

Spectral line-shape study by cavity-enhanced complex refractive index spectroscopy

D. Lisak*, A. Cygan, S. Wójtewicz, P. Wcisło, M. Zaborowski, G. Kowzan, P. Masłowski, R. Ciuryło

Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziadzka 5, 87-100 Toruń, Poland

E-mail: *dlisak@fizyka.umk.pl

Abstract. We present a unique experimental setup that enables measurement of high-resolution complex refractive index spectra of gas sample using several cavity-enhanced methods: frequency-stabilized cavity ring-down spectroscopy, cavity mode-width spectroscopy and one-dimensional cavity mode-dispersion spectroscopy. Presented examples of applications cover molecular spectral line-shape investigations, line intensities and unperturbed line center frequency measurements and high-precision detection of systematic instrumental errors of various spectroscopic methods.

1. Introduction

High-accuracy measurements of spectral line shapes are important in a growing number of fields including basic research, metrology and many gas-sensing applications. This is associated with development of new ultra-accurate spectroscopic techniques using ultra-stable and narrow laser systems. For very weak absorption lines, the cavity ring-down spectroscopy (CRDS) yields excellent performance and spectral line shapes with extremely high signal-to-noise ratios [1, 2] were demonstrated using frequency-stabilized version of CRDS (FS-CRDS) [3, 4]. The FS-CRDS is also one of the well-known and most accurate techniques that provide line-shape parameters with sub-percent combined standard uncertainties [5, 6, 7]. On the other hand, achieving 0.1% agreement between line intensities determined independently in different laboratories is very challenging [7] and this problem is still open. Apart from the determination of the physical conditions in a sample, the accuracy of most often used absorptive intensity-based spectroscopic techniques is limited by the linearity and repeatability of the detection system. Even the accurate FS-CRDS method may be prone to systematic distortions of exponential light decays caused e.g. by too low bandwidth and poor linearity of the detection system [8], frequency stability of the excited mode and multimode excitation [9], or incomplete light extinction in case of continuous-wave CRDS systems [10].

The exponential light decay measured in the CRDS is directly related to the spectral width of the cavity mode. This phenomenon was exploited in cavity mode-width spectroscopy (CMWS) [11, 12, 13] in which the absorption spectrum can be retrieved by precise measurements of half-widths of cavity modes. Analysis of the CRDS and CMWS methods revealed their complementarity in terms of achievable accuracies at different levels of intra-cavity absorption [11]. For low absorptions the best precision is expected with the CRDS technique, where ring-

down decays are long and not affected by non-exponential distortions. In the opposite case of high absorption and short ring-down decays, the cavity modes become broad and, consequently, the precision obtained by the CMWS should be higher.

Measurement of dispersive shifts of cavity modes provides another possibility for very accurate quantitative spectroscopy. Since frequency is a physical quantity that can be measured with the highest accuracy, direct measurement of absolute or differential cavity modes frequencies to obtain a dispersive spectrum should eliminate potential problems associated with nonlinearities of a detection system as well as minimize systematic instrumental errors. The recently developed one-dimensional cavity mode-dispersion spectroscopy (1D-CMDS) [13] is so far the only method that provides one-dimensional spectra and contrary to any absorptive methods both axes in the 1D-CMDS spectrum can be linked to a primary frequency standard [14]. Since the 1D-CMDS is a light intensity-independent technique, it can be considered as a reference tool for validation of other spectroscopic techniques [15]. Typical cavity mode widths used in a high-sensitivity absorption spectroscopy are of the order of a few kHz. Therefore, precise measurement of cavity mode shapes, crucial for the CMWS and 1D-CMDS methods, requires the use of extremely narrow spectrally and finely tunable lasers.

Described above new cavity-enhanced spectroscopy techniques may be especially useful in applications that require the high accuracy of weak absorption measurements, e.g. gas spectroscopy for atmospheric monitoring and gas metrology, Doppler thermometry, as well as fundamental study of spectral line shapes. Moreover, direct comparison of spectra obtained with various cavity-enhanced techniques enables identification of potential instrumental errors at sub-percent level of accuracy required in many modern applications.

Here we present a unique experimental setup that enables measurements of absorptive and dispersive spectra at the same time and with the same gas sample by three independent cavity-enhanced techniques: FS-CRDS, CMWS and 1D-CMDS. Validation of the FS-CRDS method with respect to the 1D-CMDS is presented in a broad range of pressures. A complex-fit line-shape analysis [15] is used for simultaneously recorded absorptive and dispersive spectra. Moreover, absolute frequency of an unperturbed $^{12}\text{C}^{16}\text{O}$ transition from the near-infrared (3-0) band measured with an uncertainty five-fold lower than that of previously available data is presented [14]. Both frequency axes of dispersive spectrum were linked to the primary frequency standard. Three techniques (FS-CRDS, CMWS, 1D-CMDS) and various approaches to data analysis were used to estimate potential systematic instrumental errors.

2. Experimental setup

An experimental setup enabling measurement of absorptive and dispersive spectral line shapes simultaneously by the FS-CRDS, CMWS and 1D-CMDS methods is presented in Fig. 1. A continuous-wave ECDL laser is incorporated into a two-beams configuration scheme with a careful polarization separation of the probe and locking beams. The vertical polarization is used for Pound-Drever-Hall locking [16] of the laser to one of the modes of a high-finesse optical cavity filled with the gas sample. The horizontally polarized beam, detuned up or down from the locking point center by about one cavity free spectral range, can be finely scanned across the cavity mode to record its shape. Since the laser frequency is tightly locked to the cavity, any instabilities of the comb of cavity modes caused by acoustic and mechanical vibrations of the cavity are equally transferred to absolute frequency stabilities of both beams. In this way, cavity mode shapes measured with respect to the locking point can result in high-precision determination of modes half-widths and positions. To prevent the thermal drift of the comb of cavity modes, the cavity length is actively stabilized to a Nd:YAG laser having a long-term stability of 10 kHz. A dual-AOM frequency scanning system of the probe beam is used to make dispersive measurements insensitive to the temporal drift of the laser locking point [15]. In this configuration, two acousto-optic modulators (AOMs) driven by the same RF signal are used to

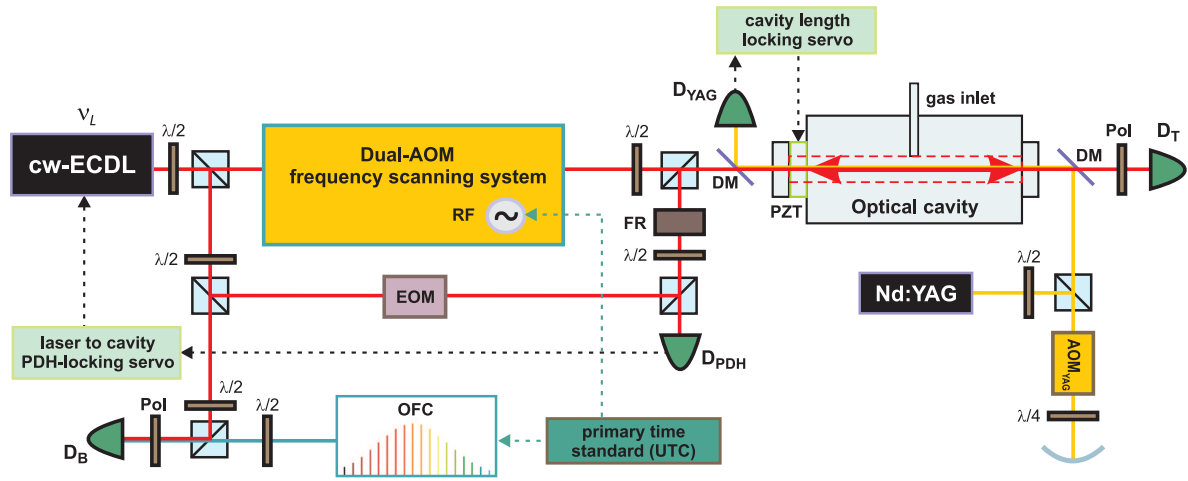


Figure 1. Schematic of an optical frequency comb (OFC)-assisted experiment for realization of three cavity-enhanced spectroscopy methods: FS-CRDS, CMWS and 1D-CMDS. Shown elements are a continuous-wave external cavity diode laser (cw-ECDL), an electro-optic modulator (EOM) for PDH locking of the cw-ECDL frequency, Faraday rotator (FR), a piezoelectric transducer (PZT), an acousto-optic modulator for the Nd:YAG laser (AOM_{YAG}), photodiodes (D_T , D_{PDH} , D_B , D_{YAG}), dichroic mirrors (DM), a quarter-wave plate ($\lambda/4$), half-wave plates ($\lambda/2$) and polarizers (Pol). The dashed lines represent electrical connections between locking electronic elements as well as reference frequency signal for the OFC and dual-AOM frequency scanning system.

point by point scan the probe laser beam alternately around the upper and lower cavity mode in relation to the locking point with relatively short switching time between them, less than 20 ms. More details about the experimental setup can be found in Refs. [13, 14, 15].

In general, a CMWS spectrum is obtained directly from determined cavity modes widths, whereas frequency intervals measured between cavity modes centers provide a differential dispersive 1D-CMDS spectrum. Ring-down decays measured in the FS-CRDS are initiated by fast switching off one of two acousto-optic modulators. As usually, the inverse of determined decay time constants form the absorptive CRDS spectrum. The absolute frequency of the ECDL laser is measured with respect to the optical frequency comb (OFC). Both the OFC as well as the RF signal for driving AOMs are referenced to the primary frequency standard, UTC(AOS), provided via the OPTIME network [17, 18] from AstroGeodynamic Observatory in Borowiec (Poland) [19, 20].

3. Results and discussion

Experimental demonstration of the cavity-enhanced complex refractive index spectroscopy was made on the P3 transition from the $^{13}\text{C}^{16}\text{O}$ (3 – 0) band as an example [15]. The recorded complex spectra (absorption from FS-CRDS and dispersion from 1D-CMDS) are shown in Fig. 2 for two gas pressures (20 and 60 Torr). It should be noted that both components of the complex spectra were measured with the same gas sample at the same time. Experimental spectra were fitted using the speed-dependent Nelkin-Ghatak profile (SDNGP) [21] which takes into account two line-shape effects beyond the Voigt profile approximation: the speed-dependence of collisional broadening and shift, with quadratic speed-dependence model, and the velocity-changing collisions, which leads to Dicke narrowing. Two schemes of data analysis were used to demonstrate the advantages of the complex spectra measurements. First, individual

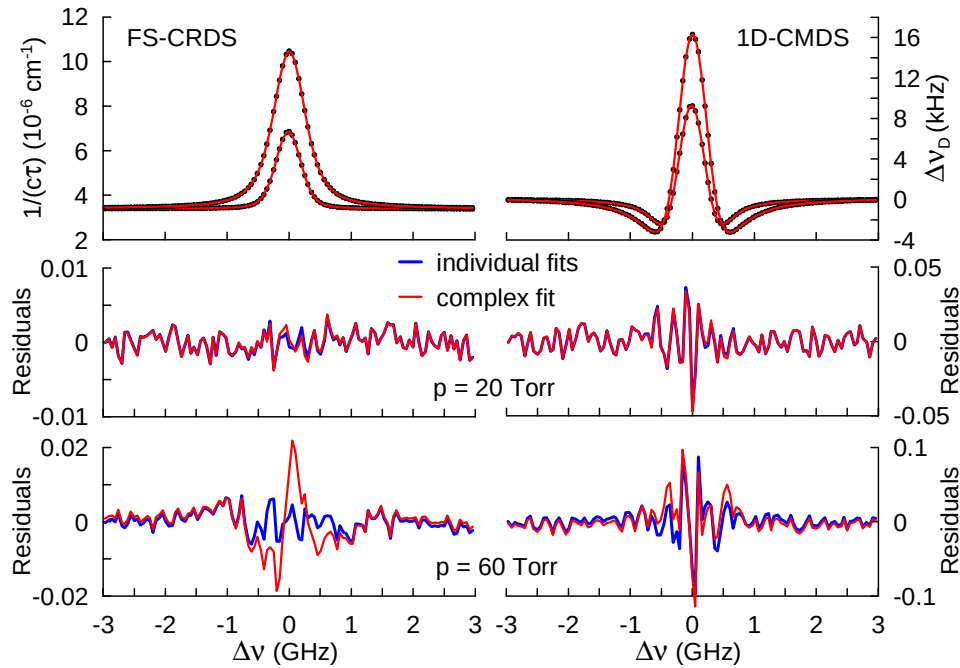


Figure 2. Experimental spectra of the $^{13}\text{C}^{16}\text{O}$ (3 – 0) band P3 line measured at pressures of 20 and 60 Torr. Absorption and differential dispersion spectra were measured with the FS-CRDS and 1D-CMDS, respectively. Below residuals of the SDNGP fits are shown for two cases: blue and red residuals correspond to individual fits of absorption or dispersion spectra and a complex line shape fits to the complex (absorption and dispersion) spectra, respectively.

fits of the real and imaginary parts of the complex SDNGP were fitted to absorption (FS-CRDS) and dispersion (1D-CMDS) spectra, respectively. Next, the complex SDNGP was fitted simultaneously to absorption and dispersion spectra. From the fit residuals shown in Fig. 2 it is clear that a perfect agreement between absorption and dispersion spectra was obtained for low-pressure spectrum (20 Torr). For the high-pressure spectrum (60 Torr) systematic distortions of the fit residuals are observed for the complex fit, but not for individual fits. This is clear indication of systematic instrumental error introduced by one of used experimental methods. In this case the ring-down time in FS-CRDS was too short to be measured properly around the line center of the 60 Torr absorption spectrum. This kind of systematic instrumental errors is difficult to detect using only one experimental technique. Especially at the accuracy level when non-Voigt line-shape effects must be taken into account, the instrumental line-shape distortions may be incorrectly interpreted as a part of the physical line-shape effects.

Another confirmation of the source of systematic line-shape distortion can be obtained by an analysis of the pressure dependence of fitted line-shape parameters which should depend linearly on gas pressure. In Fig. 3 a ratio of integrated line area A to pressure p is plotted vs pressure. Assuming that fitted SDNGP properly describe measured line shape, this A/p ratio should be constant. In Fig. 3 it is constant within the fit uncertainties only for dispersion 1D-CMDS spectra. For the FS-CRDS the instrumental effect of too short ring-down times is manifested as underestimated A/p for high absorption conditions at pressures above 20 Torr.

Similar analysis of A/p ratios obtained from fits of the Voigt profile, also shown in Fig. 3, demonstrates high sensitivity of differential dispersion spectra to a systematic error related to a wrong line-shape model. The observed nonlinearity of the line area with pressure for the

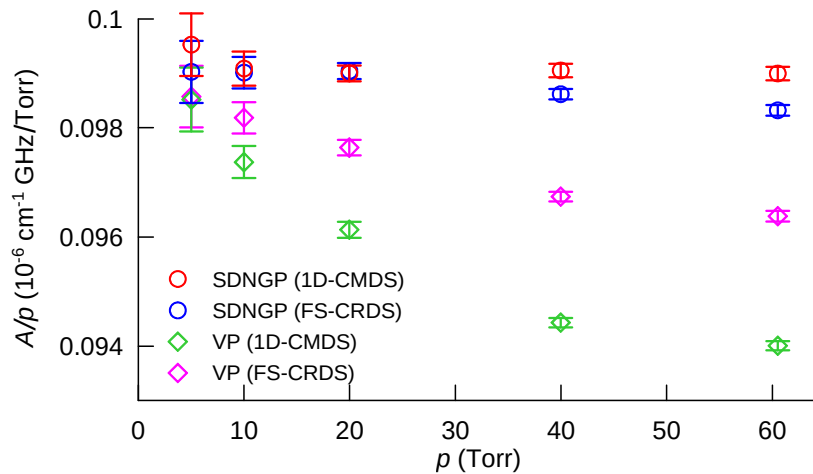


Figure 3. Dependence of a pressure scaled integrated line area of $^{13}\text{C}^{16}\text{O}$ ($3-0$) band P3 line on pressure obtained from fits of the VP and SDNGP to absorption (FS-CRDS) and differential dispersion (1D-CMDS) spectra.

1D-CMDS is twice as large as that for the FS-CRDS. This feature predestinates dispersion spectroscopy as a very sensitive tool for spectral line shape investigations. Different sensitivity of absorption and dispersion spectra to the line-shape model was also observed in the NICE-OHMS experiment [22].

The three spectroscopic methods, presented above FS-CRDS, CMWS and 1D-CMDS, were used for a high accuracy measurement of unperturbed line center frequencies and pressure shifts of $^{12}\text{C}^{16}\text{O}$ lines from the ($3-0$) band [14]. The frequency axes of the spectra were linked to the primary frequency standard UTC(AOS). It should be noted that in the case of the 1D-CMDS method both axes of the spectrum were linked to this frequency standard. In Fig. 4(a) the dependence of R24 line centers on CO pressure is shown for three experimental methods. Taking into account that the three experimental methods are not sensitive to the same kind of instrumental errors, systematic differences between FS-CRDS, CMWS and 1D-CMDS results enables estimation of systematic errors affecting determined line positions, which could not be properly estimated from results of only one method. The unperturbed line center frequencies obtained from each method by linear extrapolation of line positions to zero pressure are shown in Fig. 4(b) together with their average and a literature value of Mondelain et al. [23].

4. Conclusions

We have shown an experimental setup that enables measurements of the complex refractive index spectra using FS-CRDS in the time domain and CMWS in the frequency domain for absorption, and 1D-CMDS in the frequency domain for dispersion. This unique setup enables high-precision comparisons between absorption and dispersion spectrum of the same sample, which is tremendously useful to detect and quantify potential systematic instrumental distortions of spectra.

The purely frequency-based 1D-CMDS method is also very attractive for metrology applications because, unlike any absorption spectroscopy techniques, it is based only on frequency measurements. Therefore both axes of experimental spectra can be linked to the most accurate among standards of physical quantities.

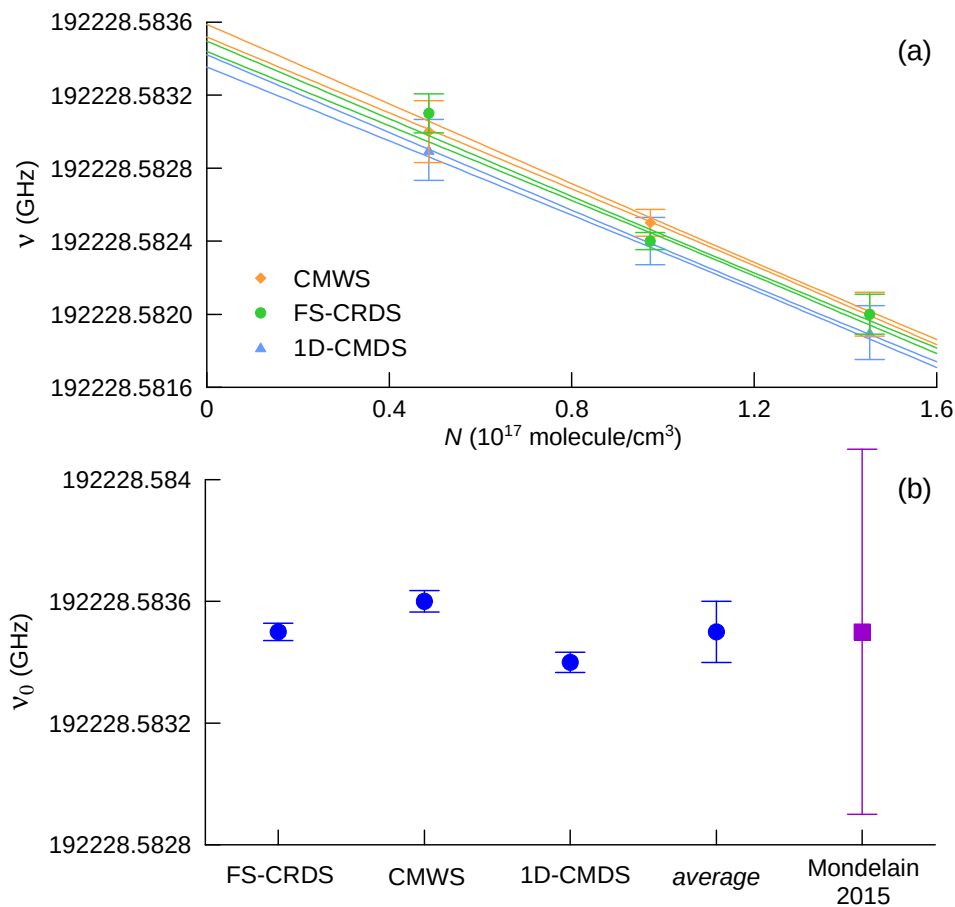


Figure 4. Graph (a): dependence of the fitted center frequencies of the $^{12}\text{C}^{16}\text{O}$ ($3-0$) band R24 line on pressure in the case of SDNGP fits to experimental spectra obtained with FS-CRDS, CMWS and 1D-CMDS (graph a). Lines indicate expanded (2σ) uncertainties and error bars correspond to scatter of individual results given by expanded (2σ) standard deviations. Graph (b): unperturbed line center frequency ν_0 obtained from the linear extrapolation of plots in graph (a) to zero pressure for three experimental methods. Additionally our average ν_0 and a literature value by Mondelain et al. [23] are shown. The error bars correspond to combined expanded (2σ) standard uncertainties.

Acknowledgments

The research is part of the program of the National Laboratory FAMO in Toruń, Poland and is supported by the National Science Centre, Poland, Project Nos. DEC-2013/11/D/ST2/02663, DEC-2012/05/D/ST2/01914, and 2015/17/B/ST2/02115, by the Foundation for Polish Science TEAM Project co-financed by the EU European Regional Development Fund and by MOLIM COST action. P.W. is supported by the Foundation for Polish Science START program.

References

- [1] Cygan A *et al* 2012 *Phys. Rev. A* **85** 022508
- [2] Lin H *et al* 2015 *J. Quant. Spectrosc. Radiat. Tr.* **161** 11
- [3] Hodges J T *et al* 2004 *Rev. Sci. Instrum.* **75**, 849
- [4] Long D A *et al* 2012 *Chem. Phys. Lett.* **536**, 1
- [5] Lisak D *et al* 2009 *Phys. Rev. A* **79** 052507

- [6] Wójtewicz S *et al* 2014 *J. Quant. Spectrosc. Radiat. Tr.* **144** 36
- [7] Polyansky O L *et al* 2015 *Phys. Rev. Lett.* **114** 243001
- [8] Wójtewicz S *et al* 2011 *Phys. Rev. A* **84** 032511
- [9] Lehmann K K and Romanini D 1996 *J. Chem. Phys.* **105** 10263
- [10] Long D A *et al* 2013 *Proc. SPIE* **8726** 87260O-6
- [11] Cygan A *et al* 2013 *Opt. Express* **21** 29744
- [12] Long D A *et al* 2014 *Appl. Phys. B* **114** 489
- [13] Cygan A *et al* 2015 *Opt. Express* **23** 14472
- [14] Cygan A *et al* 2016 *J. Chem. Phys.* **144** 214202
- [15] Cygan A *et al* 2016 *Meas. Sci. Technol.* **27** 045501
- [16] Drever R W P *et al* 1983 *Appl. Phys. B* **31** 97
- [17] Śliwczyński L *et al* 2013 *Metrologia* **50** 133
- [18] Morzyński P *et al* 2015 *Sci. Rep.* **5** 17495
- [19] Azoubib J *et al* 2003 *Metrologia* **40** S245
- [20] Jiang J *et al* 2015 *Metrologia* **52** 384
- [21] Lance B *et al* 1997 *J. Mol. Spectrosc.* **185**, 262
- [22] Wang J Y, *et al* 2014 *J. Quant. Spectrosc. Radiat. Tr.* **136**, 28
- [23] Mondelain D. *et al* 2015 *J. Quant. Spectrosc. Radiat. Tr.* **154**, 35