

# 1 Frequency Modulation

The transmittance through the gas samples  $\tau(\nu)$  can be described by the Lambert-Beer equation:

$$\tau(\nu) = e^{-\sigma(\nu)z}, \quad (1)$$

where  $z = \rho l$  is the product of the absorbing species number density  $\rho$  (in molecule/cm<sup>3</sup>) and the optical path  $l$  (in cm) of the radiation through the sample, i.e. the column amount (in molecule/cm<sup>2</sup>); the absorption cross section  $\sigma(\nu)$  is therefore expressed in cm<sup>2</sup>/molecule. If  $\sigma(\nu)z \ll 1$ , that is in the small optical depth regime, as in our case, Eq. (1) can be approximated:

$$\tau(\nu) \simeq 1 - \sigma(\nu)z. \quad (2)$$

where  $\sigma(\nu)$  must behave as the shape of the absorption line: Gaussian-like for the Doppler broadening and Lorentzian-like for the collisional broadening. Other effects, like the Dicke narrowing that occurs when the molecular mean free path is comparable to the wavelength of the radiation[1], are not taken into account here.

The Voigt function, a convolution of the Lorentz and the Gauss curves, describes the behavior of the optical absorption as a function of the radiation frequency:

$$f(\nu) = \int_{-\infty}^{+\infty} \frac{\exp[-(t - \nu_0)^2 / \Gamma_G^2 \ln 2]}{(t - \nu)^2 + \Gamma_L^2} dt, \quad (3)$$

where  $\nu_0$  is the gas resonance frequency,  $\Gamma_G$  and  $\Gamma_L$  are the Gaussian and the Lorentzian half-widths at half the maximum (HWHM) respectively.

When using the FM technique, the emission frequency of the source  $\bar{\nu}$  is sinusoidally modulated at the frequency  $\nu_m = \omega_m / 2\pi$ , resulting in

$$\nu = \bar{\nu} + a \cos \omega_m t. \quad (4)$$

In this case the transmitted intensity depends on both the line shape and the modulation parameters and can be written as a cosine Fourier series:

$$\tau(\bar{\nu} + a \cos \omega_m t) = \sum_{n=0}^{\infty} H_n(\bar{\nu}, a) \cos n\omega_m t, \quad (5)$$

where  $H_n(\bar{\nu})$  is the  $n$ -th harmonic component of the modulated signal. By using a lock-in amplifier tuned to a multiple  $n\nu_m$  ( $n = 1, 2, \dots$ ) of the modulation frequency, the output signal is proportional to the  $n$ -th component  $H_n(\bar{\nu})$  and when the amplitude  $a$  is chosen smaller than the width of the line, the  $n$ -th Fourier component is proportional to the  $n$ -order derivative of the original signal:

$$H_n(\bar{\nu}, a) = \frac{2^{1-n}}{n!} a^n \left. \frac{d^n \tau(\nu)}{d\nu^n} \right|_{\nu=\bar{\nu}}, \quad n \geq 1. \quad (6)$$

A low modulation amplitude must be used for the pressure broadening and shifting measurements and if the second harmonic component is detected ( $2f$

detection), the output signal is proportional to the second order derivative of the real absorption line. This expedient not only enhances the signal-to-noise (S/N) ratio, but also reduces to zero the unwanted background. Then a non-linear least-squares fit procedure can be used in order to extract the line parameters. In particular the Lorentzian FWHM  $\gamma_L$ , the collisional component of the line-shape, as a function of the total pressure  $p$  is interpreted by the general expression:

$$\gamma_L(p) = 2\Gamma_L(p) = \gamma_i p_i + \gamma_{\text{self}} p_o, \quad (7)$$

where  $p_o$  is the partial pressure of the studied gas,  $p_i$  is partial pressure of the buffer gas  $i$ ,  $\gamma_i$  is the FWHM broadening coefficient related to the buffer gas, and  $\gamma_{\text{self}}$  is the sample gas FWHM self-broadening coefficient.

Instead, to obtain the line positions even for the weakest lines one is obliged to use large values of the modulation amplitude parameter  $m$  ( $m = a/\Gamma = 2.2$ – $2.3$  typically). This substantially improves the S/N ratio, but does not permit the utilization of Eq. (6) any more. The approximated function that well describes the absorption line distorted by modulation has been appositely calculated in the followings.

## 1.1 Frequency modulation in the high amplitude regime

When the modulation amplitude  $a$  is increased, the derivative approximation of Eq. (6) fails and the  $n$ th harmonic component  $H_n(\nu, a)$  becomes[2]

$$H_n(\nu, a) = \frac{2}{\pi} \int_0^\pi \tau(\nu + a \cos \theta) \cos n\theta \, d\theta. \quad (8)$$

The analytical evaluation of this integral is not always possible. Arndt[3] and Wahlquist[4] derived the analytical form of the harmonic components for a Lorentzian function, valid for the collisional component of the absorption line-shape. The expression for the  $n$ th harmonic component can be obtained by inverting Eq. (5):

$$H_n(x, m) = \varepsilon_n i^n \int_{-\infty}^{+\infty} \hat{\tau}(\omega) J_n(m\omega) e^{i\omega x} \, d\omega, \quad (9)$$

where

$$\hat{\tau}(\omega) = \frac{1}{2\pi} \int \tau(x) e^{-i\omega x} \, dx \quad (10)$$

is the Fourier transform of the transmittance profile;  $x = \nu/\Gamma$  and  $m = a/\Gamma$  are respectively the frequency and the amplitude of the modulation, normalized to the line-width  $\Gamma$ ;  $J_n$  is the  $n$ th order Bessel function;  $\varepsilon_0 = 1$ ,  $\varepsilon_n = 2$  ( $n = 1, 2, \dots$ ) and  $i$  is the imaginary unit. Assuming a Lorentzian absorption line-shape centered at  $\nu = 0$  (this is acceptable when, as in this case, collisional broadening dominates) the cross-section coefficient will be

$$\sigma_L(x, m) \propto \frac{1}{1 + (x + m \cos \omega t)^2}. \quad (11)$$

Referring to the work of Arndt we recalculated the second Fourier component of the cross-section coefficient by putting  $n = 2$ :

$$H_2(x, m) = -\frac{1}{m^2} \left[ \frac{\{[(1 - ix)^2 + m^2]^{1/2} - (1 - ix)\}^2}{[(1 - ix)^2 + m^2]^{1/2}} + \text{c.c.} \right] \quad (12)$$

and by eliminating the imaginary part:

$$H_2(x, m) = \frac{2}{m^2} - \frac{2^{1/2}}{m^2} \times \frac{1/2[(M^2 + 4x^2)^{1/2} + 1 - x^2][(M^2 + 4x^2)^{1/2} + M]^{1/2} + |x|[(M^2 + 4x^2)^{1/2} - M]^{1/2}}{(M^2 + 4x^2)^{1/2}}, \quad (13)$$

where

$$M = 1 - x^2 + m^2.$$

The behavior of Eq. (13), which is proportional to the 2nd derivative of the absorption feature only for low modulation, is shown in Fig. 1 as a function of the modulation parameter  $m$ . For  $m = 3$  the 2nd derivative is completely deformed by broadening, as it happens in the reality.

## References

- [1] R.H. Dicke, Phys. Rev. 89 (1953) 472–473.
- [2] C.R. Webster, R.T. Menzies, E.D. Hinkley, Laser remote chemical analysis, Wiley, New York, 1988, p. 215.
- [3] R. Arndt R, J. Appl. Phys. 36 (1965) 2522.
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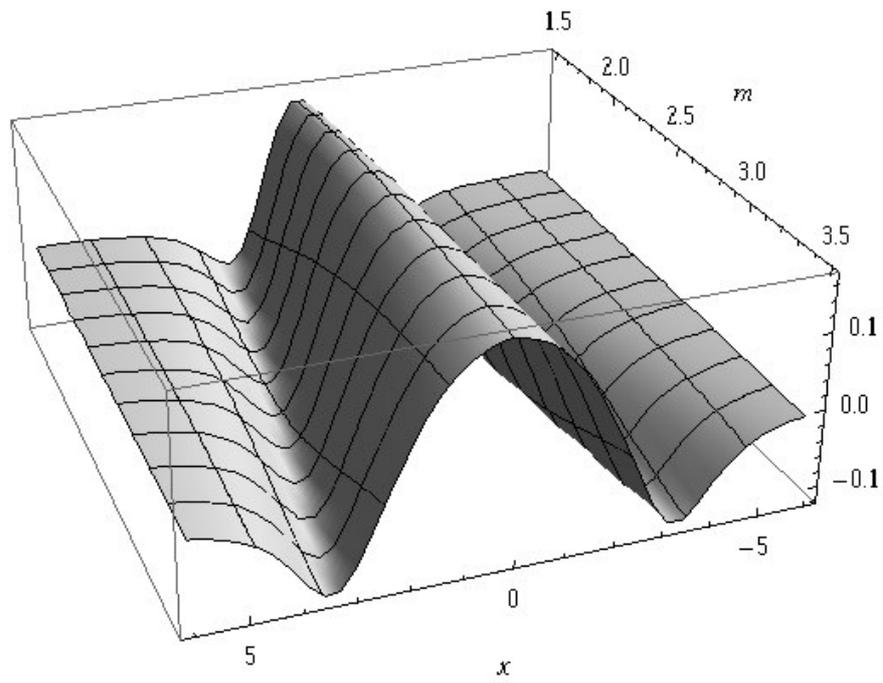


Figure 1: Behavior of Eq. (13) as a function of the modulation parameter  $m$ .