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Modeling of the *n*-th harmonic spectra used in wavelength modulation spectroscopy and their properties

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ABSTRACT In this paper a convolution model for the harmonic spectra and harmonic signals used in wavelength modulation spectroscopy (WMS) with arbitrary transmission function is given. This implies a straightforward description of the harmonic spectra in the Fourier domain, which also allows for a new general computation method. Furthermore, the model can be extended to include non-ideal behavior of practical systems by assuming a modified transmission function, e.g. a nonzero laser linewidth, laser intensity modulation during wavelength tuning and additional filtering of the harmonic signals. A recursion formula and a mean value property for *n*-th harmonic spectra has been found. The harmonic signals occurring in practical systems can be modeled with a system theoretic approach, where these are given as the output of a filter that represents the WMS system and the transmission is regarded as the input signal of the filter. This gives a very intuitive view of WMS systems.

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1 Introduction

Laser spectroscopy is an established method for sensitive gas detection. A common laser spectroscopy technique is wavelength modulation spectroscopy (WMS), which uses a sinusoidal wavelength modulation with a phase sensitive detection (lock-in amplifier) to measure the higher order harmonics of the photodetector signal [1]. The higher order harmonics are caused by the nonlinear conversion of the frequency/wavelength modulation (FM) to amplitude modulation (AM) by the gas absorption. The phase sensitive detection allows for very efficient noise and distortion suppression. Modulation spectroscopy is sometimes called derivative spectroscopy because for small FM modulation amplitudes the detected *n*-th harmonic spectra are similar to the *n*-th derivatives of the absorption line shape. However, to maximize the signal to noise ratio (SNR) a large modulation amplitude is needed so that the harmonic spectra become distinct to the *n*-th derivatives. To be able to design and implement data extraction algorithms, knowledge on the exact form or structure of these measured spectra is needed (Chapter 6H in [2]). One major non-ideal effect in WMS is that the laser intensity is not constant during wavelength tuning: the intrinsic AM of the laser diode causes significant distortion to the first harmonic spectrum, so that in WMS usually second harmonic detection with high modulation amplitudes for maximum SNR is employed [1]. For the ideal case of a constant laser intensity and unsaturated Lorentzian or Gaussian absorption lines closed form analytical formulas exist for harmonic spectra [3–6]. For arbitrary line shapes infinite series expansions are available [7], but these do not converge for all practically important cases[1]. For Voigt absorption profiles no closed form expression for the harmonic spectra has been found yet, so that curve fits have to be done with numerical calculation of the harmonic spectra [8] or by use of approximations [9].

In this paper a general approach is used to analyze WMS without any assumption of the shape of the transmission function, e.g. it is suitable for saturated line shapes or the case of non-constant laser intensity. The *n*-th harmonic spectra are expressed as a convolution of the transmission with a fixed function that is given by the Chebyshev polynomials with a square root weight function. In ESR spectroscopy convolutions have been used to describe physical effects and non-ideal behavior of the measurement system including broadening by modulation for the first order case both approximative [8, 10, 11] and exact [12], whereas in this paper it is generalized to higher order harmonics and applied to the WMS case with its own specific non-ideal behavior. The convolution expression avoids difficulties with infinities and convergence problems and provides a description for WMS that is straightforward to analyze and easy to integrate in the complete signal processing model of the measurement system, since the convolution is a very well-investigated operation in Fourier analysis and signal processing. Based on the convolution expression a system theoretic viewpoint of WMS is presented, where the transmission is considered as the input signal of a filter and the output is the corresponding *n*-th harmonic spectrum or signal. Another insight is that the *n*-th harmonic spectra at a single point are the coefficients of the Chebyshev approximation of the transmission function.

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[1] e.g. for the case of Lorentzian lines with a modulation amplitude that maximizes the SNR

The convolution model is also capable of modeling certain deviations of the ideally assumed WMS system by transferring them to a properly adjusted transmission function, as outlined in Sect. 4. It is possible to recreate the behavior of a practical system with that from an ideal system and a modified transmission function. Furthermore, with this approach it has been possible to derive a recursion formula for harmonic spectra and a general zero mean property of harmonic spectra that hold for the idealized WMS system and all non-ideal cases that can be modeled by an adjusted transmission function.

2 Model for wavelength modulation spectroscopy (WMS) systems

For WMS purposes the wavenumber of the laser light is sinusoidally modulated with frequency f_m and modulation amplitude ν_a around a center wavenumber $\bar{\nu}$

$$\nu(t) = \nu_\mathrm{a}\cos(2\pi f_\mathrm{m} t) + \bar{\nu}\,. \quad (1)$$

The light is transmitted through the gas that absorbs light of specific wavenumbers, so the frequency modulation is converted into an amplitude modulation. A photodetector together with a lock-in amplifier is then used to detect the individual harmonic components of the amplitude modulation. These corresponds to the n-th Fourier series coefficient of the periodic detector signal, and this coefficient is written as a function of the mean wavenumber $\bar{\nu}$. The variation of $\bar{\nu}$ is usually realized by linearly sweeping it in a small range around a certain wavenumber, with a frequency much lower than the modulation frequency f_m.

The ideal WMS measurement system is classified by the following assumptions:

1. The laser linewidth is zero.
2. The modulation frequency f_m does not affect the laser spectrum, i.e. f_m is small enough (otherwise we have frequency modulation spectroscopy (FMS) [13, 14]).
3. The laser intensity is constant during wavelength tuning.
4. The responsivity of the photodetector is not wavelength dependent.
5. The pre-amplifier and gain stages in the measurement system are not frequency selective.

When the mean wavenumber $\bar{\nu}$ is tuned, the n-th Fourier series coefficient of the periodic detector signal forms the harmonic spectrum $S_n(\bar{\nu})$. Since the harmonic spectrum is linear with respect to the laser intensity, detector responsivity and pre-amplifier gain, these quantities are assumed to be 1. This yields a normalized expression for the n-th harmonic spectrum

$$S_n(\bar{\nu}) = \frac{\epsilon_n}{2\pi}\int_{-\pi}^{\pi} T(\bar{\nu} + \nu_\mathrm{a}\cos(z))\mathrm{e}^{-\mathrm{i}nz}\,\mathrm{d}z \quad (2)$$

where $z = 2\pi f_\mathrm{m} t$ and $\epsilon_n = 2 - \delta_{n0}$, with the Kronecker delta δ_{ij}. $T(\nu)$ is the transmission function of the optical path including the gas. Usually this is given by the Lambert–Beer law with appropriate absorption profiles, but for our analysis, T can have an arbitrary shape. It is important to note that non-ideal behavior of practical systems can be modeled by an ideal WMS system with a properly adjusted transmission function. This includes for instance the modeling of an emission spectrum of the laser, the laser's intensity modulation under certain assumptions and additional filtering of the n-th harmonic spectrum, as explained in Sect. 4.2.

2.1 *Convolution model of harmonic spectra*

Substituting $\eta = -\nu_\mathrm{a}\cos(z)$, the integral in (2) becomes a convolution

$$S_n(\bar{\nu}) = \int_{-\infty}^{\infty} T(\bar{\nu} - \eta) Z_n(\eta)\,\mathrm{d}\eta = (T * Z_n)(\bar{\nu})\,, \quad (3)$$

with the kernel

$$Z_n(\nu) = \begin{cases} \frac{\epsilon_n\,\mathrm{C}_n(-\nu/\nu_\mathrm{a})}{\pi\sqrt{\nu_\mathrm{a}^2 - \nu^2}} & |\nu| < \nu_\mathrm{a} \\ 0 & \text{otherwise} \end{cases}. \quad (4)$$

Here $\mathrm{C}_n(x) = \cos(n\arccos(x))$ is the Chebyshev polynomial of degree n [15]. The convolution kernel depends on the modulation amplitude ν_a and the order n of the frequency component selected by the lock-in amplifier. For various orders n the kernel is shown in Fig. 1. A convolution is very similar to a correlation: the difference is just an additional minus sign in the argument of the second convolved function. So in this case the n-th harmonic spectrum is also the cross-correlation function between the transmission and the "mirrored" kernel $Z_n(-\nu)$, that is because of symmetry equal to $(-1)^n Z_n(\nu) = Z_n(-\nu)$. So the n-th harmonic spectrum (except algebraic sign) can be considered as the cross-correlation function between the transmission and the fixed kernel $Z_n(\nu)$.

When applying the Fourier transform[2] to both sides of the expression (3), the convolution turns into a multiplication

$$\widehat{S}_n(k) = \widehat{T}(k)\cdot\widehat{Z}_n(k)\,, \quad (5)$$

whereby the following definition of the Fourier transform is used

$$\widehat{X}(k) = \int_{-\infty}^{\infty} X(\nu)\mathrm{e}^{-\mathrm{i}2\pi k\nu}\,\mathrm{d}\nu\,. \quad (6)$$

The transform of the fixed kernel has a closed form that contains the Bessel function of the first kind $\mathrm{J}_n(x)$ (Chapter 9 in [15])

$$\widehat{Z}_n(k) = \epsilon_n i^n\,\mathrm{J}_n(2\pi k\nu_\mathrm{a})\,. \quad (7)$$

2.2 *Computation of the n-th harmonic spectra*

When the Fourier transform of the transmission function is known, the Fourier transform of the n-th harmonic spectrum is given by multiplication with the Bessel function of order n (see (5) and (7)). This simple structure allows for

[2] The Fourier transform of a function is denoted by a hat accent. The conjugate variable to wavenumber ν (unit cm^{-1}) is chosen to be k (unit cm).

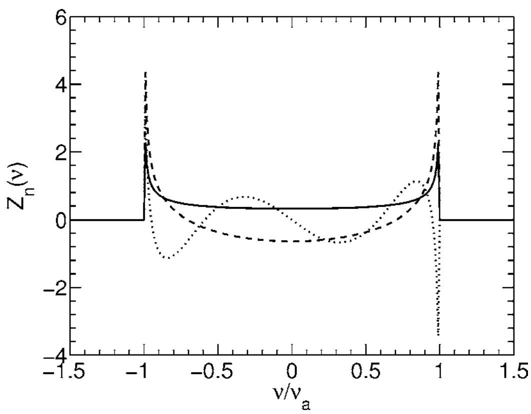

FIGURE 1 The convolution kernel Z_n for various orders n. The *solid*, *broken* and *dotted line* resemble kernels for the zeroth (Z_0), second (Z_2) and fifth (Z_5) harmonic spectra, respectively. All functions have a singularity at $|\nu/\nu_a| = 1$ and have odd and even symmetry depending on the parity of n

a fast computation of the n-th harmonic spectra in the Fourier domain. Evans et al. [8, 12] used a similar method to compute the first harmonic spectra (i.e. $n = 1$), whereas in this paper the general case is given, which allows for computation of harmonics of all orders. The Fourier transform of the transmission in (5) is either computed with the help of the FFT algorithm, or in the case of unsaturated Voigt lines, directly with known analytical formulas (which are briefly summarized in Sect. 4.1). This also works when non-ideal behavior of a practical system is modeled by an adjusted transmission function, as outlined in Sect. 4. The advantage of the computation in the Fourier domain is that all points of the n-th harmonic spectrum are computed in one step and that it works for arbitrary transmissions. However, care must be taken when using discrete Fourier transform algorithms to approximate continuous Fourier transforms.

2.3 *System theoretic view on WMS for harmonic signals*

In practical systems the n-th harmonic spectrum usually appears as a time signal, which is due to the slow linear sweep of the mean wavenumber $\bar{\nu}$

$$\bar{\nu}(t) = \beta t + \nu_{\min} , \tag{8}$$

with $\beta = (\nu_{\max} - \nu_{\min})/T_0$ being the sweep rate in wavenumbers per second. The tuning range $[\nu_{\min}, \nu_{\max}]$ is swept through in one measurement time interval $[0, T_0]$, whereas the time for one period T_0 is much higher than one sinusoidal modulation period ($T_0 \gg 1/f_m$). The n-th harmonic signal[3] $S'_n(t) := S_n(\bar{\nu}(t))$ and n-th harmonic spectrum $S_n(\bar{\nu})$ are essentially the same except for a linear change of variables, and the n-th harmonic signal is the one that occurs in practical systems.

Since the WMS system is described by a convolution, it is subject to systems theory, which is widely used in electrical engineering to describe dynamic systems like filters. Mathematically, all filters perform a convolution with their impulse

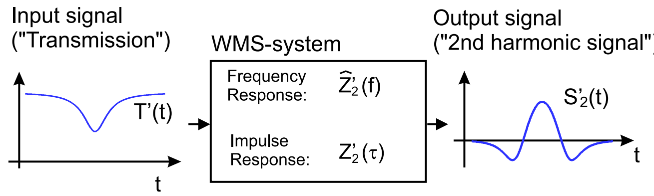

FIGURE 2 The WMS measurement system. The transmission is considered as the input signal and the output signal is the corresponding n-th harmonic signal. The WMS system is a filter with the frequency response shown in Fig. 3

response. So (3) allows for a new system theoretic viewpoint for WMS measurement systems: the transmission function is regarded as the input of the WMS system and the output is the n-th harmonic signal. Therefore the transmission function is considered as a time signal $T'(t)$. The WMS system that outputs the n-th harmonic signal $S'_n(t)$ is then simply a filter with impulse response $Z'_n(\tau)$

$$T'(t) := T(\bar{\nu}(t)) , \tag{9}$$

$$Z'_n(\tau) := \beta Z_n(\beta\tau) , \tag{10}$$

$$S'_n(t) = (T' * Z'_n)(t) . \tag{11}$$

This viewpoint is depicted in Fig. 2. Filters have the property that a sinusoidal input signal always gives a sinusoidal output signal, but with a phase shift and certain amplitude ratio, which are both frequency dependent. The Fourier transform of the impulse response of a filter is its complex valued frequency response, that describes this phase shift and amplitude ratio. The Fourier transform of the output signal is the Fourier transform of the input signal times the frequency response. This is in agreement with (5) for the Fourier transform of the harmonic spectrum. For some values of n the frequency response is shown in Fig. 3.

To visualize the meaning of $Z'_n(\tau)$ being an "impulse response", a Dirac impulse shaped transmission can be imagined. This is an infinitely narrow bandpass filter, which has an infinite gain to compensate for the infinitely narrow band. The n-th harmonic spectrum in this case will be equal to the con-

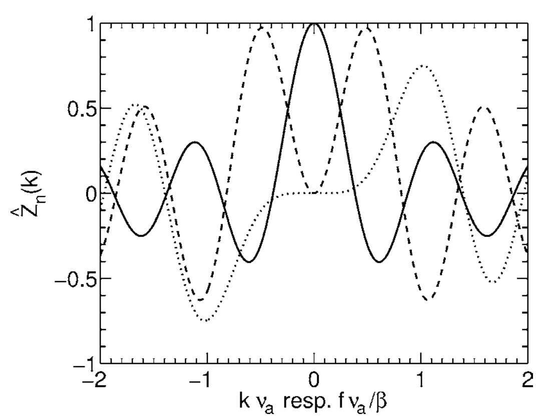

FIGURE 3 The WMS system frequency response $\widehat{Z}'_n$ for various orders n, that are essentially Bessel functions J_n. These are, except for a linear change of variable ($k\beta = f$), equal to the Fourier transform of the convolution kernel $\widehat{Z}_n$. The *solid*, *broken* and *dotted curves* resemble the response for the zeroth ($\widehat{Z}_0$), second ($\widehat{Z}_2$) and fifth ($\widehat{Z}_5$) harmonic spectra, respectively. To obtain a real valued plot the phase factor i^n has been omitted here

[3] Signals that represent spectra in systems with a wavenumber time sweep are denoted with the same symbol as the corresponding spectra but marked with an apostrophe.

volution kernel $Z_n(\nu)$ that is centered at wavenumber of the Dirac impulse. Therefore $Z_0(\nu)$ is also the amplitude density distribution for a sine wave with amplitude ν_a.

3 Basic properties of the harmonic spectra

Due to the convolution structure of the harmonic spectra many of the properties of the kernel apply to the harmonic spectra as well.

The Fourier transform of the kernel is zero for $k = 0$ and $n \neq 0$: $\widehat{Z}_n(0) = 0$. This causes all harmonic spectra with $n > 0$ to have a zero mean value.

$$\int_{-\infty}^{\infty} S_n(\bar{\nu})\,\mathrm{d}\bar{\nu} = 0\,, \quad \text{for} \quad n \neq 0\,. \tag{12}$$

Since the Bessel functions fulfill a recursion property with respect to order n, the harmonic spectra do as well. When in the relation (Eq. 9.1.27 in [15])

$$\mathrm{J}_{n+1}(x) = \frac{2n}{x}\mathrm{J}_n(x) - \mathrm{J}_{n-1}(x)\,. \tag{13}$$

$\mathrm{J}_n(x)$ is replaced by $Z_n(k)$ (see (7)) and multiplied with the Fourier transform of the transmission, the following recursion formula for the Fourier transform of the n-th harmonic spectra is obtained

$$\widehat{S}_{n+1}(k) = -\frac{n\epsilon_{n+1}}{\epsilon_n \nu_a i\pi k}\widehat{S}_n(k) + \frac{\epsilon_{n+1}}{\epsilon_{n-1}}\widehat{S}_{n-1}(k)\,. \tag{14}$$

After transforming back, a recursion formula for the harmonics is found. Note that the multiplication with $1/(2i\pi k)$ corresponds to an integration, because $n\widehat{S}_n(0)$ is zero for all n.

$$S_{n+1}(\bar{\nu}) = -\frac{2n\epsilon_{n+1}}{\epsilon_n \nu_a}\int_{-\infty}^{\bar{\nu}} S_n(\bar{\nu})\,\mathrm{d}\bar{\nu} + \frac{\epsilon_{n+1}}{\epsilon_{n-1}}S_{n-1}(\bar{\nu})\,. \tag{15}$$

It is important to remark that for $n = 1$ prior to application of (15) the offset of the zeroth harmonic spectrum has to be removed. This is due to the fact that in (14) the limit for $k = 0$ is mathematically incompatible with a generalized function Dirac delta in $\widehat{T}(k)$:

$$\lim_{x\to 0}\left(\frac{1}{x}\mathrm{J}_n(x)\right)\delta(x) \neq \lim_{x\to 0}\frac{1}{x}\left(\mathrm{J}_n(x)\,\delta(x)\right)\,. \tag{16}$$

The Dirac delta in $\widehat{T}(k)$ is created from the Fourier transform of the offset of the transmission $T(k)$. However, it is not severe because the general shape of the $(n+1)$-th harmonic spectrum is always predicted correctly. Also this only occurs at $n = 1$ and affects the offset of the predicted second harmonic spectrum because (14) is just at $k = 0$ possibly incorrect.

4 Including non-ideal behavior in the ideal WMS model

In this section it will be shown how to include non-ideal behavior of practical systems in the model for ideal WMS by assuming a special transmission function. The n-th harmonic spectra for a real (i.e. non-ideal) WMS system will be written as $\widetilde{S}_n(\nu)$. A real WMS system, for example, uses a laser that changes the light intensity during wavelength tuning, has a nonzero linewidth or performs additional filtering of the n-th harmonic signal. Of course the harmonic spectra in such a WMS system are not the same as in an ideal system. Now the goal is to find a function $\widetilde{T}(\nu)$, so that the output of the ideal WMS system with an assumed transmission $\widetilde{T}(\nu)$ gives the harmonic spectrum $\widetilde{S}_n(\nu)$ for the non-ideal case, i.e.

$$\widetilde{S}_n(\nu) = \left(\widetilde{T} * Z_n\right)(\nu)\,. \tag{17}$$

The true transmission of the optical path will still be called $T(\nu)$, and firstly, the model for the true gas transmission is presented. The analytical expression of the Fourier transform of the harmonic spectra (7) together with the presented line profiles and modeling of non-ideal behavior can be used to compute efficiently the n-th harmonic spectrum with the help of a numerical Fourier transform algorithm.

4.1 *Transmission of the gas*

The optical transmission function $T(\nu)$ of a gas is given by the Lambert–Beer law

$$T(\nu) = \exp(-Cla(\nu))\,. \tag{18}$$

C is the gas concentration, l the optical path length and $a(\nu)$ the absorption coefficient. For small (i.e. unsaturated) absorptions ($Cla(\nu) \ll 1$) this can be approximated by

$$T(\nu) \approx 1 - Cla(\nu)\,. \tag{19}$$

The absorption coefficient is given as the sum of the individual absorption lines

$$a(\nu) = \sum_j L_j \varphi(\nu - \nu_j;\, \alpha_j)\,. \tag{20}$$

Here φ is the normalized line profile, ν_j the center wavenumber and L_j and α_j the line strength and line width of the j-th absorption line, respectively.

Due to the exponential function in (18) the Fourier transform of the transmission can not be analytically simplified in the general case. However, in the case of unsaturated absorptions, the Fourier transform of the transmission can be expressed in terms of Fourier transform of the line profiles:

$$\widehat{T}(k) \approx \delta(k) - Cl\sum_j L_j \widehat{\varphi}(k;\, \alpha_j)\mathrm{e}^{-\mathrm{i}2\pi k\nu_j}\,. \tag{21}$$

ν_j is usually independent of gas temperature and pressure in contrast to the line strength and line broadening coefficient which both depend on these factors. The temperature or pressure range determines which line profile to choose. For room temperature usually three different line shapes are of importance. The Gauss line shape models broadening due to the Doppler effect, the Lorentz profile pressure broadening and the Voigt profile the combination of both effects:

$$\varphi_\mathrm{L}(\nu;\, \alpha_\mathrm{L}) := \frac{\alpha_\mathrm{L}/\pi}{\alpha_\mathrm{L}^2 + \nu^2} \tag{22}$$

$$\varphi_{\mathrm{G}}(\nu;\alpha_{\mathrm{G}}) := \frac{\sqrt{\ln 2/\pi}}{\alpha_{\mathrm{G}}} \exp\left(-\ln 2\,(\nu/\alpha_{\mathrm{G}})^2\right) \tag{23}$$

$$\varphi_V(\nu;\alpha_{\mathrm{L}},\alpha_{\mathrm{G}}) := (\varphi_{\mathrm{L}} * \varphi_{\mathrm{G}})(\nu)\,, \tag{24}$$

whereby α_{L} and α_{G} are the half width at half maximum (HWHM) of the Lorentz and Gauss profile, respectively. Their Fourier transform is given by

$$\widehat{\varphi}_{\mathrm{L}}(k) = \mathrm{e}^{-2\pi\alpha_{\mathrm{L}}|k|}\,, \tag{25}$$

$$\widehat{\varphi}_{\mathrm{G}}(k) = \mathrm{e}^{-(\pi\alpha_{\mathrm{G}}k)^2/\ln 2}\,, \tag{26}$$

$$\widehat{\varphi}_V(k) = \mathrm{e}^{-2\pi\alpha_{\mathrm{L}}|k|}\mathrm{e}^{-(\pi\alpha_{\mathrm{G}}k)^2/\ln 2}\,. \tag{27}$$

It is important to note that the convolution of two Lorentz and Gauss profiles form a Lorentz or Gauss profile again, respectively. The HWHMs simply add in the first case and are the square mean in the second case.

4.2 *Adjustment of the transmission to include non-ideal behavior*

4.2.1 A nonzero laser linewidth. If a laser with center wavenumber ν_0 has an emission spectrum of $L(\nu-\nu_0)$ and the light is passed through a transmission $T(\nu)$, the detector will detect an intensity that is proportional to

$$I(\nu_0) = \int_{-\infty}^{\infty} T(\nu)L(\nu-\nu_0)\,\mathrm{d}\nu = (T(\nu) * L(-\nu))(\nu_0)\,. \tag{28}$$

It can be clearly seen that the harmonic spectra in a system with a laser linewidth would be the same as the spectra in an ideal system (laser with no linewidth) with a transmission function $\widetilde{T}(\nu_0) = (T(\nu) * L(-\nu))(\nu_0)$ that is the convolution of the real transmission and the mirrored laser line profile. Usually the spectrum of a cw (continuous wave) laser is Lorentzian i.e. $L(\nu) = \varphi_{\mathrm{L}}(\nu;\alpha_{\mathrm{Laser}})$ with α_{Laser} being the HWHM of the emission spectrum. Since the convolution of two Lorentz functions is simply a Lorentz function again, the integration of the linewidth effect in the model with unsaturated Lorentz or Voigt shaped absorption lines is very simple. The laser linewidth simply adds to the Lorentzian half width of the gas absorption. Similar considerations can be made if the laser spectrum has both Lorentzian and Gaussian components.

4.2.2 Laser intensity modulation. For tunable lasers the laser intensity practically also changes when the frequency of the light is tuned. If there is a unique relation between instantaneous wavenumber and instantaneous intensity for the laser used, the intensity modulation can be included in this model. Let $P(\nu)$ be the intensity of the laser at a given wavenumber. Then the n-th harmonic spectrum of the real WMS system is equal to the output of the ideal system with an assumed transmission of

$$\widetilde{T}(\nu) = T(\nu)P(\nu)\,. \tag{29}$$

The assumption of a unique relation between wavenumber and intensity is usually fulfilled when there is no dynamic effect in the frequency or intensity modulation, i.e. there is no phaseshift between frequency and intensity modulation and no drop in wavelength modulation efficiency.

However in the other case no convolution form like (3) can exist for $\widetilde{S}_n(\bar{\nu})$. This can be overcome when a generalized convolution is used where either the convolution kernel or the assumed transmission function $\widetilde{T}$ depend on the second variable $\bar{\nu}$. The first case is given as

$$\widetilde{S}_n(\bar{\nu}) = \int_{-\infty}^{\infty} T(\bar{\nu}-\eta)\widetilde{Z}_n(\bar{\nu},\eta)\,\mathrm{d}\eta\,, \tag{30}$$

where

$$\widetilde{Z}_n(\bar{\nu},\eta) = \sum_{m=0}^{M} A_{\mathrm{m}}(\bar{\nu})Z_{\mathrm{m}}(\eta)\,. \tag{31}$$

This is because the real harmonic spectrum $\widetilde{S}_n(\bar{\nu})$ with arbitrary laser AM effects can be expressed as a weighted sum of several ideal harmonic spectra $S_{\mathrm{m}}(\bar{\nu})$ [16, 17]. The weight factors $A_{\mathrm{m}}(\bar{\nu})$ are defined through the relationship

$$\widetilde{S}_n(\bar{\nu}) = \sum_{m=0}^{M} A_{\mathrm{m}}(\bar{\nu})S_{\mathrm{m}}(\bar{\nu}) \tag{32}$$

and can be determined with the theory given in [16, 17].

4.2.3 Subsequent filtering of the n-th harmonic signal. In a practical system additional filtering of the n-th harmonic signal may occur, i.e. the n-th harmonic signal is passed through some analog or digital filter. Since the WMS system can be modeled as a filter and the order of the filters can be exchanged, the additional filtering can be applied to the transmission function. Let $h(\tau)$ be the impulse response and $H(f)$ the frequency response of the additional filter. The ideal model with the following transmission function $\widetilde{T}$ reproduces the additional filtering:

$$\widetilde{T}(\nu) = \frac{1}{|\beta|}\left(T(\eta) * h(\eta/\beta)\right)(\nu)\,. \tag{33}$$

Note that the Fourier transform of $\widetilde{T}(\nu)$ is given as the product of the Fourier transform $\widehat{T}(k)$ and the frequency response $H(k\beta)$ of the filter. This allows for an easy determination of how much distortion by the additional filter is added to the transmission.

5 Conclusion

A general convolution model for the harmonic spectra (and harmonic signals) used in wavelength modulation spectroscopy has been developed. It expresses the harmonic spectra as a convolution of transmission function with a fixed function that depends on the modulation amplitude and the order of the harmonic spectra.

The basic concept is to examine an ideal WMS system and to investigate the properties the n-th harmonic spectra have for an arbitrary transmission function. It has been shown that some non-ideal behavior can be reproduced with an ideal

WMS system with a modified transmission function. This approach has the essential advantage, that all properties for the ideal harmonic spectra are also valid for the given non-ideal cases. It was found out that the description of the n-th harmonic spectra in the Fourier domain has a significant advantage because explicit expressions for the Fourier transform of different absorption profiles exist. Secondly, a computation of n-th harmonic spectra in the Fourier domain has the advantage that the complete harmonic spectrum is obtained in one step. It has been shown that all higher harmonic spectra ($n > 0$) for arbitrary transmission always have a mean value of zero. Furthermore, a recursion formula that allows expression of the $(n+2)$-th harmonic spectrum in terms of the two previous ($(n+1)$-th and n-th) harmonic spectra was found.

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