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Analytical expression for the n^{th} Fourier coefficient of a modulated Lorentzian dispersion lineshape function

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Abstract

Modulated spectroscopic detection techniques that rely on dispersion, e.g. Faraday modulation/rotation spectroscopy and wavelength-modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy, are often described in terms of Fourier coefficients of the modulated dispersion lineshape function. This work derives a non-complex analytical expression for the n^{th} Fourier coefficient of a modulated Lorentzian dispersion lineshape function, which is easier to implement, and orders of magnitude faster to execute, than previous approaches involving numerical calculations of integrals. The first six Fourier coefficients are illustrated for their optimum modulation amplitudes. An analytical expression for the first Fourier coefficient is explicitly given.

Keywords: Modulated Lorentzian dispersion lineshape, Fourier coefficient, Phase-sensitive detection, Faraday modulation/rotation spectrometry, FAMOS/FRS, NICE-OHMS

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1. Introduction

The spectroscopic detection techniques that rely on dispersion and are simultaneously modulated are often described in terms of the first Fourier coefficient of the modulated dispersion lineshape function, which, in turn, is given by an integral containing a product of a modulated dispersion lineshape function and a sinusoidal function. Examples of such techniques are Faraday modulation/rotation spectroscopy (FAMOS/FRS), which is used for detection of paramagnetic gaseous species, in particular NO [1–9], and wavelength-modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy, commonly referred to as wm-NICE-OHMS [10]. It has been shown that the signals from these techniques can be written in terms of such first Fourier coefficients [1, 2, 7, 11–13].

To the authors’ knowledge, no analytical expression for any Fourier coefficient of a modulated dispersion lineshape function, for any type of lineshape, has so far been derived, why they normally are calculated numerically. Although perfectly legitimate, such procedures involve time-consuming numerical calculations that prevents efficient real-time curve-fitting.

In this work, an analytical expression is derived for the general n^{th} Fourier coefficient of a modulated Lorentzian dispersion lineshape function, which thus is valid for pressure broadened media [11], and, for the case with wm-NICE-OHMS, also for sub-Doppler detection [13–15]. The expression is first derived with a complex notation but later expressed in a non-complex form, which makes it easily implemented in computer code for simulations and curve-fitting. The expression for the first Fourier coefficient is explicitly

given.

2. Fourier expansion of a modulated general lineshape function

In order to derive the n^{th} Fourier coefficient of a modulated Lorentzian dispersion lineshape function, and following the calculations outlined by Arndt [16] for the case of the corresponding absorption lineshape function, the lineshape function will be written in terms of a Fourier series.

Let $F(\nu_d)$ denote an arbitrary lineshape function, where ν_d is the frequency detuning from the center frequency of the transition given in suitable units. For the case of a sinusoidally modulated detuning given by $\nu_d(t) = \nu_d + \nu_a \cos \Omega t$, where ν_d is the frequency detuning in the absence of modulation, ν_a the modulation amplitude, and Ω the modulation frequency, the time-dependent modulated lineshape function, $F[\nu_d(t)] = F(\nu_d + \nu_a \cos \Omega t)$, can be expressed in terms of a Fourier series by Fourier transformation.

By denoting the Fourier transform of $F(\nu_d)$ by $f(\tau)$, defined by

$$f(\tau) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(\nu_d) e^{-i\nu_d \tau} d\nu_d, \quad (1)$$

where τ is the conjugate variable to ν_d , and using some properties of Fourier analysis¹, it is possible to write the time-dependent Fourier transform of $F[\nu_d(t)]$, $f(\tau, t)$, as

$$f(\tau, t) = f(\tau) e^{i\nu_a \tau \cos \Omega t}, \quad (2)$$

¹Given that $f(\tau)$ is the Fourier transform of $F(\nu_d)$, the Fourier transform of $F(\nu_d + a)$ is $f(\tau) e^{ia\tau}$.

where $f(\tau)$ is the Fourier transform of the unmodulated lineshape function, given by equation (1). By utilizing the Jacobi-Anger formula² this Fourier transform can be written in terms of a sum of harmonic components of the modulation frequency, $\cos(n\Omega t)$, *viz.* as

$$f(\tau, t) = \sum_{n=0}^{\infty} (2 - \delta_{n0}) i^n f(\tau) J_n(\nu_a \tau) \cos(n\Omega t), \quad (3)$$

where δ_{n0} is Kronecker's delta function and J_n is the n^{th} Bessel function.

Using the inverse Fourier transform, which is defined as

$$F(\nu_d) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(\tau) e^{i\nu_d \tau} d\tau, \quad (4)$$

it is finally possible to write $F[\nu_d(t)]$ succinctly as

$$F[\nu_d(t)] = \sum_{n=0}^{\infty} \bar{\chi}_n(\nu_d, \nu_a) \cos(n\Omega t), \quad (5)$$

where $\bar{\chi}_n(\nu_d, \nu_a)$ is the n^{th} (in-phase) Fourier coefficient of the time-dependent modulated lineshape function $F[\nu_d(t)]$, given by

$$\bar{\chi}_n(\nu_d, \nu_a) = (2 - \delta_{n0}) \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} i^n f(\tau) J_n(\nu_a \tau) e^{i\nu_d \tau} d\tau. \quad (6)$$

²The Jacobi-Anger formula states that $e^{iz \cos \theta} = \sum_{n=0}^{\infty} (2 - \delta_{n0}) i^n J_n(z) \cos n\theta$.

3. Derivation of an analytical expression for the n^{th} Fourier coefficient of a modulated Lorentzian dispersion signal

The normalized Lorentzian dispersion lineshape function (which corresponds to the area-normalized Lorentzian absorption lineshape function by the Kramer-Kronigs' relations [17, 18]) can be expressed in terms of a normalized frequency, $\bar{\nu}_d$, given by ν_d/Γ , where Γ is the half-width-half-maximum (HWHM) of the Lorentzian absorption profile, as [19]

$$F(\bar{\nu}_d) = \frac{1}{\pi} \frac{\bar{\nu}_d}{1 + \bar{\nu}_d^2}. \quad (7)$$

Using equation (1) its Fourier transform is found to be

$$f(\bar{\tau}) = -\frac{i}{\sqrt{2\pi}} e^{-|\bar{\tau}|}, \quad (8)$$

where $\bar{\tau}$ is a normalized time given by $\tau\Gamma$.

When the frequency is modulated according to $\bar{\nu}(t) = \bar{\nu}_d + \bar{\nu}_a \cos \Omega t$, where $\bar{\nu}_d$ and $\bar{\nu}_a$ are the normalized detuning and the normalized modulation amplitude, respectively, the n^{th} Fourier coefficient of the modulated Lorentzian dispersion lineshape function is given by equation (6). Inserting equation (8) into equation (6) implies that $\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a)$ can be expressed as

$$\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a) = -\frac{1}{\pi} \left(1 - \frac{\delta_{n0}}{2}\right) \int_{-\infty}^{\infty} i^{n+1} e^{-|\bar{\tau}|} J_n(\bar{\nu}_a \bar{\tau}) e^{i\bar{\nu}_d \bar{\tau}} d\bar{\tau}. \quad (9)$$

This integral is similar to that for a Lorentzian absorption lineshape function [16], whereby $\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a)$ can be written as,

$$\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a) = -\frac{1}{\pi} \left(1 - \frac{\delta_{n0}}{2}\right) \frac{i^{n+1} \left\{ [(1 - i\bar{\nu}_d)^2 + \bar{\nu}_a^2]^{\frac{1}{2}} - (1 - i\bar{\nu}_d) \right\}^n}{\bar{\nu}_a^n [(1 - i\bar{\nu}_d)^2 + \bar{\nu}_a^2]^{\frac{1}{2}}} + c.c., \quad (10)$$

where *c.c.* stands for the complex conjugate.

4. Conversion of the analytical expression for the n^{th} Fourier coefficient to a non-complex form

Even though the expression given in equation (10) is mathematically correct, it is not given in its most useful form. It is possible to rewrite equation (10), following the procedures outlined by Axner et al. [20], in a non-complex form, making it more suitable for fast simulations and curve-fitting.

4.1. Elimination of the power dependence of the order n on $\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a)$

The power dependence of the order n on $\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a)$ can be eliminated by using the following variable substitutions

$$\begin{aligned} M &= 1 + \bar{\nu}_a^2 - \bar{\nu}_d^2 \\ R &= \sqrt{M^2 + 4\bar{\nu}_d^2} \\ A_n &= -\frac{(2 - \delta_{n0})}{\pi}, \end{aligned} \quad (11)$$

which gives

$$\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a) = \frac{A_n}{2\bar{\nu}_a^n} \sqrt{M + 2i\bar{\nu}_d} \frac{[\sqrt{M - 2i\bar{\nu}_d} - (1 - i\bar{\nu}_d)]^n}{R} i^{n+1} + c.c.. \quad (12)$$

It is furthermore possible to rewrite $[\sqrt{M - 2i\bar{\nu}_d} - (1 - i\bar{\nu}_d)]^n$ in the numerator by using the binomial expansion theorem [21],

$$[\sqrt{M - 2i\bar{\nu}_d} - (1 - i\bar{\nu}_d)]^n = \sum_{j=0}^n \binom{n}{j} (M - 2i\bar{\nu}_d)^{\frac{n-j}{2}} (-1)^j (1 - i\bar{\nu}_d)^j, \quad (13)$$

where, in turn,

$$(1 - i\bar{\nu}_d)^j = \sum_{k=0}^j \binom{j}{k} (-1)^k i^k \bar{\nu}_d^k, \quad (14)$$

and

$$(M - 2i\bar{\nu}_d)^{\frac{n-j}{2}} = \begin{cases} \sum_{l=0}^{(n-j)/2} \binom{\frac{n-j}{2}}{l} M^{[(n-j)/2-l]} (-1)^l 2^l i^l \bar{\nu}_d^l \\ \sqrt{M - 2i\bar{\nu}_d} \sum_{l=0}^{(n-j-1)/2} \binom{\frac{n-j-1}{2}}{l} M^{[(n-j-1)/2-l]} (-1)^l 2^l i^l \bar{\nu}_d^l, \end{cases} \quad (15)$$

where the two cases in equation (15) refer to when $n - j$ is even and odd, respectively. To handle the two different cases, it is convenient to introduce two new variables, κ_a^+ and κ_a^- , defined as

$$\kappa_a^+ = \frac{1 + (-1)^a}{2} = \begin{cases} 1 & \text{when } a \text{ is even,} \\ 0 & \text{when } a \text{ is odd,} \end{cases} \quad (16)$$

$$\kappa_a^- = \frac{1 - (-1)^a}{2} = \begin{cases} 0 & \text{when } a \text{ is even,} \\ 1 & \text{when } a \text{ is odd.} \end{cases} \quad (17)$$

Utilizing these variables equation (15) can be rewritten as

$$(M - 2i\bar{\nu}_d)^{\frac{n-j}{2}} = (\kappa_{n-j}^+ + \kappa_{n-j}^- \sqrt{M - 2i\bar{\nu}_d}) \sum_{l=0}^{l_{max}} (-1)^l \binom{l_{max}}{l} 2^l M^{(l_{max}-l)} \bar{\nu}_d^l i^l, \quad (18)$$

where we have introduced

$$l_{max} = Int^- \left(\frac{n-j}{2} \right), \quad (19)$$

where the $Int^-(x)$ function is defined as $sign(x)floor(|x|)$, where $sign(x)$ represents the sign of the argument, x , and $floor(x)$ extracts the nearest lower integer of the argument, x . Inserting the equations (14) and (18) into the equations (12) and (13) gives

$$\begin{aligned} \bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a) &= \frac{A_n}{2\bar{\nu}_a^n} \sum_{j=0}^n \sum_{k=0}^j \sum_{l=0}^{l_{max}} \left[(-1)^{j+k+l} \binom{n}{j} \binom{j}{k} \binom{l_{max}}{l} 2^l M^{(l_{max}-l)} \bar{\nu}_d^{(k+l)} \right. \\ &\quad \times \left. \left(\frac{\kappa_{n-j}^+ \sqrt{M + 2i\bar{\nu}_d}}{R} + \kappa_{n-j}^- \right) i^{n+k+l+1} \right] + c.c.. \end{aligned} \quad (20)$$

By using our previously defined κ -functions it is possible to express $i^{n+k+l+1}$ as

$$i^{n+k+l+1} = (\kappa_{n+k+l+1}^+ + i\kappa_{n+k+l+1}^-) (-1)^\Gamma, \quad (21)$$

where Γ is given by

$$\Gamma = Int^- \left(\frac{n+k+l+1}{2} \right). \quad (22)$$

This implies that $\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a)$ can be written as

$$\begin{aligned} \bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a) = & \frac{A_n}{2\bar{\nu}_a^n} \sum_{j=0}^n \sum_{k=0}^j \sum_{l=0}^{l_{max}} \left\{ (-1)^{j+k+l+\Gamma} \binom{n}{j} \binom{j}{k} \binom{l_{max}}{l} 2^l M^{(l_{max}-l)} \bar{\nu}_d^{(k+l)} \right. \\ & \times \left[\left(\kappa_{n+k+l+1}^+ + i\kappa_{n+k+l+1}^- \right) \left(\kappa_{n-j}^- + \frac{\kappa_{n-j}^+ \sqrt{M+2i\bar{\nu}_d}}{R} \right) + c.c. \right] \Big\} \end{aligned} \quad (23)$$

where all complex parts have been collected in the bracket.

4.2. Reduction of $\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a)$ to a non-complex form

Although expressed by complex notation, equation (23) is a fully real expression. $\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a)$ can be reduced to a non-complex form by expanding the bracket in equation (23) which gives rise to four components:

$$\begin{aligned} \kappa_{n+k+l+1}^+ \kappa_{n-j}^- + c.c. &= 2\kappa_{n+k+l+1}^+ \kappa_{n-j}^-, \\ \kappa_{n+k+l+1}^+ \kappa_{n-j}^+ \frac{\sqrt{M+2i\bar{\nu}_d}}{R} + c.c. &= \kappa_{n+k+l+1}^+ \kappa_{n-j}^+ \frac{\sqrt{2}S_+}{R}, \\ i\kappa_{n+k+l+1}^- \kappa_{n-j}^- + c.c. &= 0, \\ i\kappa_{n+k+l+1}^- \kappa_{n-j}^+ \frac{\sqrt{M+2i\bar{\nu}_d}}{R} + c.c. &= -\kappa_{n+k+l+1}^- \kappa_{n-j}^+ \text{sign}(\bar{\nu}_d) \frac{\sqrt{2}S_-}{R}, \end{aligned} \quad (24)$$

where we have introduced the two variables S_+ and S_- defined by

$$\begin{aligned} S_+ &= \sqrt{R+M} \\ S_- &= \sqrt{R-M}. \end{aligned} \quad (25)$$

Since all imaginary parts have been eliminated, it is possible to write the non-complex expression for the n^{th} Fourier coefficient of a modulated Lorentzian dispersion lineshape function succinctly as ³

$$\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a) = \frac{A_n}{\bar{\nu}_a^n} \left[B_n + \frac{C_n S_+ + D_n S_-}{\sqrt{2}R} \right], \quad (26)$$

where the B_n , C_n , and D_n coefficients are given by

$$B_n = \sum_{j=0}^n \sum_{k=0}^j \sum_{l=0}^{l_{max}} \left[(-1)^{j+k+l+\Gamma} \binom{n}{j} \binom{j}{k} \binom{l_{max}}{l} \right. \\ \left. \times 2^l M^{(l_{max}-l)} \bar{\nu}_d^{(k+l)} \kappa_{n-j}^- \kappa_{n+k+l+1}^+ \right], \quad (27)$$

$$C_n = \sum_{j=0}^n \sum_{k=0}^j \sum_{l=0}^{l_{max}} \left[(-1)^{j+k+l+\Gamma} \binom{n}{j} \binom{j}{k} \binom{l_{max}}{l} \right. \\ \left. \times 2^l M^{(l_{max}-l)} \bar{\nu}_d^{(k+l)} \kappa_{n-j}^+ \kappa_{n+k+l+1}^+ \right], \quad (28)$$

³This expression is of the same general form as that for the n^{th} Fourier coefficient of a modulated Lorentzian absorption lineshape function [20]. The B_n , C_n , and D_n coefficients are similar but slightly different from those derived for that lineshape function [20].

and

$$D_n = -\text{sign}(\bar{\nu}_d) \sum_{j=0}^n \sum_{k=0}^j \sum_{l=0}^{l_{max}} \left[(-1)^{j+k+l+\Gamma} \binom{n}{j} \binom{j}{k} \binom{l_{max}}{l} \right. \\ \left. \times 2^l M^{(l_{max}-l)} \bar{\nu}_d^{(k+l)} \kappa_{n-j}^+ \kappa_{n+k+l+1}^- \right] \quad . \quad (29)$$

4.3. Simplification of the B_n , C_n , and D_n coefficients

It is possible to further simplify the expressions for the B_n , C_n , and D_n coefficients, expressing them only in terms of normalized detuning, $\bar{\nu}_d$, and normalized modulation amplitude, $\bar{\nu}_a$. Utilizing the same method as is outlined in Appendix A of Axner et al. [20] implies that they can be written as

$$B_n(\bar{\nu}_d, \bar{\nu}_a) = \sum_{a=0}^{a_{max}} \sum_{b=0}^a \sum_{r=0}^{a-b} \sum_{s=0}^r \sum_{c=c_{min}}^{c_{max}} \left[(-1)^{a-b-r+c+1} \right. \\ \left. \times \binom{n}{n-2a-1} \binom{a}{b} \binom{a-b}{r} \binom{r}{s} \binom{n-2a-1}{2c-n-b-1} 2^b \bar{\nu}_a^{2s} \bar{\nu}_d^{2(a-b-r+c)-n-1} \right], \quad (30)$$

$$C_n(\bar{\nu}_d, \bar{\nu}_a) = \sum_{d=0}^{d_{max}} \sum_{e=0}^d \sum_{r=0}^{d-e} \sum_{s=0}^r \sum_{f=f_{min}}^{f_{max}} \left[(-1)^{d-e-r+f+1} \right. \\ \left. \times \binom{n}{n-2d} \binom{d}{e} \binom{d-e}{r} \binom{r}{s} \binom{n-d}{2f-n-e-1} 2^e \bar{\nu}_a^{2s} \bar{\nu}_d^{2(d-e-r+f)-n-1} \right], \quad (31)$$

and

$$D_n(\bar{\nu}_d, \bar{\nu}_a) = \text{sign}(\bar{\nu}_d) \sum_{d=0}^{d_{max}} \sum_{e=0}^d \sum_{r=0}^{d-e} \sum_{s=0}^r \sum_{g=g_{min}}^{g_{max}} \left[(-1)^{d-e-r+g+1} \right. \\ \left. \times \binom{n}{n-2d} \binom{d}{e} \binom{d-e}{r} \binom{r}{s} \binom{n-d}{2g-n-e} 2^e \bar{\nu}_a^{2s} \bar{\nu}_d^{2(d-e-r+g)-n} \right], \quad (32)$$

where the summation indices are given in Table 1.

For convenience of the reader the expressions for the B_n , C_n and D_n coefficients for the first six Fourier components are explicitly given in Tables 2-4.

This implies that the first Fourier coefficient, $\bar{\chi}_1(\bar{\nu}_d, \bar{\nu}_a)$, which is the entity that is most often used, can be explicitly written as

$$\bar{\chi}_1(\bar{\nu}_d, \bar{\nu}_a) = \frac{2}{\bar{\nu}_a \pi} \left[1 - \frac{S_+ + \text{sign}(\bar{\nu}_d) \bar{\nu}_d S_-}{\sqrt{2} R} \right] = \\ = \frac{2}{\bar{\nu}_a \pi} \left\{ 1 - \frac{\sqrt{2}}{2 \sqrt{(1 + \bar{\nu}_a^2 - \bar{\nu}_d^2)^2 + 4 \bar{\nu}_d^2}} \right. \\ \times \left[\sqrt{\sqrt{(1 + \bar{\nu}_a^2 - \bar{\nu}_d^2)^2 + 4 \bar{\nu}_d^2} + 1 + \bar{\nu}_a^2 - \bar{\nu}_d^2} \right. \\ \left. \left. + |\bar{\nu}_d| \sqrt{\sqrt{(1 + \bar{\nu}_a^2 - \bar{\nu}_d^2)^2 + 4 \bar{\nu}_d^2} - 1 - \bar{\nu}_a^2 + \bar{\nu}_d^2} \right] \right\} \quad (33)$$

5. Illustration of the first six Fourier coefficients of a modulated Lorentzian dispersion lineshape function

The two panels (a) and (b) in Fig. 1 display the first three even and odd Fourier coefficients, $\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a)$, i.e. for $n = 0, 2, 4$ and $n = 1, 3, 5$, respectively,

Table 1: Expressions for the summation indices given in equations (30)-(32).

Summation index	Expression ^a
a_{max}	$Int^-\left(\frac{n-1}{2}\right)$
c_{min}	$Int^+\left(\frac{n+b-1}{2}\right)$
c_{max}	$n - a + Int^-\left(\frac{b-2}{2}\right)$
d_{max}	$Int^-\left(\frac{n}{2}\right)$
f_{min}	$Int^+\left(\frac{n+e+1}{2}\right)$
f_{max}	$n - d + Int^-\left(\frac{e+1}{2}\right)$
g_{min}	$Int^+\left(\frac{n+e}{2}\right)$
g_{max}	$n - d + Int^-\left(\frac{e}{2}\right)$

^a Mathematically the $Int^+(x)$ and $Int^-(x)$ functions are defined as $sign(x)ceil(|x|)$ and $sign(x)floor(|x|)$, respectively, where $sign(x)$ represents the sign of the argument, x , and $ceil(x)$ and $floor(x)$ extract the nearest upper and lower integer of the argument, x , respectively.

Table 2: Expressions for the first six B_n coefficients.

Summation index	Expression
B_0	0
B_1	-1
B_2	$2\bar{\nu}_d$
B_3	$4 + \bar{\nu}_a^2 - 4\bar{\nu}_d^2$
B_4	$-24\bar{\nu}_d - 4\bar{\nu}_a^2\bar{\nu}_d + 8\bar{\nu}_d^3$
B_5	$-16 - 12\bar{\nu}_a^2 - \bar{\nu}_a^4 + 96\bar{\nu}_d^2 + 12\bar{\nu}_a^2\bar{\nu}_d^2 - 16\bar{\nu}_d^4$

Table 3: Expressions for the first six C_n coefficients.

Summation index	Expression
C_0	0
C_1	1
C_2	$-4\bar{\nu}_d$
C_3	$-4 - 3\bar{\nu}_a^2 + 12\bar{\nu}_d^2$
C_4	$32\bar{\nu}_d + 16\bar{\nu}_a^2\bar{\nu}_d - 32\bar{\nu}_d^3$
C_5	$16 + 20\bar{\nu}_a^2 + 5\bar{\nu}_a^4 - 160\bar{\nu}_d^2 - 60\bar{\nu}_a^2\bar{\nu}_d^2 + 80\bar{\nu}_d^4$

Table 4: Expressions for the first six D_n coefficients.

Summation index	Expression
D_0	$-sign(\bar{\nu}_d)$
D_1	$sign(\bar{\nu}_d)\bar{\nu}_d$
D_2	$-sign(\bar{\nu}_d)(-2 - \bar{\nu}_a^2 + 2\bar{\nu}_d^2)$
D_3	$-sign(\bar{\nu}_d)(12\bar{\nu}_d + 3\bar{\nu}_a^2\bar{\nu}_d - 4\bar{\nu}_d^3)$
D_4	$-sign(\bar{\nu}_d)(8 + 8\bar{\nu}_a^2 + \bar{\nu}_a^4 - 48\bar{\nu}_d^2 - 8\bar{\nu}_a^2\bar{\nu}_d^2 + 8\bar{\nu}_d^4)$
D_5	$-sign(\bar{\nu}_d)(-80\bar{\nu}_d - 60\bar{\nu}_a^2\bar{\nu}_d - 5\bar{\nu}_a^4\bar{\nu}_d +$ $+160\bar{\nu}_d^3 + 20\bar{\nu}_a^2\bar{\nu}_d^3 - 16\bar{\nu}_d^5)$

as a function of normalized detuning $\bar{\nu}_d$. Each Fourier coefficient has been evaluated at its optimum modulation amplitude, $\bar{\nu}_a$, which corresponds to 0, 1.27, 2.84, 3.15, 4.44 and 5.10 for the 0th, 1st, 2nd, 3rd, 4th and 5th Fourier coefficient, respectively. The optimum modulation amplitude can be extracted from Fig. 2 in which the maximum of the first three even [panel (a)] and odd [panel (b), on resonance] Fourier coefficients are given as a function of normalized modulation amplitude.

The Fourier coefficients derived above and illustrated in Fig. 1 are indistinguishable from those calculated numerically using the integral

$$\frac{2}{\tau} \int_0^{\tau} F[\bar{\nu}_d(t)] \cos(n\Omega t) dt, \quad (34)$$

where $F[\bar{\nu}_d(t)]$ is given by equation (7) and where $\bar{\nu}_d(t) = \bar{\nu}_d + \bar{\nu}_a \cos(\Omega t)$, which previously have appeared in the literature, e.g. in Westberg et al. [12],

Lathdavong et al. [22], and Foltynowicz et al. [11].

Figure 1: Panel (a): the first three even Fourier coefficients ($n = 0, 2, 4$) of a modulated Lorentzian dispersion lineshape function as a function of normalized detuning evaluated at their optimum normalized modulation amplitudes (which correspond to 0, 2.84 and 4.44 for the 0th, 2nd and 4th Fourier coefficients, respectively). Panel (b): the first three odd Fourier coefficients ($n = 1, 3, 5$) as a function of normalized detuning evaluated at their optimum normalized modulation amplitudes (which correspond to 1.27, 3.15 and 5.10 for the 1st, 3rd and 5th Fourier coefficients, respectively).

Figure 2: Panel (a): maximum value of the first three even Fourier coefficients ($n = 0, 2, 4$) of a modulated Lorentzian dispersion lineshape function as a function of normalized modulation amplitude. The optimum modulation amplitudes for the various harmonics are 0, 2.84 and 4.44 for the 0th, 2nd and 4th Fourier coefficients, respectively. Panel (b): on-resonance value of the first three odd Fourier coefficients ($n = 1, 3, 5$) as a function of normalized modulation amplitude. The optimum modulation amplitudes for the various harmonics are 1.27, 3.15 and 5.10 for the 1st, 3rd and 5th Fourier coefficients, respectively.

6. Discussion and Conclusion

It has previously been shown by Westberg et al. [12] that the FAMOS signal from a vibrational Q -transition in NO can be expressed succinctly in terms of the 1st Fourier coefficient of the modulated dispersion counterpart of an area-normalized lineshape function. Likewise, it has been shown that the dispersion wm-NICE-OHMS signal is proportional to the same type of integral, both in the cases of Doppler-broadened [11] and sub-Doppler [13–15] detection. However, up until now no analytical expression for such a coefficient has existed, wherefore the integrals of the lineshape functions so far have been evaluated by time-consuming numerical procedures.

In this paper we have demonstrated that for the cases when the lineshape function has a Lorentzian shape, e.g. in collision broadened media [19], or for sub-Doppler detection [15], it is possible to express the n^{th} Fourier coefficient solely in terms of the normalized detuning and the normalized modulation amplitude, in a succinct non-complex form, *viz.* as

$$\bar{\chi}_n(\bar{\nu}_d, \bar{\nu}_a) = \frac{A_n}{\bar{\nu}_a^n} \left[B_n + \frac{C_n S_+ + D_n S_-}{\sqrt{2}R} \right], \quad (35)$$

where S_+ , S_- and R are given by the equations (11) and (25) and the $A_n - D_n$ coefficients are in general given by the equations (11), (30), (31) and (32). Explicit expressions for the first six B_n , C_n , and D_n coefficients are given in the Tables 2-4, respectively. The full expression for the commonly used

$\bar{\chi}_1(\bar{\nu}_d, \bar{\nu}_a)$ coefficient is given in equation (33).⁴

Moreover, the optimum modulation amplitude, $\bar{\nu}_a^{opt}$, for the 1st Fourier coefficient, which often is the coefficient of interest, is calculated and found to be $\bar{\nu}_a^{opt} = 1.272$, which is in excellent agreement with that given by Blake et al. [2] who predicted an optimum modulation amplitude of 1.27 in the Lorentzian limit. Access to an analytical expression for $\bar{\chi}_1(\bar{\nu}_d, \bar{\nu}_a)$ will make fast on-line fitting possible also for modulated techniques relying on dispersion, e.g. FAMOS/FRS and wm-NICE-OHMS. Execution of equation (33) is two-to-three orders of magnitude faster than the numerically calculated integral.

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References

- [1] Kaldor, A., Maki, A.G., Olson, W.B.. Pollution monitor for Nitric Oxide - Laser device based on Zeeman modulation of absorption. Science 1972;176:508–510.

⁴The 1st Fourier coefficient of the modulated dispersion lineshape function for the FAMOS technique, given by Westberg et al. [12], $\bar{\chi}_1^F(\bar{\nu}_d, \bar{\nu}_a)$, is given in its Doppler-peak-normalized form, which relates to that of this paper, $\bar{\chi}_1(\bar{\nu}_d, \bar{\nu}_a)$, by $\bar{\chi}_1^F(\bar{\nu}_d, \bar{\nu}_a) = \bar{\chi}_1(\bar{\nu}_d, \bar{\nu}_a)/\hat{\chi}_0$, where $\hat{\chi}_0$ is the peak value of the area-normalized Gaussian absorption lineshape function.

- [2] Blake, T.A., Jr., C.C., Podolske, J.R.. Prognosis for a mid-infrared magnetic rotation spectrometer for the in situ detection of atmospheric free radicals. *Applied Optics* 1996;35(6).
- [3] Ganser, H., Urban, W., Brown, A.M.. The sensitive detection of NO by Faraday modulation spectroscopy with a quantum cascade laser. *Molecular Physics* 2003;101:545–550.
- [4] Ganser, H., Horstjann, M., Sushek, C.V., Hering, P., Murtz, M.. Online monitoring of biogenic nitric oxide with a QC laser-based Faraday modulation technique. *Applied Physics B* 2004;78:513–517.
- [5] Fritsch, T., Horstjann, M., Halmer, D., Sabana, H., Hering, P., Murtz, M.. Magnetic Faraday modulation spectroscopy of the 1-0 band of ^{14}NO and ^{15}NO . *Applied Physics B* 2008;93:713–723.
- [6] Fritsch, T., Brouzos, P., Heinrich, K., Kelm, M., Rassaf, T., Hering, P., et al. NO detection in biological samples: Differentiation of ^{14}NO and ^{15}NO using infrared laser spectroscopy. *Nitric Oxide - Biology and Chemistry* 2008;19:50–56.
- [7] Lewicki, R., Doty, J.H., Curl, R.F., Tittel, F.K., Wysocki, G.. Ultra-sensitive detection of nitric oxide at $5.33\text{ }\mu\text{m}$ by using external cavity quantum cascade laser-based Faraday rotation spectroscopy. *Proceedings of the National Academy of Sciences* 2009;106:12587–12592.
- [8] Sabana, H., Fritsch, T., Onana, M.B., Bouba, O., Hering, P., Murtz, M.. Simultaneous detection of ^{14}NO and ^{15}NO using Faraday modulation spectroscopy. *Applied Physics B* 2009;96:535–544.

- [9] Kluczynski, P., Lundqvist, S., Westberg, J., Axner, O.. Faraday rotation spectrometer with sub-second response time for detection of nitric oxide using a cw DFB quantum cascade laser at 5.33 μm . Submitted for publication to Journal of Applied Physics B 2010;.
- [10] Foltynowicz, A., Schmidt, F.M., Ma, W., Axner, O.. Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy: Current status and future potential. Applied Physics B 2008;92(3):313–326. doi: 10.1007/s00340-008-3126-z.
- [11] Foltynowicz, A., Ma, W., Schmidt, F.M., Axner, O.. Wavelength-modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy signal line shapes in the Doppler limit. Journal of the Optical Society of America B 2009;26(7):1384–1394.
- [12] Westberg, J., Lathdavong, L., Dion, C.M., Shao, J., Kluczynski, P., Lundqvist, S., et al. Quantitative description of Faraday modulation spectrometry in terms of the integrated linestrength and 1st Fourier coefficients of the modulated lineshape function. Journal of Quantitative Spectroscopy and Radiative Transfer 2010;111:2415 – 2433.
- [13] Foltynowicz, A., Ma, W., Axner, O.. Characterization of fiber-laser-based sub-Doppler NICE-OHMS for quantitative trace gas detection. Optics Express 2008;16(19):14689–14702.
- [14] Ma, L., Ye, J., Dube, P., Hall, J.. Ultrasensitive frequency-modulation spectroscopy enhanced by a high-finesse optical cavity: theory and ap-

- plication to overtone transitions of C_2H_2 and C_2HD . Journal of the Optical Society of America B 1999;16(12):2255–2268.
- [15] Axner, O., Ma, W., Foltynowicz, A.. Sub-Doppler dispersion and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy revised. Journal of the Optical Society of America B 2008;25(7):1166–1177.
 - [16] Arndt, R.. Analytical line shapes for Lorentzian signals broadened by modulation. Journal of Applied Physics 1965;36(8):2522 – 2524.
 - [17] Kronig, R.L.. On the theory of dispersion of x-rays. Opt Soc Am 1926;12:547–555.
 - [18] Kramer, H.A.. La diffusion de la lumire par les atomes. Atti Congr Int Fis Como 1927;2:545–557.
 - [19] Milonni, P.W., Eberly, J.H.. Lasers. John Wiley and Sons Inc.; 1988.
 - [20] Axner, O., Kluczynski, P., Lindberg, A.M.. A general non-complex analytical expression for the n th Fourier component of a wavelength-modulated Lorentzian lineshape function. Journal of Quantitative Spectroscopy and Radiative Transfer 2001;68:299–317.
 - [21] Abramowitz, M., Stegun, I.A.. Handbook of mathematical functions. Dover Publications, Inc.; 9 ed.; 1972.
 - [22] Lathdavong, L., Westberg, J., Shao, J., Dion, C.M., Kluczynski, P., Lundqvist, S., et al. Faraday modulation spectrometry of nitric oxide

addressing its electronic $X^2\Pi - A^2\Sigma^+$ band: I. theory. *Applied Optics* 2010;49(29).