Journal of Quantitative Spectroscopy & Radiative Transfer 187 (2017) 490–504

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Overcoming the detection bandwidth limit in precision spectroscopy: The analytical apparatus function for a stepped frequency scan

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A R T I C L E I N F O

Article history:
Received 7 June 2016
Received in revised form
20 September 2016
Accepted 20 September 2016
Available online 8 October 2016

Keywords:
Laser spectroscopy
Absorption line-shape
Spectrometer apparatus function
Doppler Broadening Thermometry
Boltzmann constant measurement

A B S T R A C T

In a previous paper [Rohart et al., Phys Rev A 2014;90(042506)], the influence of detection-bandwidth properties on observed line-shapes in precision spectroscopy was theoretically modeled for the first time using the basic model of a continuous sweeping of the laser frequency. Specific experiments confirmed general theoretical trends but also revealed several insufficiencies of the model in case of stepped frequency scans. As a consequence in as much as up-to-date experiments use step-by-step frequency-swept lasers, a new model of the influence of the detection-bandwidth is developed, including a realistic timing of signal sampling and frequency changes. Using Fourier transform techniques, the resulting time domain apparatus function gets a simple analytical form that can be easily implemented in line-shape fitting codes without any significant increase of computation durations. This new model is then considered in details for detection systems characterized by 1st and 2nd order bandwidths, underlining the importance of the ratio of detection time constant to frequency step duration, namely for the measurement of line frequencies. It also allows a straightforward analysis of corresponding systematic deviations on retrieved line frequencies and broadenings. Finally, a special attention is paid to consequences of a finite detection-bandwidth in Doppler Broadening Thermometry, namely to experimental adjustments required for a spectroscopic determination of the Boltzmann constant at the 1-ppm level of accuracy. In this respect, the interest of implementing a Butterworth 2nd order filter is emphasized.

1. Introduction

Since several tens of years, spectroscopy was revealed as a privileged tool for a large variety of scientific domains, including fundamental studies as well as applications. More recently with the advent of lasers, new experimental techniques have emerged increasing tremendously measurement accuracies. As an example, molecular properties such as absorption line intensities, transition frequencies and collisional broadenings are routinely investigated in view of applications to analytical chemistry or to atmosphere remote sensing [1]. More subtle effects such as pressure induced line frequency shifts are now currently considered and, thanks to large signal to noise ratios achieved, a great interest is devoted in deviations from the time-honored Voigt profile, including influences of velocity/speed changing collisions (Dicke effect) and speed dependence of relaxation rates [2,3]. Spectroscopic techniques are also presently developed for more fundamental studies, for instance tests of quantum electrodynamics,

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http://dx.doi.org/10.1016/j.jqsrt.2016.09.019

drift of proton-electron mass ratio, or parity violation [4–6]. In addition, a great interest is devoted to metrological applications such as measurements of Rydberg and Boltzmann constants [7,8].

Dealing with the determination of the Boltzmann constant k_B, a large effort is presently devoted to Doppler Broadening Thermometry (DBT) [9,10], a technique that allows the k_B-value to be retrieved from precise measurements of the Doppler width of absorption profiles of low pressure gaseous samples at thermal equilibrium [9–19, and Refs. therein]. Indeed, the Boltzmann constant value is expected to be fixed within a few years, giving a more convenient definition of the temperature scale [20,8; see also 21]. In this context, the target is an experimental measurement of k_B with a combined uncertainty in the 1-ppm range. Such a challenge requires a very careful analysis of possible systematic errors that have already been considered in several papers [11–19, 22–25, and Refs. therein]. However, the particular problem of the influence of the detection-bandwidth has emerged very recently [13,16,26]. Although Townes and Schawlow succinctly evoked this problem as far back as 1955 [27], it is relevant for a number of other experiments, such as the “fast-scan” technique where frequency varies rapidly [28,29] or the fundamental studies already evoked [4–8], but a first theoretical model of the consequences of a finite detection-bandwidth was only published in 2014 [26].

In Ref. [26], it was shown that the finite bandwidth of the detection system entails, at increasing orders, a shift of transition frequencies, then an extra broadening of linewidths, and finally asymmetry and deformation of lineshapes. These theoretical results were derived using the model of a continuous sweeping of the laser frequency. Analytical solutions were obtained, allowing the analysis of the finite bandwidth influence on frequency and broadening determinations to be done, and general theoretical trends were confirmed by ad-hoc experiments performed on NH_3 at 10 µm and $H_2^{18}O$ at 1.3 µm. As a matter of fact, these experiments were done using a step-by-step sweeping mode of laser frequencies, but precise measurements of line frequencies clearly showed that the continuous frequency-sweeping model was insufficient. So the step-by-step sweeping model was also considered in [26], but shortly and only via preliminary numerical simulations. However, a closer look of results reveals that this numerical solution is far from satisfactory. First, quoted difficulties in frequency measurements are not properly solved, unless introducing effective bandwidth parameters, the values of which are not easily estimated. Secondly, some theoretical behaviors of extra line broadenings are unexpected, so they need to be well understood in view of a safe application to DBT experiments. At last, this numerical solution seems difficult to be incorporated in line-shape fitting codes and most of all, calculations are time consuming, which could be inapplicable for accurate line-shape analysis of extended amounts of data as currently encountered in DBT [11,14] or in remote sensing of atmospheres.

Nowadays, up-to-date experiments devoted to precise spectroscopic measurements implement a frequency-stabilized laser that is step-by-step controlled via a frequency synthesizer. So, it is opportune to develop a new detection-bandwidth model suitable for stepped frequency scan experiments, namely with the purpose of obtaining an apparatus function that can be easily incorporated in line-shape fitting codes with a reasonable increase of computation times. Using signal processing and Fourier transform techniques, the present study shows that corresponding results can be set in analytic forms, namely the apparatus function. Thanks to this remarkable result, the implementation of the model in numerical codes is straightforward with a negligible modification of calculation durations. By comparison with numerical simulations of [26], it is worth noting that the new model now includes the actual timing of signal sampling and frequency changes. In this way, above quoted difficulties in frequency measurements or extra line broadening behaviors are properly understood and solved, which supports the model validity. Finally, consequences of a finite detection-bandwidth on absorption line frequency and broadening measurements are easily obtained, namely the influence of the ratio of detection time constant to frequency step duration.

The arrangement of the paper is as follows. Section 2 is devoted to the modeling of the absorption signal recorded via a detection system having a finite bandwidth: the case of a laser operating in the step-by-step frequency-sweeping mode is described in details and includes a realistic description of the timing of signal sampling and frequency changes. The case of a 1^{st} order detection-bandwidth is analyzed in details in Section 3, which allows highlighting the influence of the ratio of detection time constant to frequency step duration. Then, 2nd order detection-bandwidths are considered. Section 4 is devoted to the case of the usual 2nd order filter (quality factor $Q=1/2$) and previous experiments [26] are revisited for the purpose of a comparison of step-by-step and continuous frequency-sweeping models, namely for line frequency measurements. Taking account of its interest for DBT experiments, the Butterworth 2nd order filter ($Q=\sqrt{1/2}$) is considered in Section 5. Finally, consequences of a finite detection-bandwidth in DBT experiments are discussed in details in Section 6. At last, conclusions and recommendations for precise spectroscopic measurements, namely line frequencies or the Boltzmann constant, are resumed in Section 7. Note that for clarity, general analytical results dealing with 2nd order detection-bandwidths are reported in Appendix A.

2. Theoretical model

The modeling of the absorption signal recorded via a finite detection-bandwidth can be obtained via usual signal treatment methods for linear systems, namely Fourier transform techniques that allow expressing theoretical results as a function of the Fourier transform of the sample absorbance.

Let us consider the case of an isolated line, the absorbance $A(\nu)$ of which is small enough so that the Beer–Lambert law is considered in its linear form [the sample transmittance $T(\nu)$ is given by $T(\nu)=1–A(\nu)$]. In up-to-date