Demonstration of the extremely high signal-to-noise ratio and advanced O\textsubscript{2} B-band line shape analysis in the PDH-locked FS-CRDS experiment

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Abstract. We demonstrate an extremely high signal-to-noise ratio of 220000 : 1 obtained by the long-term spectra co-adding and averaging in the Pound-Drever-Hall-locked frequency-stabilized cavity ring-down experiment. The connection of this laser spectroscopy technique with the careful line-shape analysis revealed very subtle line-shape asymmetry of the R7 Q\textsubscript{8} \textsuperscript{16}O\textsubscript{2} rovibronic B-band transition probed at pressure 933 Pa. This asymmetry could be ascribed to the speed dependence of the collisional shift, as will be shown. Reduction of the minimum detectable absorption coefficient of 2 \times 10^{-10} \text{ cm}^{-1} by an order of magnitude, according to the $1/\sqrt{N}$ dependence, shifted the bottom limit of measured line intensities toward values as low as 1.3 \times 10^{-30} \text{ cm}^{-1}/(\text{molecule cm}^{-2}). The demonstrated measurement precision enabled the quantification of systematic line-shape deviations, which were approximately 1 part in 80000 of the peak absorption. The influence of slowly drifting etaloning effects on the accuracy of the line-shape analysis is discussed.

1. Introduction

The combination of the high-resolution and high-signal-to-noise ratio absorption spectroscopy with an advanced line-shape analysis is crucial for understanding and solving many of physical problems investigated today. Study of molecular and atomic collisions [1, 2, 3], verification of interaction potentials [4, 5, 6], optical determination of physical constants [7, 8, 9, 10, 11] and testing their stability [12, 13], detection of isotopic composition [14], and deconvolution of hyperfine spectra [15] are only some of tasks considered by modern spectroscopy. Application of the difference frequency generation laser spectroscopy for absorption spectra measurements in the near- and mid-infrared regions [16, 17] provided for decades signal-to-noise ratios (SNR) high enough to detect many subtle line-shape effects in molecular spectra. The development of tunable diode lasers gave similar results in the visible and near-infrared regions [18, 19, 20, 21]. The precision of the Fourier-transform spectroscopy (FTS), usually used for complex molecular spectra study, was significantly improved in the past few years. In 2008 Brown et al. [22] obtained SNR of 200000 : 1 in the microwave region, while three years later Gerecht et al. [23] reported SNR of 100000 : 1 in the terahertz region. In both cases the FTS spectroscopy with the chirped-pulse technique was used. The cavity-enhanced spectroscopy techniques are well-known...
tools for probing very weak absorption spectra. That is why their range of applications concerns mainly an atmospheric study. High-accurate line parameter data designated by cavity-enhanced experiments and careful line-shape analysis allow for remote sensing of trace gases concentration with the subpercent precision demanded in satellite-based measurements. The highest previously reported SNR of 28000 : 1 was obtained by Long et al. [24] in 2011 for a single CO$_2$ spectrum measured at 1.6 µm by the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) technique. Review describing a development and application of the FS-CRDS technique can be found in [25]. This technique was also recently combined with the optical frequency comb in order to provide absolute frequency axis of recorded absorption spectra [26].

Here we demonstrate the extremely high SNR of 220000 : 1 we recently obtained by probing the R7 Q8 $^{16}$O$_2$ B-band transition near 687 nm by the Pound-Drever-Hall-locked frequency-stabilized spectrometer (PDH-locked FS-CRDS). To our knowledge, this is the highest SNR ever reported in the optical absorption spectroscopy experiment. The ultra-high precision of our spectrometer allowed us to observe very subtle asymmetry in the shape of the self-broadened R7 Q8 $^{16}$O$_2$ line recorded at low pressure 933 Pa. An improvement of the spectrometer detection limit, by spectra averaging technique and an investigation of an influence of etaloning effects on the line-shape analysis is presented in this work.

2. Experiment precision improvements
An early version of our CRDS spectrometer [27] was based on an active stabilization of cavity modes technique introduced by Hodges et al. in 2004 [28, 29] and provided spectra with SNR of about 2000 : 1. In 2011 the Pound-Drever-Hall (PDH) technique [30] of laser frequency stabilization was incorporated to the system [31]. Such solution allowed to inject more laser power to the cavity resonance and significant increase of ring-down events repetition rate made possible to average more (3000) decay signals for each spectrum point. Defined as a minimum detectable absorption loss (MDAL) the detection limit of the PDH-locked FS-CRDS spectrometer ($2 \times 10^{-10}$ cm$^{-1}$) was improved five times compared to the previous FS-CRDS version. Despite the fact that the typical value of the SNR of 6000 : 1 obtained in the PDH-locked FS-CRDS experiment was relatively high, we showed in [32] that it was not high enough to distinguish between fit qualities obtained from O$_2$ lines analysis with different theoretical line-shape models, more complex than the standard Voigt profile, at low pressure range. Further improvements of the PDH-locked FS-CRDS spectrometer were related to eliminate the PDH error signal offset, which interfered a stable work of the system, and some changes in the measurement procedure. The description of the control procedure and electronic setup for an active correction of the PDH error signal offset can be found in [33]. The more reliable work of the spectrometer together with the actively stabilized relative frequency axis gave an opportunity to improve spectrometer precision by spectra co-adding and averaging technique. Proceeding in this way the SNR of the order of 220000 : 1 has been achieved [34]. The history of our spectrometer precision improvements was shown in Fig. 1.

3. Analysis
In the line-shape analysis of the strongest in the $^{16}$O$_2$ B-band R7 Q8 transition, recorded at pressure 933 Pa, the Voigt profile and more sophisticated theoretical profiles were considered. Such line-shape effects as speed dependence of collisional broadening and shifting [35] and Dicke narrowing in case of soft [36] and hard [37, 38] collision model were incorporated. Mathematical expressions of these models were collected in [39]. In the cases of speed-dependent profiles we used a quadratic models for the speed dependence of collisional broadening and shifting as given by Priem et al. [40]. In this way formulas for reduced collisional width $B_W(x)$ and shift $B_S(x)$ functions are as follows:
The self-broadened spectrum of the R7 Q8 $^{16}$O$_2$ B-band line recorded at pressure 933 Pa by subsequent versions of our CRDS spectrometer: (a) - FS-CRDS spectrometer from 2009 [27] (single spectrum), (b) - PDH-locked FS-CRDS spectrometer from 2011 [31] (single spectrum), (c) - PDH-locked FS-CRDS spectrometer with the PDH error signal offset correction procedure from 2012 [33, 34] (spectrum averaged from 1040 scans).

\[ B_W(x) = 1 + a_W(x^2 - 3/2), \quad B_S(x) = 1 + a_S(x^2 - 3/2), \]

where $x$ denotes reduced absorber velocity and $a_W$, $a_S$ are fitted parameters. We should note that in our previous investigations of the R7 Q8 $^{16}$O$_2$ transition, the speed dependence of the collisional shifting was ignored because of the small value of the pressure self-shifting determined for this line [27, 32]. Moreover, the value of SNR obtained in our previous experiments was too low to observe a possible subtle line-shape asymmetry caused by the speed dependence of the collisional shifting. However, in the present work, the enhanced spectrum SNR that we demonstrated for the R7 Q8 transition enabled us to carefully investigate the shape of this line. For this reason in the analysis with different line-shape models the parameter of the collisional shift was fitted and in case of speed-dependent profiles the $a_S$ parameter was constrained to be equal to $a_W$.

In order to quantify and distinguish random effects and systematic distortions of the line profile we introduce two quantities: the signal-to-noise ratio (SNR) which specify statistical noise and the quality of the fit (QF) which is defined as the ratio of the peak absorption signal $\alpha_{\text{max}} - \alpha_{\text{min}}$ to the standard deviation $\tilde{S}_R$ of the fit residuals calculated from the whole spectrum:

\[ \text{QF} = (\alpha_{\text{max}} - \alpha_{\text{min}})/\tilde{S}_R. \]

Beyond the random noise, the QF parameter takes into account also systematic effects caused for example by etaloning effects or limitations in the line-shape model. Under conditions of low SNR, the value of the QF parameter is close to the value of SNR.

### 3.1. Asymmetry of the R7 Q8 O$_2$ B-band line

In Fig. 2, results of the line-shape analysis of the single and averaged (from 1040 scans) spectrum of the R7 Q8 $^{16}$O$_2$ transition with the use of the Voigt (VP) and speed-dependent Nelkin-Ghatak profiles (SDNGP) were presented. Unlike the VP profile, the SDNGP profile takes also into account speed-dependent effects and Dicke narrowing. Systematic limitations of the VP profile are clearly seen both in case of averaged as well as single spectrum of the investigated line [see
Figure 2. The self-broadened single and averaged from 1040 scans spectrum of the R7 Q8 $^{16}$O$_2$ B-band line recorded at pressure 933 Pa. Below are residuals from VP (a) and SDNGP (b), (c) fits. The abbreviation SD visible in the graph legend denotes Speed Dependence.

diamonds and circles in graph (a)]. The SDNGP analysis gives flat residuals with SNR equal to 7637 for single recorded scan of the R7 Q8 line, regardless of the consideration of the speed dependence of the collisional shift [compare squares and triangles in graph (b)]. However, in case of the averaged spectrum clear structure emerges on residuals [squares in graph (c)] when the speed dependence of the collisional shift is not incorporated into analysis and it disappears when the speed-dependent effect of the collisional shifting is taken into account [triangles in graph (c)]. The asymmetry we found is the smallest one ever observed for the self-broadened molecular line recorded at such a low pressure. Recently De Vizia et al. [41] observed a small speed-dependent asymmetry for self-colliding H$_2$O molecules at pressure 500 Pa with SNR of 15000 : 1. We should note that under this precision we could not observed asymmetry for the studied R7 Q8 $^{16}$O$_2$ line. Simple comparison of ratios of the collisional shift to the total line width suggest that ten-fold smaller speed-dependent asymmetry should be expected in case of O$_2$ – O$_2$ system rather than in H$_2$O – H$_2$O. In this work we ascribed the asymmetry of the R7 Q8 line to the speed dependence of the collisional shift based only on the observation of fit residuals. However, observed asymmetry can also be caused by several other physical effects, such as correlations between velocity- and phase-changing collisions, finite collision duration, or line mixing. In general, physical cause of this effect will be identified if advanced line-shape analysis will be realized in wider range of pressures.

3.2. Systematic effects in the line-shape analysis

Signal-to-noise ratio of 220000 : 1 that allowed us to observe the R7 Q8 line asymmetry is extremely high and previously was completely unattainable in optical absorption spectroscopy. However, the true information about the fit quality gives the QF parameter which is almost 3-fold smaller than SNR. Such big discrepancy between QF and SNR parameters could be explained by residual systematic effects introduced to line-shape analysis by imperfections of the used SDNGP model and etaloning effects observed as sine structures on the line profile background. In general, techniques of spectra co-adding and averaging should very well average and dissipate periodic
4. Detection limit improvements

Spectra averaging technique is the easiest way to improve data precision. In order to quantify the detection limit of our PDH-locked FS-CRDS spectrometer under conditions of spectra co-adding process we probed a very weak R41 R41 $^{16}$O$_2$ B-band line having intensity at room temperature equal to $2.716 \times 10^{-29}$ cm$^{-1}$/(molecule cm$^{-2}$). Line-shape analysis of the investigated transition was realized at pressure 2.67 kPa and demanded an incorporation of the R7 Q8 line, 15 times stronger than the R41 R41 line and distant from it by $-5.182(9)$ GHz. Single and averaged from 405 scans spectrum of the R41 R41 is presented in Fig. 3. (a). Below are residuals from the VP fits to the averaged spectrum. As seen under conditions of SNR equal to 1.9 the examined line is completely non-observable. However SNR of 21 is high enough to do research. In Fig. 3 (b) the dependence of $\tilde{S}_R$ on the number of averaged scans $N$ for R41 R41 $^{16}$O$_2$ line is shown. As would be expected in case of weak absorption the $\tilde{S}_R(N)$ function is close to the $1/\sqrt{N}$ dependence. Determined $a$, $a_0$, and $\mu$ parameters of the power-law functions $a N^{-0.5}$ and $a_0 N^{-\mu}$ fitted to experimental data are $0.00052 \times 10^{-6}$ cm$^{-1}$, $0.00053 \times 10^{-6}$ cm$^{-1}$ and 0.45, respectively. The detection limit read from the graph is $2 \times 10^{-11}$ cm$^{-1}$ and is an order of magnitude lower than this obtained without spectra averaging. This detection limit corresponds to the line intensity of $1.3 \times 10^{-30}$ cm$^{-1}$/(molecule cm$^{-2}$) measured with SNR of 1 : 1 at pressure 2.67 kPa.

5. Conclusions

In this work we discussed improvements of our CRDS spectrometer realized during last three years. Uncommon signal-to-noise ratio of 220000 : 1 we are able to get nowadays thanks to...
spectra averaging method allowed us to observe very subtle asymmetry in the shape of the R7 Q8 $^{16}$O$_2$ B-band line recorded at pressure 933 Pa. This is the first observation of such small asymmetry for self-colliding molecules investigated at such a low pressure. We ascribed this asymmetry to the speed dependence of the collisional shift, but we suggested further analysis of the R7 Q8 line for different pressures to find truly physical interpretation of this line-shape effect. During this study we also discussed influence of etaloning features and their drift on the quality of the line-shape analysis. We indicate the non-$\sqrt{N}$ dependence of the fit quality under presence of systematic effects. In case of low absorption we showed that improvement of the measurement precision follows the $1/\sqrt{N}$ relation. The detection limit of our spectrometer we have demonstrated is of the order of $2.4 \times 10^{-11}$ cm$^{-1}$ and allows us to measure absorption lines having intensities of the order of $10^{-30}$ cm$^{-1}$/(molecule cm$^{-2}$) or even weaker depending on the absorber pressure.

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