ and $x = 5.16$, and with the modulation indices of $M = 1$, $M = 1.7$, $M = 2.5$. The results are shown in Figs. 5 – 7 for the second, fourth, and sixth harmonics, respectively. In the figures the measured data are signed by squares, the numerical simulations by Fourier expansion are depicted by solid lines.

For the second harmonic signal, the maximal positions were measured to be at C = 8.5%, 10.7%, and 15.5% corresponding to $x = 1.37$, 1.73, 2.5 for $M = 1$, 1.7, and 2.5 respectively. Similarly, the maxima for the fourth and sixth harmonic signals were measured experimentally. In addition, nulls were found in the fourth and sixth harmonic in the range of gas concentration below 32%. Some of the null positions were in good agreement with the theoretically calculated results, for example, the fourth harmonic with $M = 1.7$, and the sixth harmonic with $M = 2.5$. There were also some differences between

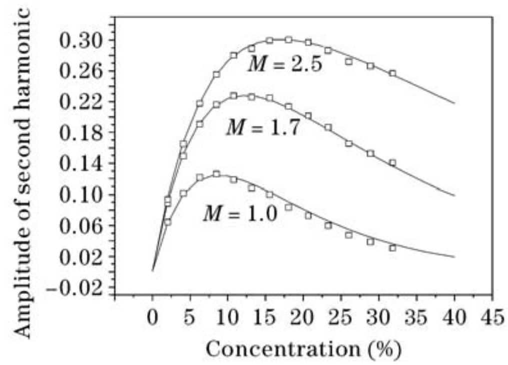

Fig. 5. Second harmonic varies with methane concentration.

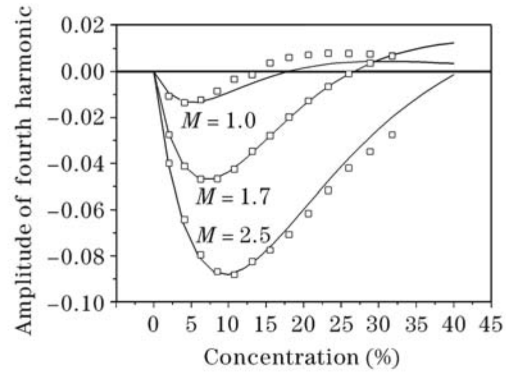

Fig. 6. Fourth harmonic varies with methane concentration.

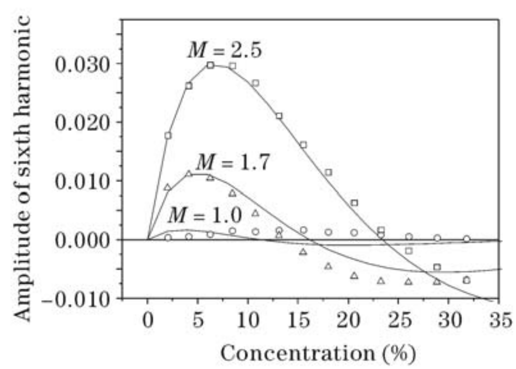

Fig. 7. Sixth harmonic varies with methane concentration.

experimental results and theoretical calculations, especially in low modulation indices such as $M = 1$. There might be higher experimental errors since the signals were very low in that case.

In summary, the behaviors of the harmonic signals in WMS are investigated theoretically and experimentally under high absorption, especially for the relation between the harmonic amplitude and the absorption strength. Approximate analytic expressions of the dependence of the second, fourth and sixth order harmonic signals on the strength are given, which are more explicit than the infinite series given by previous publications. The simulation shows that the approximate expressions are coincident with the exact Fourier expansion by means of numerical integration, especially in low absorption strength range. The observed characteristics varying with the modulation index are also in good agreement with the theoretical analysis. The non-monotonic behavior is an important property to be noticed, that would produce dual values when using the harmonic signal to measure gas concentration. The null point and non-monotonic behavior lead to additional restrictions for some parameters, such as modulation depth, the order of harmonics and the length of gas cell. The conclusion of this work will facilitate proper design and reliable application of the WMS.

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