

On the measurement of pressure induced shift by diode lasers and harmonic detection

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Abstract

In this paper we present an analysis of the line shape of the ro-vibrational molecular absorptions, in case of frequency modulation spectroscopy with diode lasers, and in presence of a residual amplitude modulation. Subtle effects, such as pressure induced shift, can be measured with sufficient accuracy also for the weak transition lines of the overtone and the combination bands of the molecules, under the proviso of considering the correct fit function in order to avoid possible systematic errors. Some results are given for acetylene overtone absorptions in the derivative spectroscopy limit (small amplitude of modulation) and in the case of large amplitude of modulation.

Key words: Spectral line shapes; Diode laser spectroscopy; Frequency modulation spectroscopy

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1 Introduction

Overtone and combination ro-vibrational bands of many molecules site in the near infrared (NIR) region of the electromagnetic spectrum. The absorptions due to these bands are weaker than the ones coming from the fundamentals, thus they are more difficult to be detected. Usually it is necessary to have a longer optical path through the sample, and this can be fulfilled or by using a multipass cell [1–3], or by an intracavity spectroscopy technique [4], or one can reduce the noise of the absorption signal by adopting a frequency modulation technique with harmonic detection [5–8]. Sometime both requirements must be fulfilled.

Tunable diode lasers (TDLs) are radiation sources suitable for high resolution spectroscopy, in the NIR [9,10], with particular regard to high precision measurements of line shape parameters, such as the positions and the widths, and their dependence on the pressure, i. e. pressure induced shift and broadening.

In this paper we discuss the possibility to correctly determine the line shape parameters, when a frequency modulation (FM) technique is used and phase-sensitive detection is performed at a multiple of the modulation frequency; in particular we concentrate on the crucial role played by the amplitude modulation, that necessarily comes with the frequency modulation of a TDL. Indeed, when the injection current of a TDL changes, apart from the variation of the emission frequency, a simultaneous variation of the intensity of the emitted radiation occurs, also called residual amplitude modulation (RAM). Thus the TDL's emission profile, as a function of the emission frequency, is not constant. The most evident result of this amplitude modulation is an asymmetry of the detected signal, which must be kept into account for a correct determination of the position of the center of the line and of the coefficient of the pressure induced shift [11,12]. A similar asymmetry has also been observed in line shape measurements in the microwave region of the spectrum [13] when, due to etalon effects in the absorption cell, a frequency dependence of the radiation occurs; in that specific case this effect has not properly been taken into account for a correct determination of the shift. Recently an extension of the theory of the frequency modulation has been proposed, including the effect of the amplitude modulation and showing how the phase difference between frequency and amplitude modulation is the origin of the asymmetry in the detected signal [14]. In the followings we show an approximate though correct way to account for the presence of RAM in the second derivative absorption signal and we present our first results of pressure induced shift obtained by this analysis. Yet more we also consider the general case of second harmonic detection when the amplitude of the modulation is not small respect to the width of the absorption line. We present an approximated analytical expression for a general harmonic-detected Voigt profile, which has been implemented in a

fit routine for the case of second harmonic signals.

2 Analysis of the FM line shapes

When a harmonic detection is adopted [15], the emission frequency $\bar{\nu}$ of the diode laser is modulated sinusoidally by varying the injection current, so that

$$\nu = \bar{\nu} + m \cos \Omega t ,$$

where $\Omega = 2\pi\nu_m$, ν_m and m are respectively the frequency and the amplitude of the modulation. If the frequency $\bar{\nu}$ is slowly scanned over an interval across the chosen transition, one gets a signal $I(\bar{\nu} + m \cos \Omega t)$, which depends on both the line shape and the modulation parameters. Since it is an even function of the time, it can be written as a cosine Fourier series,

$$I(\bar{\nu} + m \cos \Omega t) = \sum_{n=0}^{\infty} H_n(\bar{\nu}, m) \cos n\Omega t , \quad (1)$$

where $H_n(\bar{\nu})$ is the n -th harmonic component of the modulated signal. Then, demodulating the signal with a lock-in amplifier at a multiple $n\nu_m$ ($n = 1, 2, \dots$) of the modulation frequency, an output signal that is proportional to the n -th component $H_n(\bar{\nu})$ is collected. In the limit of small modulation amplitude, i.e. the amplitude m is smaller than the width of the transition line ($m \ll \gamma$), the n -th Fourier component is proportional to the n -order derivative of the original signal,

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

2.1 Derivative spectroscopy limit

In this section, working in the approximation of derivative spectroscopy, we carefully analyze the effect that the variation of the TDL emission intensity has on the modulated signal.

In a rather general way, the intensity of the radiation transmitted through a sample can be written as the product

$$I(\nu) = I_0(\nu) T(\nu) , \quad (3)$$

of the incoming intensity $I_0(\nu)$ and the transmittance $T(\nu)$ (or spectral transmission), where ν is the distance from the central frequency of the line. According to the Lambert-Beer law, $T(\nu)$ is generally given by

$$T(\nu) = e^{-\alpha(\nu) d},$$

where $d = n l$ is the optical density of the sample, which is the product of the gas density n and the optical path l of the radiation through the sample, $\alpha(\nu)$ is the absorption coefficient.

In the following we assume that the absorption intensity is weak, $\alpha(\nu) d \ll 1$, so we can approximate

$$T(\nu) \simeq 1 - \alpha(\nu) d. \quad (4)$$

Let us assume a laser emission profile that varies linearly with the frequency; this is experimentally true for frequency sweeping up to tens of GHz. Putting

$$I_0 = \bar{I}_0 (1 + s \nu),$$

where \bar{I}_0 is the intensity at $\nu = 0$ and s is the fractional variation per frequency unit, the second derivative of the transmitted power, Eq. (3), will be

$$I''(\nu) = \bar{I}_0 (1 + s \nu) T'' + 2 s \bar{I}_0 T'. \quad (5)$$

Fig. 1 displays the signals corresponding to an absorption line and its second derivative, in presence of a constant emission profile (a,b) and a linear varying emission profile (c,d). In the first case the signals are symmetrical respect to the center of the line, where the second derivative have a maximum. On the contrary, as a linear profile occurs, the signal and its second derivative are not symmetric, and the center of the line displaces from the maximum of the second derivative. Moreover the apparent shifting of the center depends on the slope s of the profile and on the width γ of the transition line. This characteristic is very important when the pressure induced shift is considered. As the pressure increases, the width of the line becomes larger, then a displacement of the center due to the linear sloping background occurs and apparently it seems to be proportional to the pressure, in a way similar to the *real* pressure induced shift. If this apparent shift is not correctly considered, a systematic error will affect the measurement of the pressure induced line shift.

For the sake of simplicity, let us assume for the absorption coefficient $\alpha(\nu)$, a Lorentzian shaped function centered at $\nu = 0$, with an half width (HWHM)

γ_L ,

$$\alpha(\nu) = S \frac{\gamma_L}{\pi} \frac{1}{\nu^2 + \gamma_L^2},$$

where S is the line strength. In the weak absorption approximation, Eq. (4), the transmittance is

$$T(\nu) = 1 - S d \frac{\gamma_L}{\pi} \frac{1}{\nu^2 + \gamma_L^2}. \quad (6)$$

The second derivative of Eq. (6) can be easily expanded around $\nu = 0$, getting the displacement of the maximum as a function of the slope of the emission profile and of the linewidth,

$$\nu_{\max} = \frac{1}{4} \gamma_L \left(\xi - \frac{5}{16} \xi^3 + \dots \right),$$

where $\xi = s \gamma_L$ is the fractional variation of the intensity of the background relative to its value $I(0)$, at a distance γ_L from the center of the line.

For a numerical estimate we can reasonably assume $\xi = 0.1$, and calculate the displacement of the maximum as a function of the HWHM,

$$\frac{\nu_{\max}}{\gamma_L} = \frac{1}{4} \xi \simeq 0.025.$$

The displacement of about 2.5% of the width could be of the same order of magnitude of the pressure induced shift. Thus, if the maximum of the second derivative signal is used to determine the center of the line, a systematic error can occur, which is proportional to the width and can give an additional incorrect contribution to the measurement of the pressure induced shift coefficient. A more refined knowledge of the line shape parameters can be obtained by fitting the second derivative signal. When an accurate value for the center of the line is required, the choice of the fitting function will be critical. Sometimes the asymmetry of the signal is not evident, and it could be reasonable to choose as a fitting function the derivative of the pure absorption $\alpha(\nu)$, which is symmetric. Otherwise the asymmetry of the signal could be matched by multiplying the second derivative of the pure absorption function by a linear ramp with an appropriate slope. This is equivalent to consider only the first term of r.h.s. of Eq. (5). In both cases the estimate of the position of the line center can be still affected by the above mentioned error.

A more correct choice is the function that is the total second derivative of the signal, Eq. (5), that implicitly takes into account the presence of a non

constant background. Moreover the slope of the background can be easily determined by the direct absorption signal.

A detailed description of the experimental apparatus used for the measurements is given in Ref. [16], where the following results have been presented. Briefly, the radiation is emitted by a tunable diode laser, which is driven by a low-noise current supply and is thermally controlled within 0.002 K by a high-stability temperature controller. The slow frequency scanning is obtained by adding to the driving current a low frequency (~ 1 Hz) sawtooth signal. The radiation is split in two beams that go through two different cells containing the sample gas: the first one is kept at constant pressure and is used as reference, while the pressure is successively increased in the second one. A third beam goes through a Fabry-Perot interferometer which marks the frequency scan. The transmitted radiation is then collected by three photodiodes. For the modulation detection a sinusoidal modulated current at ~ 10 KHz is mixed to the diode laser injection current. The collected signals are sent to two lock-in amplifiers to extract the desired harmonic components.

The analysis of the experimental data has been made using the LINEFIT 2.0 software package [17], properly modified to fit the harmonic detected signals.

Fig. 2 shows the results concerning the measurement of the pressure induced shift for the acetylene transition R(21) of the combination band $\nu_1 + 3\nu_3$ at 12714.73 cm^{-1} . The absorption intensity was strong enough to be directly detected over a path length of 3 m, but it could be still considered a small absorption for which Eq. (2) is still satisfied. Then both the direct absorption signals and the second derivative ($2f$) signals were acquired and subsequently fitted. The $2f$ signals have been fitted both with the total second derivative function, and with the second derivative of the pure absorption but multiplied by an appropriate linear ramp. The line shape parameters obtained in the first case agree very well with the corresponding ones got from fitting the direct absorption signals, $c_s = (-0.7 \pm 0.2) \text{ MHz/Torr}$, while in the other case, even if there is no considerable deviation from linearity in the shift dependence on the pressure, the final value of the shift coefficient, $(-1.1 \pm 0.1) \text{ MHz/Torr}$, is considerably lower, as it could be predicted by observing the sign of the slope of the laser emission profile, i.e. $s < 0$. By using this approach, we got some more pressure-shift coefficients for the $\nu_1 + 3\nu_3$ acetylene overtones [16]; to our knowledge they are the first ever measured in this band.

For what concerns the linewidth, the results of the three different fitting procedures are equal, and the width does not seem to depend significantly on the adopted fitting function. This can be qualitatively explained considering how the width of the second derivative signal changes when a sloping emission profile occurs. For the sake of simplicity we still assume a Lorentzian absorption line shape and consider the intersection width γ_I , which is the distance

between the two points where the second derivative of the shape intersects the zero line — for a Lorentzian profile is $\gamma_I = (2/\sqrt{3}) \gamma_L$. The intersection width can be expanded as a series around $\xi = 0$

$$\gamma_I = 2\frac{\sqrt{3}}{3} \gamma_L \left(1 + \frac{4}{27}\xi^2 + \dots \right).$$

If we assume $\xi = 0.1$, the relative change in the width is

$$\frac{\Delta\gamma_I}{\gamma_I} = \frac{4}{27} \xi^2 \simeq 0.0025$$

that is smaller than the relative experimental error affecting the measurement of the width. It can be shown also that the relative change the intensity of the signal due to a non constant background is of the same order of magnitude of what calculated for the width.

For a Gauss or Voigt line shape the behavior is qualitatively the same, apart from the coefficient of the series. Indeed, as the collisional effects are concerned, when the pressure changes, only the Lorentzian contribution to the total width changes, and the effect of a sloping background is related to the weight of the Lorentz width on the total linewidth.

2.2 Large modulation amplitude

In order to improve the signal to noise ratio, often a larger value of the modulation amplitude is required.

When the amplitude m of the modulation is increased, the derivative approximation of Eq. (2) fails, and the n -th harmonic component $H_n(\nu, m)$ is generally given as [15]

$$H_n(\nu, m) = \frac{2}{\pi} \int_0^\pi \alpha(\nu + m \cos \theta) \cos n\theta \, d\theta. \quad (7)$$

The analytical evaluation of this integral is not always possible. Arndt [18] and Wahlquist [19] derived the analytical form for the harmonic components $H_n(\nu, m)$ for a Lorentzian absorption function α , while numerical methods must be adopted for Gaussian or Voigt absorption functions. Reid and Labrie [5] have found an excellent agreement between the theoretical expression of Eq. (7) and the experimental $2f$ line shape for different values of modulation amplitude and for various absorption functions.

Even if it is not possible to get an analytical expression for the derivatives of a Voigt function, we can adopt the Martin and Puerta approximation of the Voigt [20,21] and write down a representation of the second harmonic component according to Ref. [18], which takes into account the laser emission profile too.

An expression for the n-th harmonic component can be given by inverting Eq. (1):

$$H_n(x) = \epsilon_n i^n \int_{-\infty}^{+\infty} \hat{I}(\omega) J_n(a\omega) e^{i\omega x} d\omega, \quad (8)$$

where

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

is the Fourier transform of the transmittance profile; $x = \nu/\gamma_D$ and a/γ_D are respectively the frequency and the amplitude of the modulation, normalized to the Doppler width; J_n is the n-th order Bessel function; $\epsilon_0 = 1$, $\epsilon_n = 2$ ($n = 1, 2, \dots$) and i is the imaginary unit. According to Martin and Puerta, a Voigt function can be approximated by a sum of N generalized Lorentzian functions [20],

$$V(x) = \sum_{j=1}^N \frac{c_j (q - a_j) + d_j (x - b_j)}{(q - a_j)^2 + (x - b_j)^2},$$

where $q = \gamma_L/\gamma_D$ and a_j, b_j, c_j, d_j are fixed parameters which optimize the approximation. For small absorption intensities, and in presence of a linear background, the signal will be

$$I(x) = -I_0(1 + sx) V(x) = -I_0 \sum_{j=1}^N S_j(x), \quad (9)$$

where

$$\begin{aligned} S_j(x) &= (1 + s\gamma_D x) \frac{c_j(q - a_j) + d_j(x - b_j)}{(q - a_j)^2 + (x - b_j)^2} \\ &= \alpha_{1j} \frac{1}{1 + x_j^2} + \alpha_{2j} \frac{x_j}{1 + x_j^2} + \alpha_{3j} \frac{x_j^2}{1 + x_j^2} \\ &= S_j(x_j) \end{aligned} \quad (10)$$

and

$$\begin{aligned}
x_j &= \frac{x - b_j}{q - a_j} \\
\alpha_{1j} &= c_j \frac{1 + s b_j}{q - a_j} \\
\alpha_{2j} &= s c_j + d_j \frac{1 + s b_j}{q - a_j} \\
\alpha_{3j} &= s d_j .
\end{aligned}$$

The Fourier transform of Eq. (9) can be easily calculated; then, by substituting it in Eq. (8) we obtain,

$$H_n(x) = \frac{\epsilon_n}{2} \sum_{j=0}^N (\alpha_{1j} - \alpha_{3j} + i\alpha_{2j}) M(x_j) + \text{c.c.},$$

where

$$M(x_j) = \left[i^n \frac{1}{a^n} \frac{\{[(1 - i x_j)^2 + a]^1/2 - (1 - i x_j)\}^n}{[(1 - i x_j)^2 + a^2]^1/2} \right].$$

Such an expression has been used in a specifically designed fit routine for LINEFIT 2.0.

Hence we acquired the second harmonic signal for the same transition line, but with different values of the pressure and for three different values of the modulation amplitude: 0.5, 1.2, 1.6 GHz. The modulation amplitude was evaluated by measuring the splitting of the peaks in the Fabry-Perot transmitted signal. These signals have been successively fitted (see Fig. 3), and the results for the self-broadening (HWHM) and shift of the R(18) line of the $\nu_1 + 3\nu_3$ band of acetylene (12710.63 cm^{-1}) are shown in Fig. 4. The values of the self-broadening and shift coefficients obtained by fitting the three sets of data are pretty the same within the errors, giving respectively: $c_b = (4.9 \pm 0.1) \text{ MHz/Torr}$ and $c_s = (-1.0 \pm 0.1) \text{ MHz/Torr}$. It has been noted that for larger modulation amplitude the effect of the sloping background is reduced. This can be qualitatively explained by considering the presence of an additional broadening: the modulation broadening. This is constant for a fixed modulation amplitude, therefore in this condition the actual width of the second harmonic signal is larger than in the derivative limit, and the weight of the relative Lorentzian contribution, which is the only one depending on the pressure, comes to be smaller.

3 Conclusions

An analysis of the line shape of some molecular transitions when using the harmonic detection technique has been presented. In this context it has been shown how the presence of RAM influences the determination of the line shape parameters. Some approximations, that apparently fit the experimental data, can lead to erroneous results. A more correct, though approximate, way to fit those signals has been discussed both in the derivative limit and in the general case of large amplitude of modulation. Appropriate algorithms have been implemented in a fit routine for $2f$ signals. The results of the fits have been compared to what obtained by direct the absorption signals and a good agreement has been found. This agreement confirms the validity of the presented analysis and makes possible a study of line shape in the case of weak absorptions too. The wavelength modulation spectroscopy with the second harmonic detection technique, and the correct interpretation of the collected data permitted to obtain for the first time some pressure-shift coefficients for the $\nu_1 + 3\nu_3$ acetylene ro-vibrational band.

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Figure captions

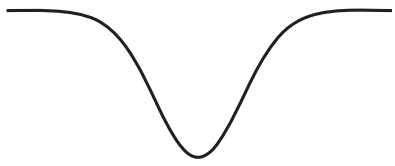
Fig. 1. Pure absorption (a) and its second derivative (b); absorption in presence of a non-constant emission profile (c) and its second derivative (d). The dashed line is the zero axis.

Fig. 2. Shift vs. pressure for the R(21) line of the $\nu_1 + 3\nu_3$ band of acetylene (12714.73 cm^{-1}). The squares are from the direct absorption signals; the $2f$ signals have been fitted both with the total derivative of the whole absorption signal (triangles) and with the symmetric derivative of the pure absorption, multiplied by an *ad hoc* ramp (circles); the dotted lines are the best fits of the three sets of data.

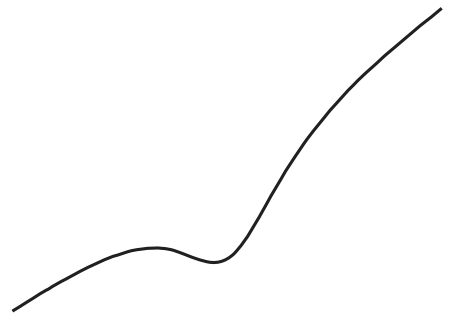
Fig. 3. Example of a $2f$ signal (dotted line) for the R(18) line of the $\nu_1 + 3\nu_3$ band of acetylene (12710.63 cm^{-1}), along with the fitted Voigt profile (solid line) and (below) the residual of the fit in the same units. The amplitude of the modulation was $\sim 1.6 \text{ GHz}$.

Fig. 4. Lorentzian HWHM (a) and shift (b) vs. pressure of the R(18) line of the $\nu_1 + 3\nu_3$ band of acetylene. The $2f$ detection has been made at three different values of modulation amplitude. The linear fits of the three sets of data give the same value of the broadening coefficient, $c_b = (4.9 \pm 0.1) \text{ MHz/Torr}$, and of the shift coefficient, $c_s = (-1.0 \pm 0.1) \text{ MHz/Torr}$.

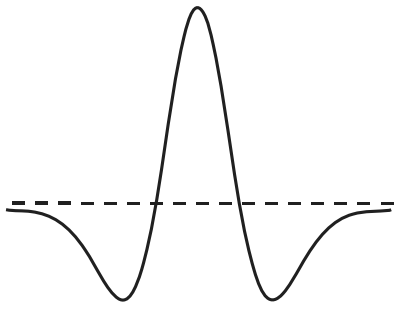
(a)



(c)

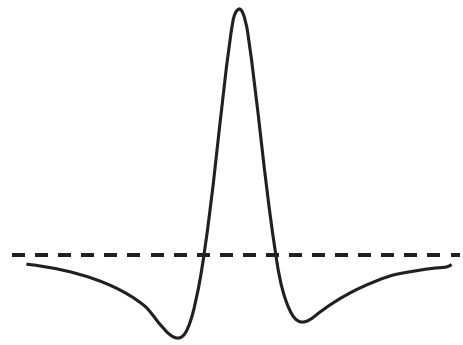


(b)



$s = 0$

(d)



$s > 0$

