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Methodology for fast curve fitting to modulated Voigt dispersion lineshape functions

Jonas Westberg, Junyang Wang, Ove Axner*

Department of Physics, Umeå University, SE-901 87 Umeå, Sweden

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ABSTRACT

Faraday rotation spectroscopy (FAMOS) as well as other modulated techniques that rely on dispersion produce lock-in signals that are proportional to various Fourier coefficients of modulated dispersion lineshape functions of the molecular transition targeted. In order to enable real-time curve fitting to such signals a fast methodology for calculating the Fourier coefficients of modulated lineshape functions is needed. Although there exist an analytical expression for such Fourier coefficients of modulated Lorentzian absorption and dispersion lineshape functions, there is no corresponding expression for a modulated Voigt dispersion function. The conventional computational route of such Fourier coefficients has therefore so far either consisted of using various approximations to the modulated Voigt lineshape function or solving time-consuming integrals, which has precluded accurate real-time curve fitting. Here we present a new methodology to calculate Fourier coefficients of modulated Voigt dispersion lineshape functions that is significantly faster (several orders of magnitude) and more accurate than previous approximative calculation procedures, which allows for real-time curve fitting to FAMOS signals also in the Voigt regime.

1. Introduction

Dispersion lineshape functions are the basis for spectroscopic techniques that measure the interference between two (or several) light fields. Examples of such techniques are Faraday modulation/rotation spectroscopy (FAMOS/FRS) [1–4], frequency modulation spectroscopy (FMS), and thereby noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) [5–7], and chirped laser dispersion spectroscopy (CLaDS) [8–11]. They are often used to assess the concentration of molecular species in gas phase, most frequently in trace concentrations. In order to perform such assessments with high accuracy the laser light is often scanned across the transition after which a model expression of the expected signal is fitted to the measured data. The concentration is then given by the value (s) of one (or several) parameter(s) in the fitted function.

To improve on the signal-to-noise ratio in the measurements and to increase the detection sensitivity, some spectroscopic detection techniques incorporate a modulation of either the transition frequency, e.g. as FAMOS, or the wavelength of the laser light, as wavelength-modulated tunable diode-laser absorption spectrometry (TDLAS). It has previously been shown that the signal from modulated absorption techniques can be expressed in terms of one or several Fourier coefficients of the modulated lineshape function [12,13]. As has recently been demonstrated, the same is valid for techniques based on dispersion [14,15]. This has both facilitated the theoretical description of modulated techniques and, for the cases when a given Fourier coefficient can be expressed as an analytical function in closed form, speeded up the fitting processes.

However, a limitation of this approach has been that it is only possible to find analytical expressions for the

* Corresponding author. Tel.: +46 90 786 6754.
E-mail address: ove.axner@physics.umu.se (O. Axner).

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Fourier coefficients of modulated lineshape functions (absorption or dispersion) when the samples are fully pressure broadened, i.e. when the lineshape has a Lorentzian form [14]. For measurement conditions that do not fulfill this assumption, e.g. when the transition needs to be described by a Voigt lineshape, the modulated lineshape function has been calculated by numerical means, e.g. in terms of a modulated plasma dispersion function or a modulated error function. Since this is utterly time consuming [16], it has, up to recently, precluded real-time curve fitting to signals from transitions with Voigt lineshapes assessed by modulated dispersion techniques. A remedy to this for techniques that rely on absorption was recently given by Westberg et al. by the development of the WWA-methodology (Westberg–Wang–Axner), which reduces the computation time of various Fourier coefficients of a modulated Voigt absorption lineshape function by three orders of magnitude, from the second to the millisecond range, with no loss of accuracy [17]. No such remedy has yet been demonstrated for techniques that rely on dispersion. Therefore, we demonstrate in this work how the WWA methodology can be extended to modulated Voigt dispersion lineshape functions just as easily, which makes it applicable also to the modulated detection techniques that rely on dispersion addressing Voigt lineshape functions.

Although the new WWA-methodology is applicable to all modulated techniques that detect dispersive signals it is, in this work, demonstrated on measurements of NO performed by the FAMOS technique. FAMOS is a technique that is based upon the fact that in the presence of a magnetic field a transition in a paramagnetic molecule will rotate the plane of polarization of linearly polarized light. The reason for this is that linearly polarized light can be seen as a superposition of two circularly polarized components of light with oppositely helicity, left-handed and right-handed circularly polarized light (LHCP and RHCP), respectively. When the two circularly polarized components of the light propagate through a gas containing paramagnetic species exposed to an external magnetic field, they will experience dissimilar indices of refraction, and therefore propagate at different speed through the sample, which, in turn, results in a tilting of the polarization plane of the linearly polarized light. By placing the sample between two polarizers and modulating the magnetic field it is possible to detect this tilting as a modulation of the intensity of the transmitted light. The signal is proportional to the difference between two or several modulated dispersive lineshape functions [14].

The FAMOS signal is, in this work, modeled by a theoretical description developed by Westberg et al. [14] that is based on the integrated linestrength of the transition addressed and the first (even) Fourier coefficient of a modulated dispersive line shape function but also takes the influence of polarization imperfections that give rise to asymmetric lineshape functions into account [18]. This description requires calculations of the 1st Fourier coefficients of both modulated dispersion and absorption Voigt lineshape functions, which is exceedingly time consuming by standard numerical calculation procedures. It is shown that the new methodology presented here can model the FAMOS signal more appropriately than previously used approaches, and that it is several (up to four) orders of magnitude faster than the ordinary numerical solution procedure.

2. Theory

2.1. Calculation of the 1st Fourier coefficient of a modulated Lorentzian dispersion lineshape function

When pressure broadening is the dominating broadening mechanism the lineshape function takes a Lorentzian form. The Lorentzian dispersion lineshape function that corresponds to an area normalized Lorentzian absorption lineshape function can be written as

$$\chi_L^{disp}(\nu) = -\frac{1}{\pi\delta\nu_L}\frac{\nu-\nu_0}{(\nu-\nu_0)^2+\delta\nu_L^2}, \tag{1}$$

where ν is the frequency of the laser light, ν_0 is the center frequency of the transition, and $\delta\nu_L$ is the half-width-half maximum (HWHM) of the Lorentzian profile. For the case when modulation is applied, either to the laser frequency or the transition, the corresponding modulated lineshape function can be written as

$$\chi_L^{disp}(\overline{\nu}_d,\overline{\nu}_a) = -\frac{1}{\pi\delta\nu_L}\frac{\overline{\nu}_d+\overline{\nu}_a\cos(2\pi ft)}{[\overline{\nu}_d+\overline{\nu}_a\cos(2\pi ft)]^2+1} \tag{2}$$

where $\overline{\nu}_d$ is the width-normalized detuning, given by $(\nu_c-\nu_0)/\delta\nu_L$, where ν_c is the center frequency of the laser, $\overline{\nu}_a$ is the width-normalized modulation amplitude, given by $\nu_a/\delta\nu_L$, where ν_a is the modulation amplitude, defined as positive or negative for the case when the laser frequency or the transition is modulated, respectively, f is the modulation frequency, and t is the time.

It has previously been shown that the nf-signal from a modulated technique (irrespectively of whether it detects absorption [12,13] or dispersion [15]) can be written in terms of the nth (even) Fourier coefficient of the modulated lineshape function. In the case of a modulated Lorentzian dispersion lineshape function, this Fourier coefficient can be written as

$$\chi_{L,n}^{disp,even}(\overline{\nu}_d,\overline{\nu}_a) = -\frac{1}{\pi\delta\nu_L}\frac{2}{\tau}\int_{-\infty}^{\infty}\frac{\overline{\nu}_d+\overline{\nu}_a\cos(2\pi ft)}{[\overline{\nu}_d+\overline{\nu}_a\cos(2\pi ft)]^2+1} \times\cos(2\pi nft)\,\mathrm{d}t, \tag{3}$$

where τ is given by $1/f$ (or an integer thereof).

Moreover, it has been shown by Westberg et al. [14] that this Fourier coefficient can be expressed expediently as

$$\chi_{L,n}^{disp,even}(\overline{\nu}_d,\overline{\nu}_a) = -\frac{1}{\pi\delta\nu_L}\frac{A_n}{\overline{\nu}_a^n}\left[B_n+\frac{C_nS_++D_nS_-}{\sqrt{2}R}\right], \tag{4}$$

where S_+ and S_- are given by $\sqrt{R+M}$ and $\sqrt{R-M}$, respectively, where, in turn, $R=\sqrt{M^2+4\overline{\nu}_d^2}$ and $M=1+\overline{\nu}_a^2-\overline{\nu}_d^2$. The coefficient A_n is given by Eq. (16) in Ref. [14] whereas the coefficients B_n, C_n, and D_n are given in Tables 2–4 in the same reference.

For the case with 1f-detection, which is the coefficient that most often is used, as for example in the FAMOS