Precise cavity enhanced absorption spectroscopy

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Abstract. A short review of recent achievements in high-precision cavity enhanced absorption spectroscopy is presented. Actual challenges and development paths in modern line shape study are indicated and discussed. The importance of identification and quantification of systematic instrumental errors affecting the measured line shape is highlighted. New, alternative measurement methods based on cavity enhanced spectroscopy are proposed.

1. Introduction
Satellite and ground-based studies of the atmosphere [1–3], control of the composition and purity of the gas mixtures used in production processes [4], determination of physical constants [5–9] as well as calibration of measurement equipment continuously increase demands on precision molecular spectroscopy. Recent progress in development of precise spectrometers revealed that the main reason of systematic errors of measurement of gas concentration, temperature and pressure is a simplified description of the spectral line shape. Particularly in the case of very weak molecular lines, important in the study of the atmosphere, the lack of a unified theoretical model and reference data inhibit the progress in these applications. Hence a strong effort is nowadays put into proper analysis of experimental spectral line shapes with the use of the complex line-shape models [10], incorporation of advanced and fast algorithms of the line shapes computation [11–13] as well as elimination of numerical correlations between fitted line-shape parameters by application of the multispectrum fitting procedure [14,15].

Cavity enhanced absorption spectroscopy (CEAS) using high Q-factor optical cavities yields the highest sensitivity of absorption measurements and enables study of weak molecular spectra with potentially very high resolution and precision [16]. Combination of cavity ring-down spectroscopy (CRDS) with frequency stabilization of cavity modes realized at NIST in 2004 [17,18] provided the proper tool for probing the absorption lines with unprecedented precision. Further evolution of this technique [19] including spectral narrowing and frequency stabilization of the probe laser [20–22] as well as the use of optical frequency combs [23,24] resulted in the signal-to-noise ratio exceeding $10^5$ [25,26] and control of the frequency axis with the kilohertz level of accuracy [27]. This created favorable conditions for testing advanced line-shape models and above all it allowed to determine spectral parameters with subpercent accuracy [28–34] demanded in satellite research.

This paper is a condensed review about recent achievements in development of precise cavity enhanced absorption spectroscopy. At extremely high level of precision of spectroscopy experiments systematic instrumental errors affecting the shape of investigated line can be
exposed as well. In this paper alternatives to the CRDS method for the measurement of weak spectral lines will be presented. One of them bases on dependence of the width of the optical cavity mode on the absorption coefficient [35, 36]. This method seems to be complementary to CRDS and under certain conditions more attractive.

2. Line shape description
A proper description of the line shape is a nontrivial task. It demands careful preparation of high-precision experimental data, only slightly affected by systematic distortions, and choosing adequate theoretical model which allows to reproduce experimental line shape with the highest possible accuracy. During recent years it was demonstrated many times that the Voigt profile (VP), which is just a simple convolution of Lorentzian and Doppler shapes, cannot be valid and cannot provide subpercent accuracy of line-shape parameters even at low pressures [31]. Instead of the VP other more complex line-shape models are often considered. They take into account Dicke narrowing [37], both in case of soft (Galatry profile, GP) [38] and hard (Nelkin-Ghatak profile, NGP) [39, 40] collision model, the speed dependence of collisional broadening and shifting [41] marked mostly by abbreviation SD, as well as line-mixing and correlations between phase- and velocity-changing collisions [40]. Recently, partially-correlated speed-dependent Nelkin-Ghatak profile (pCSDNGP) [42] with quadratic speed dependence of absorber speed was
tested in a wide range of pressures, from single Torrs to atmospheric pressures [12]. Its high flexibility, unification and variety of physical effects accounted for in this model, as well as recent development of fast numerical computation of this model [13] based on the SDVP algorithm introduced by Boone et al. [43], caused that the pCSDNGP became attractive especially for atmospheric study and development of new generation of spectroscopic data bases. Recently, the pCSDNGP was recommended by IUPAC as a proper isolated line-profile for representing high-resolution spectroscopic transitions [44].

Typical thorough analysis of the line shape looks like this presented in Fig. 1. Fifteen weak self-broadened spectra of the R1 Q2 line from the oxygen B band [33] were recorded by CRDS at pressures from 2 to 22 Torr. Below are residuals from fits with VP and other more sophisticated profiles. As would be expected the VP gives the worst quality of the fit. High measurement precision as well as the wide range of investigated pressures allows to distinguish which line-narrowing mechanism, Dicke narrowing or speed dependence of collisional broadening, is dominating in case of the R1 Q2 line. As seen all profiles taking into account speed dependence of collisional broadening give better fit quality. Moreover, it is clear that the hard collision model in the NGP reproduces experimental data worse than the soft collision model provided by the GP.

A complication of line-shape model implies growth of number of fitted line-shape parameters and hence increase of degree of numerical correlations between them. Such numerical correlations may strongly affect the line-shape analysis and perturb achieving results, especially when the range and values of investigated pressures are small. To overcome this problem, the multispectrum fit procedure [14, 15] is used. It is based on analysis of spectral line shapes simultaneously for all measured pressures, see Fig. 1. It should be noted as well, that the multispectrum fit analysis can help to determine line-shape parameters even when spectra are affected by instrumental errors introduced by the measurement procedure [45, 46].

3. CEAS precision and accuracy

Systematic increase of CEAS precision observed during last 15 years is mainly caused by techniques of frequency stabilization of probing light as well as frequency modulation methods [47, 48] allowing for realization of spectroscopy near the shot noise limit. Narrowing of laser linewidth much below the width of the cavity resonance, possible thanks to Pound-Drever-Hall (PDH) [50] or optical feedback [51, 52] methods, increased significantly the number of coincidences between probing light and the cavity mode and hence improved a repetition rate of ring-down events in CRDS. A detection limit of $1 \times 10^{-12} \text{cm}^{-1}\text{Hz}^{-1/2}$ obtained in this way by Spence et al. [53] in 2000 is the lowest achieved in CRDS to this day. A table presented in Fig. 2 (c) includes the most sensitive cavity-enhanced spectrometers reported in the literature. As seen the highest precision of $1 \times 10^{-14} \text{cm}^{-1}\text{Hz}^{-1/2}$ provides so far the NICE-OHMS (Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy) technique [54] which combines two methods: PDH laser linewidth narrowing and phase modulation of laser light at frequency equal to the cavity free spectral range. It should be noted as well, that two modes of detection (absorption and dispersion) occurring in NICE-OHMS allows for quantitative comparison of differences in accuracy of determined line-shape parameters in case of both modes, as was shown recently by Wang et al. [49]. The third, also very sensitive technique mentioned in table in Fig. 2 (c) is a frequency-agile, rapid scanning CRDS (FARS-CRDS) developed recently by Truong et al. [55]. This modified CRDS method allows for fast spectra recording, for example a 2 GHz spectrum within several milliseconds.

Active stabilization of the comb of cavity modes provides a stable relative frequency axis for recorded spectra. Moreover, it gives an opportunity for effective spectra averaging leading to further improvement of measurement sensitivity. In Figs. 2 (a) and (b) two recent spectra demonstrating extremely high signal-to-noise ratio are presented. The former was obtained in
Figure 2. (a) - The R7 Q8 O$_2$ B band spectrum and residuals from fit with speed-dependent billiard ball profile. Source: [11]. (b) - The R26e CO$_2$ spectrum and residuals from fit with SDNGP. Source: [26]. (c) - The most sensitive cavity-enhanced spectrometers reported in the literature. Source: [35].

Currently the strong effort is put into reduction of systematic instrumental errors as well as development of new, more accurate spectroscopic techniques. For example, parasitic etaloning effects appear as sine structures on line-shape residuals were firstly subtracted or fitted as artificial background [56]. Later, techniques of spectra averaging allowed for significant suppression of etalons amplitude because the etalon phase changes randomly in time during spectra measurement [25, 26]. Recently, Courtois et al. [26] discussed how etalons are caused by coupled-cavity interactions between primary ring-down cavity and other optical elements in the experiment. They also proposed differential technique which under conditions of carefully selected frequency interval between measurements points provided spectra free from unwanted interferences.

Standard CEAS experiments are based on measurements of attenuation of light transmitted through the cavity filled with absorbing medium. Such approach although provide fast data acquisition is very sensitive to power variations of probing light. For this reason, CRDS methods are considered as more promising for accurate measurements. However, light rapidly decaying
from the cavity needs to be recorded by a fast-response detector characterized by high linearity both in amplitude as well as gain for whole bandwidth. Any nonlinearities of detection system lead to distortions of measured ring-down events which strongly affect determined line-shape parameters. In paper [31] we demonstrated comparison of two different high-speed analog-to-digital converters (ADC) used as detectors in CRDS experiment. Their influence on recorded ring-downs is presented in Figs. 3 (a) and (b), for the worse and better ADC, respectively. Reported systematic errors of determined line intensity were 5 % and 0.5 % for those cases, respectively. Apart from the high-quality detection system, also the system of light beam interruption in CRDS has to be fast enough. In general, it consists of an acoustooptic or an electrooptic modulator driven by the RF signal which is switched off when the laser beam has to be blocked. If the shut-off of the excitation laser is incomplete, the residual optical power couples to the excited cavity mode. Since the coherence time of most lasers is less than the cavity storage time, this extra field adds with random phase to the ring-down decay creating additional interference noise on it. It is worth noting that the tight locking of the laser to the cavity, leading to laser line width narrowing, positively affects also on the reduction of unwanted interference noise. The impact of the RF signal extinction ratio on the recorded ring-down decay was discussed in recent papers [57, 58] and is presented in Figs. 3 (c) and (d). As seen to get undistorted ring-down decay, beam extinction ratio has to be at least 80 dB which, however, is

**Figure 3.** (a), (b) - Registered ring-down decays and fit residuals from a single-exponential fit for two different ADC measurement cards. Source: [31]. (c), (d) - Measured ring-down decays and fit residuals from a single-exponential fit for two different beam extinction ratios. Source: [58].
Figure 4. (a) - Spectral broadening and dispersion shift of cavity modes in the vicinity of absorber. (b) - Experimental spectrum of P3 \((3 \leftarrow 0) ^{13}C^{18}O\) line recorded at pressure 4.8 Torr and residuals from VP and GP fits. Below graphs (a) and (b) - mathematical formulas for calculation of physical quantities measured in CRDS, CMWS and CMDS experiments, respectively.

much larger than typical extinction ratios of 50 dB offered in commercial devices. A description of a home-made microwave switch with the extinction ratio variable in range 30-80 dB can be found in Ref. [57].

4. Alternative measurement methods

As was mentioned above identification and quantification of systematic instrumental errors is the most challenging task of modern line shape study. To solve this problem alternatives to the CRDS method for the measurement of weak spectral lines are now being developed.

The photon lifetime \(\tau(\nu)\) in the cavity, commonly measured from the ring-down decays in CRDS, is directly related to the spectral width of the cavity resonant modes which also are shifted due to dispersion, see Fig. 4 (a). This first phenomenon inspires relatively new technique named cavity mode-width spectroscopy (CMWS) in which absorption information can be retrieved by precise measurements of widths \(\delta\nu_{m}(\nu)\) of cavity modes. In 1994 Nakagawa et al. [59] reported
for the first time that a higher intracavity absorption coefficient is accompanied by a larger cavity mode width. Since then no one explored this phenomenon until 2013. Very recently experimental spectrum determined from cavity mode widths measurement was demonstrated by Long et al. with the use of the FARS technique [35, 55]. At the same time we have measured CMWS spectrum of the oxygen line with the use of ultranarrow and tunable in the range of 40 GHz external cavity diode laser [36]. The CMWS seems to be an intermediate technology between CRDS and CEAS. No need to use fast detectors in CMWS results in a wide dynamic range of absorption measurements, as was also indicated in [35]. Also possibility to measure high absorptions by the use of lower-reflectivity mirrors makes CMWS technique similar to CEAS. However, low sensitivity of CMWS to laser power variations allows to find similar features with CRDS technique. Qualitative and intuitive comparison of CRDS and CMWS methods reveals their complementarity in the sense that they achieve their best precision in different pressure ranges. For low absorptions the best precision is achieved with the CRDS technique, where the ring-downs are long and hence they can be well determined. In the opposite case, where the absorption is high and hence cavity modes become more broadened, the precision of CMWS is enhanced. In Fig. 4 (b) very recent experimental spectra of P3 (3 ← 0) $^{13}$C$^{16}$O line and residuals from VP and GP fits are presented both in case of CMWS and CRDS experiments. We found 0.7% and 0.3% agreement between collisional widths and line areas obtained from CRDS and CMWS measurements, respectively.

It is worth noting that measurement of dispersion shift of cavity modes delivers another way for potentially accurate studies of molecular spectra. Direct use of frequency domain quantities to obtain absorption coefficient thanks to Kramers-Kröning relation [60] in here-called cavity mode-dispersion spectroscopy (CMDS) may prevent from nonlinearities of detection system and hence may minimize contribution of systematic instrumental errors in the total shape of investigated spectral lines.

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