Extending the applicability of the Arndt formula in wavelength modulation spectroscopy for absorbance in the lower percent range

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ABSTRACT

The Arndt formula for Lorentzian signals broadened by modulation is enhanced for the usage on 2f WMS (wavelength modulation spectroscopy) signals produced by spectroscopic lines with high absorption (percent range). Next to the first order approach of the Beer–Lambert law, which is covered by the Arndt formula, a second order term is included for a better approximation of the damped Lorentzian line shape. This second order approximation of the 2f signal can be described by a combination of several components created by the Arndt formula. The error of a pure Arndt evaluation and the improvement of the Arndt extended technique are illustrated in the example of a humidity measurement performed at 100 °C and up to 100 vol%. The energy transition at $\nu = 10,526.274910$ cm^{-1} is used in this setup. With the presented technique, the error is reduced by a factor of 90.

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1. Introduction

Wavelength modulation spectroscopy is a widely spread technique in molecular spectroscopy. Applying a wavelength modulation, which covers an absorption line, and analyzing the harmonic components of this modulation, by means of phase sensitive detection, eliminate the laser background and supply a very good signal-to-noise ratio [1]. In 1965, Arndt developed an analytical expression for the different harmonic components of a Lorentzian signal broadened by modulation [2], which enables a fast computation of the signals created by wavelength modulation spectroscopy. Basically, this expression covers a pure Lorentzian line shape, but molecular spectroscopic signals are also subject to the nonlinearity of the Beer–Lambert law.

However, for low absorption (< 0.01), the exponential function can be approximated and the Arndt expression becomes applicable [3].

For signals with larger absorption, other techniques, e.g. direct absorption measurement, are applied. Problems occur for systems, which have to cover a wide absorption range. Calculating the WMS signal for large absorption with the Arndt formula includes systematical deviations. For low absorption, it is difficult to distinguish between the laser background and the absorption signal in direct spectroscopy. Additionally high-resolution analog–digital converters are needed to measure a very low signal on a high background [4].

In the literature a lot of approaches for calculating WMS signals for the extension of the Lorentzian line shape by a Gaussian part (the so-called Voigt line shape) exist [5,6]. Since most authors try to measure very low signals, a lack occurs for research on the influence of the Beer–Lambert law on WMS signals for optically thick conditions. Only the group around Axner [7,8] analyzes the applicability of

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WMS to absorption signals with higher absorbances using simulations, but there is also no closed solution given. Basically, the WMS line shape influenced by the Beer–Lambert law could be calculated with a numerical approach based on the discrete Fourier transform. However, this calculation is quite time consuming and almost not applicable on a microcontroller hardware.

First of all the presented paper analyzes the theoretical Lorentzian line shape influenced by the Beer–Lambert law and then develops an extension of the Arndt formula with a more exact approximation. Then, the technique is applied to humidity measurements with a wide range of absorption and compared with the results of an exact full model approach and the Arndt approximation.

2. Theory

2.1. Error resulting from the Arndt approximation for high absorption

The absorption of light is characterized by the Beer–Lambert law as follows:

$$I(\nu) = I_0 \exp(-\alpha(\nu)cl) \approx I_0(1 - \alpha(\nu)cl) \tag{1}$$

with I_0 being the initial light intensity, $\alpha(\nu)$ the wave number dependent absorption coefficient, c the gas concentration and l the length of the optical path. The term $\alpha(\nu)cl$ is further referred to as *absorbance*. For simplicity, the initial light intensity is assumed to be constant. This expression could be expanded to a Taylor series and, for low absorbance ($\alpha(\nu)cl < 0.01$), approximated with the constant and the first order term. With modulation of the wave number the expression becomes

$$I(\nu + m \cdot \cos(\omega t)) \approx I_0(1 - \alpha(\nu + m \cdot \cos(\omega t))cl) \tag{2}$$

with m being the modulation amplitude, ω the angular frequency and t the time. As a line profile, a Lorentzian line shape is used. Since a lot of conditions exist, where the absorption line shape is almost completely dominated by the Lorentzian part, this assumption is applicable for many gases. As an example, in case of water vapor lines, the Lorentzian line shape dominates for high temperatures and high concentrations due to the huge self-broadening of the lines. Also for the CO_2 lines at 2 μm almost no Gaussian part exists at room conditions.

After replacing the absorption coefficient with the Lorentzian profile the expression is expanded into a Fourier series, whose coefficients are given by the Arndt formula as follows:

$$I(\nu + m \cdot \cos(\omega t)) \approx I_0(1 - Scl/(1 + (\nu + m \cdot \cos(\omega t))^2)$$
$$= I_0\left(1 - Scl \sum_{n=0}^{\infty} S_n(\nu) \cos(n\omega t)\right) \tag{3}$$

$$S_n(\nu) = \frac{1}{2*m^n}\varepsilon_n i^n \frac{\{[(1-i\nu)^2 + m^2]^{1/2} - (1-i\nu)\}^n}{[(1-i\nu)^2 + m^2]^{1/2}} + c.c. \tag{4}$$

with S being the line strength, n the number of the Fourier component, i the imaginary unit and *c.c.* the conjugate complex part. The factor ε_n is 1 for $n=0$, otherwise 2.

If absorbance < 0.01 is not fulfilled, the deviation of the first order approximation to the real signal quickly rises to
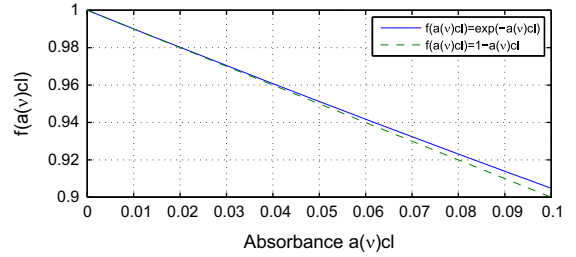

Fig. 1. Exponential function (solid) and its first order approximation (dashed).
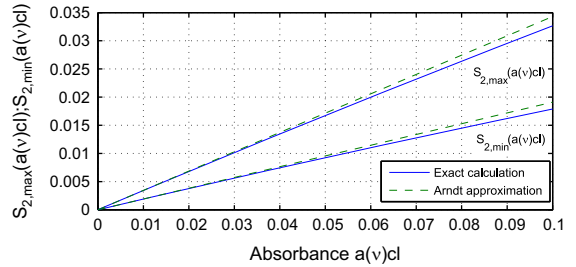

Fig. 2. Exact calculation (solid) and Arndt approximation (dashed) of 2*f* maximum and minima.

several percent (Fig. 1). For example, for an absorbance of 0.04, the deviation to the exact signal is already 2%. By means of a more extended Taylor expansion of the natural exponential function, the deviation can be estimated as follows:

$$y(x) = \exp(x) = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \cdots = 1 - x + r(x) \tag{5}$$

$$r(x) = \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \cdots \tag{6}$$

$$\Rightarrow \frac{x^2}{2!} > r(x) > \frac{x^2}{2!} - \frac{x^3}{3!} \tag{7}$$

with $r(x)$ being the residual function. Since the value of each polynomial term is smaller than the value of one lower order, the residual is smaller than the second polynomial term but at least as high as the second minus the third term (Eq. (7)).

The effect of the approximation on the 2*f* spectroscopic signal is not as easily estimated as for the direct signal, due to the missing information of the 2*f* behavior on the residual function (Eq. (7)). Since the exact 2*f* signal can be calculated numerically by means of the discrete Fourier transform, the deviation of the Arndt-2*f* to the exact calculation can be numerically determined. This deviation, depending on the absorbance, is illustrated in Fig. 2 for the maximum 2*f* value at the line center and the two minima. The differences behave very similar to the deviation in the direct spectroscopic signal. Again, for an absorbance of 0.04, the difference of the maximum is around 2%. For the minima, it is with approximately 2.7% a bit higher.

A least-squares curve fit of an Arndt approximated model to the exact 2*f* signal (absorbance 0.04) with only