Self-presentation

1. Name

Agata Cygan

2. Diplomas and scientific degrees

2008-2012 Ph.D. studies in physics, Nicolaus Copernicus University

19.09.2012 Ph.D. degree in physics, Nicolaus Copernicus University
thesis title: *Cavity ring-down spectroscopy with active frequency stabilization*
advisor: prof. dr hab. Ryszard Stanisław Trawiński

2003-2008 M.Sc. studies in physics, Nicolaus Copernicus University

09.06.2008 M.Sc. degree in physics, Nicolaus Copernicus University
thesis title: *Study of pressure broadening of spectral line 326.1 of cadmium isotope 113 perturbed by neon*
advisor: prof. dr hab. Ryszard S. Trawiński

3. Employment in academia

od 10.2016 research assistant at the Institute of Physics of Nicolaus Copernicus University

10.2012-10.2016 research and teaching assistant at the Institute of Physics of Nicolaus Copernicus University

od 10.2016 postdoc in the NCN Sonata Bis project *Temperature effects in spectroscopy of molecular collisions*, Institute of Physics, Nicolaus Copernicus University
principal investigator: dr hab. Daniel Lisak

11.2012-06.2015 postdoc in the TEAM FNP project *Optical Control and Metrology in Quantum Systems*, Institute of Physics, Nicolaus Copernicus University
principal investigator: prof. dr hab. Roman Ciuryło

07.2011-12.2011 internship at the National Institute of Standards and Technology, Gaithersburg, Maryland (USA)
supervisor: dr Joseph T. Hodges

4. Main scientific achievement

4.1 Title of the achievement

Ultra-accurate frequency-based spectroscopy in an optical cavity

4.2 Publications that are part of the achievement

H1. **A. Cygan**, D. Lisak, P. Morzyński, M. Bober, M. Zawada, E. Pazderski, R. Ciuryło, *Cavity mode-width spectroscopy with widely tunable ultra narrow laser*, Optics Express **21**, 29744-29754 (2013)

H2. **A. Cygan**, P. Wcisło, S. Wójtewicz, P. Masłowski, J. T. Hodges, R. Ciuryło, D. Lisak, *One-dimensional frequency-based spectroscopy*, Optics Express **23**, 14472-14486 (2015)

H3. **A. Cygan**, S. Wójtewicz, M. Zaborowski, P. Wcisło, R. Guo, R. Ciuryło, D. Lisak, *One-dimensional cavity mode-dispersion spectroscopy for validation of CRDS technique*, Measurement Science and Technology **27**, 045501 (2016)

H4. **A. Cygan**, S. Wójtewicz, G. Kowzan, M. Zaborowski, P. Wcisło, J. Nawrocki, P. Krehlik, Ł. Śliwczyński, M. Lipiński, P. Masłowski, R. Ciuryło, D. Lisak, *Absolute molecular transitions frequencies measured by three cavity-enhanced spectroscopy techniques*, Journal of Chemical Physics **144**, 214202 (2016)

H5. S. Wójtewicz, **A. Cygan**, J. Domysławska, K. Bielska, P. Morzyński, P. Masłowski, R. Ciuryło, D. Lisak, *Response of an optical cavity to phase-controlled incomplete power switching of nearly resonant incident light*, Optics Express **26**, 5644 (2018)

4.3 Description of the achievement

Introduction and motivation

Spectroscopy, a rich source of our knowledge about the Universe, is at the basis of many fields of science ranging from atomic and molecular research to astronomical and cosmological observations. The tremendous progress that has been made in laser techniques has recently resulted in the development of high-finesse optical cavities with stable construction parameters, ultra-stable and spectrally narrow lasers, optical frequency combs and optical, atomic frequency standards. These achievements have resulted in new, precise and extremely sensitive spectroscopic techniques using enhancement cavities, in which the frequency of the laser radiation can be measured and controlled with at least Hz-level precision. This has significantly increased the accuracy of determined line-shape parameters such as position, intensity, Doppler and collisional broadening, or collisional shift of the spectral line. Until recently, spectroscopic data with accuracy of several percent deserves recognition among spectroscopic, metrological, theoretic and atmospheric researchers. Currently, in the world's leading spectroscopic laboratories, line-shape parameters with accuracy of 0.2-0.5%[1,2] are achieved. However, spectroscopic data with sub-per-mille accuracy is already expected. A major challenge for modern molecular spectroscopy are atmospheric studies in which the increasing precision of satellite and ground-based Earth atmosphere monitoring devices imposes sub-per-mille requirements on the accuracy of spectroscopic reference data[3], ultra-accurate measurements of molecular structure[1,4] and isotope ratios[5,6], study of exoplanet atmosphere[7] and search for extraterrestrial life[8], in which the support of theoretical calculations by accurate laboratory spectroscopic measurements is extremely

1 O. L. Polyansky et al., *Phys. Rev. Lett.* **114**, 243001 (2015)
2 J. Domysławska et al., *J. Quant. Spectrosc. Radiat. Transfer* **169**, 111 (2016)
3 D. R. Thompson et al., *J. Quant. Spectrosc. Radiat. Transfer* **113**, 2265 (2012)
4 S. Yu et al., *J. Chem. Phys.* **137**, 024304 (2012)
5 I. Galli et al., *Phys. Rev. Lett.* **107**, 270802 (2011)
6 S. Koulikov et al., *Talanta* **184**, 73 (2018)
7 P. F. Bernath et al., Phil. Trans. R. Soc. A **372**, 20130087 (2014)
8 S. Seager, W. Bains, *Sci. Adv.* **1**, e1500047 (2015)

important, testing of quantum electrodynamics in molecular systems[9] and searching for physics beyond the Standard Model[10].

The cavity ring-down spectroscopy (CRDS) is a commonly and readily used method for high-accuracy measurements. The great success of this technique lies in its insensitivity to fluctuations in the laser power, thanks to measurement of time of interaction of light with the optical cavity filled with the absorbing medium. In addition, due to the appropriate stabilization of the comb of cavity modes and frequency of the measuring laser, the CRDS method can also provide great measurement precision. In 2012, we demonstrated the world's first optical spectroscopy with a signal-to-noise ratio of 220000:1[11]. The weak molecular oxygen line was measured by the CRDS technique with active stabilization of the comb of cavity modes and tight locking of the laser to the cavity mode[12,13] using the Pound-Drever-Hall technique (PDH)[14]. In 2013, at NIST (USA), the spectrum of the CO_2 molecule was demonstrated with a signal-to-noise ratio of 170000:1[15], and two years later the spectrum of CO molecule was obtained with the highest so far signal to noise ratio of 1500000:1[16]. It quickly turned out that with such a great precision of measurements, the accuracy of the measuring method itself begins to play a key role.

In the case of mentioned CRDS method, a common source of systematic errors is related to propagation and detection of laser radiation in the spectrometer system. The most common problems include the use of systems that switch off the laser beam (eg acoustooptical modulator) with too low optical signal attenuation[17], excitation of multiple transverse cavity modes[18] as well as non-linear detection of optical signal by a detector with limited bandwidth[19]. These effects lead to noticeable distortions of light decays recorded by the CRDS technique and can cause even a few percent systematic error of determined line-shape parameters[19]. In addition, too slow detection of decay signals imposes strong limitations of the CRDS applicability to only weakly absorbing systems. In general, similar accuracy limits characterize all spectroscopic techniques that require intensity-based detection of laser radiation.

The scientific achievement for habilitation is the development of two new ultra-sensitive spectroscopic techniques using frequency measurement to detect concentration changes in the medium placed inside the optical cavity: cavity mode-width spectroscopy (CMWS) and cavity mode-dispersion spectroscopy (CMDS). The basis of both techniques is the precise measurement of the transmission spectrum of the cavity modes. In CMWS information on the absorption coefficient of the investigated medium comes from measurements of the cavity mode width. The CMWS method is complementary to CRDS and allows for a significant extension of the dynamic range of absorption measurements in relation to CRDS. The CMDS spectroscopy is a dispersive technique involving the measurement of cavity resonance positions, modified by the dispersion of the medium. The CMDS method offers a dynamic range of absorption/dispersion measurements essentially the same as CMWS. However, unlike all known spectroscopic techniques, it is a one-dimensional technique that owes its uniqueness to the measurement of only one physical quantity - frequency. The current possibility of measuring the frequency with a relative accuracy of even 10^{-18} determines the huge potential of the CMDS method to implement the most accurate spectroscopy in the world at the level of the highest metrological standards. In addition, frequency detection in the microwave range, in CMDS spectroscopy, gives the possibility of convenient reference of both axes of the

[9] E. J. Salumbides et al., *Phys. Rev. Lett.* **107**, 043005 (2011)
[10] E. J. Salumbides et al., *Phys. Rev. D* **87**, 112008 (2013)
[11] A. Cygan et al., *Phys. Rev. A* **85**, 022508 (2012)
[12] A. Cygan et al., *Rev. Sci. Instrum.* **82**, 063107 (2011)
[13] A. Cygan, et al., *Eur. Phys. J.-Spec. Top.* **222**, 2119 (2013)
[14] R. W. P. Drever et al., *Appl. Phys. B* **31**, 97 (1983)
[15] J. Courtois, K. Bielska, J. T. Hodges, *J. Opt. Soc. Am. B* **30**, 1486 (2013)
[16] H. Lin et al., *J. Quant. Spectrosc. Radiat. Transfer* **161**, 11 (2015)
[17] H. Huang, K. K. Lehmann, *Appl. Phys. B* **94**, 355 (2009)
[18] J. T. Hodges, J. P. Looney, R. D. van Zee, *J. Chem. Phys.* **105**, 10278 (1996)
[19] S. Wójtewicz et al., *Phys. Rev. A* **84**, 032511 (2011)

dispersion spectrum to the atomic frequency standard. This approach makes it much easier to compare measurement data from different laboratories around the world and is a very desirable feature in the case of spectroscopic reference methods. The methods of ultra-accurate frequency-based spectroscopy in the optical cavity, developed and implemented at the National Laboratory FAMO in Toruń, are the result of 5 years of research including:

- development in the years 2013-2015 of a new CMWS absorption spectroscopy method based on the measurement of the spectral width of the optical cavity modes in the frequency domain and significantly extending the dynamic range of absorption measurements in relation to the CRDS [H1, H2];
- transition in 2015 from the measurement of absorption to the measurement of dispersion in the optical cavity leading to the development of a new one-dimensional CMDS spectroscopy, based solely on frequency measurement [H2, H3];
- completed in 2016-2018 a comparison of CRDS, CMWS and CMDS methods and estimation of systematic errors distorting experimental spectra and leading to incorrect analysis of the physical effects of the absorption and dispersion shape of the molecular line [H3-H5].

Results

The first demonstration of the absorptive broadening of the optical cavity modes, constituting the basis for the future CMWS method, was presented in 1994 by Nakagawa and co-workers[20]. Narrow resonances of the optical cavity (with a spectral width > 18 kHz) were recorded, within the absorption spectrum of the C_2H_2 line, using the Nd: YAG laser with a spectral linewidth of around 5 kHz. In the paper of Nakagawa et al.[20] a statement about the relation of inverse proportionality between the absorption coefficient and the width of the cavity mode was made, but the quantitative analysis of experimental data was not performed. Instead, the conclusion was given that the spectroscopy based on the width of the cavity modes has the potential for ultrasensitive detection of molecular absorption, but requires the use of narrow spectral lasers, several orders of magnitude narrower than the measured modes of the optical cavity. Potential techniques for narrowing the laser spectral linewidth, such as frequency modulation or optical laser feedback, have also been indicated. Probably just due to the high technological requirements, i.e. the need to minimize the instrumental function of the spectrometer, the method has lost interest for almost 17 years.

In the work of Lisak et al.[21] from 2012, which was primarily a report on the construction of the first laser in Poland with a Hz-level spectral linewidth and stability determined by the ultra-stable optical cavity, we presented the potential use of a laser system for high-resolution spectroscopy on the example of measurement of narrow optical cavity resonances. For the first time, a comparison of the measurement results of the optical cavity mode widths obtained by direct measurement of the mode transmission spectrum and measurement of the time constant of the light decay from the cavity by the CRDS method was presented. Very good consistency of results was obtained. Proper construction of the cavity and its very good acoustic and thermal insulation from the environment ensured high precision measurement of transmission of the 22 kHz-wide cavity mode at the level better than 100 Hz. In addition, due to the use of a narrow linewidth laser, it was also a measurement characterized by high accuracy, because the laser instrumental function was negligible in comparison with the width of the cavity mode.

In the paper [H1] from 2013, we introduced the name of CMWS spectroscopy for the first time and proposed a technique for measuring the transmission spectrum of cavity modes using a system of phased-locked diode lasers with a Hz-level spectral linewidth and long-term stability determined by the ultrastable optical cavity, tunable in the range up to 20 GHz. It was one of two

[20] K. Nakagawa et al., *Opt. Commun.* **107**, 369 (1994)
[21] D. Lisak et al., *Acta Phys. Pol. A* **121**, 614 (2012)

(second parallel and independently was developed at NIST (USA)[22]) first implementations of molecular spectroscopy CMWS. In the paper [H1], the optical cavity with the investigated gas medium was in a laboratory other than the laser system, and the communication between the laboratories was carried out using a 100-meter fiber-optic connection. The uncompensated Doppler noise of a laser radiation in the optical fiber and the lack of stabilization of the length of the optical cavity were responsible for the mutual vibrations of the laser and the comb of the cavity modes. As a result, measured on the background of a weak oxygen molecular absorption line, the transmission spectrum of the cavity modes was characterized by significant noise of frequency origin. The widths of the cavity modes have been determined with kHz precision. In the paper [H1] the theory of the CMWS method was described and the scope of applicability of made approximations was estimated. An important result of the work [H1] was also simulation of the precision of CRDS and CMWS methods under conditions of high absorption. Unlike CRDS spectroscopy, the CMWS method does not require very fast light detectors. Despite the same decrease in the intensity of light transmitted through the cavity, along with the increase in absorption the cavity modes are broadening and can be more accurately measured than the very short light decays measured by CRDS in these conditions. The main advantage of CMWS spectroscopy is its potentially wide dynamic range of absorption measurements. It can be considered as a complementary technique to the CRDS one, giving satisfactory results also for relatively high absorption, which are practically unachievable for CRDS methods. This proves high attractiveness of the CMWS method in the application to comprehensive measurements of spectral line shapes in a wide range of pressures, from Doppler up to collisional (atmospheric) regime. Such research enables accurate testing of the theory of molecular collisions important, among others for basic research, as well as atmospheric and astrophysical research. The development of the CMWS technique in the application to precise line shape measurements of the weak absorption transitions of O_2 and CO molecules was continued in the years 2014-2017, as part of the NCN Sonata 6 project headed by me, entitled "Cavity mode-width spectroscopy (CMWS) as a new ultra-sensitive absorption spectroscopy technique".

An improved technique for measuring the transmission of cavity modes is presented in the paper [H2]. In the new approach, the beam of the continuous-wave laser is divided into two, one of which is used for tight locking of the laser frequency to the optical cavity mode with the PDH technique, and the second one, tunable in the range of several MHz by the acousto-optic modulator, is used to measure the transmission spectrum of the cavity modes. At the same time, the cavity mode comb is actively stabilized against the Nd:YAG laser stabilized on the iodine spectral line. The applied solution finally eliminated the problem of mutual vibrations between the laser and the comb of cavity modes leading previously to kHz frequency noise on the measured cavity modes. As a result, a sub-Hz-level precision in the measurement of the position and width of the cavity mode was demonstrated for the first time. This achievement not only contributed to a significant improvement (by two to three orders of magnitude) of the signal-to-noise ratio of the absorption spectra recorded by the CMWS technique, but also showed that even small changes in the position of the cavity modes caused by the dispersion of the intracavity medium can be measured with high precision. In this way, a new, ultra-sensitive, one-dimensional, dispersive CMDS spectroscopic technique was developed, based solely on the measurement of frequency changes in the positions of the cavity resonances in relation to the laser-to-cavity locking point. Preliminary results of dispersion measurement of cavity modes have been presented in post-conference works by Cygan et al.[23] and Hodges et al.[24]. The work [H2] contains a theoretical description of the CMDS method, its measurement procedure and the first comparison of absorption and dispersion spectra registered simultaneously with the CRDS, CMWS and CMDS techniques. The frequency nature of

[22] D. A. Long et al., *Appl. Phys. B* **114**, 489 (2014)
[23] A. Cygan et al., *J. Phys.: Conf. Ser.* **548**, 012024 (2014)
[24] J. T. Hodges et al., *Imaging and Applied Optics 2014*, OSA Technical Digest (Optical Society of America, 2014), paper LW3D.3

the CMDS technique and its very low sensitivity (especially in conditions far from saturation with light power) on the detection of light intensity indicate a high potential of CMDS spectroscopy for ultraaccurate measurements of molecular spectra. The CMDS spectrum shown in [H2] was characterized by a high signal-to-noise ratio of 1600:1, although lower than those obtained for CRDS and CMWS absorption spectra. This was due to the technical problem of the slow drift of the error signal offset in the feedback loop stabilizing the laser to the cavity mode. This drift little affects the measurement of the cavity mode width, but in the case of the measurement of the cavity resonance positions can ultimately lead to asymmetric distortion of the determined dispersion profile of the spectral line. For example, the drift of the offset in the laser stabilizing loop and the lack of stabilization of the length of the optical cavity were responsible for the significant deformation of the dispersion spectrum demonstrated in the work of Hodges et al.[24]. In the paper [H2], the minimization of the offset problem was done by the procedure of active offset correction, and its idea was similar to that described in the work of Cygan et al.[25]. The final elimination of the problem occurred after using two instead of one acoustooptical modulators in the system of the probe beam tuning, and the description of the improvements was included in the paper [H3].

The experimental setup from the work [H2] made it possible to perform absorption and dispersion spectroscopic measurements simultaneously with three CRDS, CMWS and CMDS methods. This simultaneous measurement of absorption and dispersion is very important as it provides complete information on the complex refractive index of the investigated medium. In the work [H3], for the first time, simultaneous analysis of the absorptive and dispersive spectrum was demonstrated based on the complex theoretical line-shape model fitted to experimental data. It can be seen as a new tool for testing and validating models of spectral line shapes. We have also shown that a complex analysis of experimental spectra can also be a very convenient method for detecting systematic errors of absorption measurement techniques. By adopting CMDS frequency spectroscopy as the reference method, we analyzed the accuracy of the absorption CRDS method. The fit of the complex line-shape profile simultaneously to absorptive CRDS and dispersive CMDS spectra was compared with the individual fits of the real and imaginary part of the complex line-shape profile to absorptive CRDS and dispersive CMDS spectrum, respectively. Good consistency of results was obtained only in the case of low pressures, while for the highest analyzed pressure there was a clear discrepancy between the complex line-shape fit and individual fits. This is directly related to the fact that with the increase in absorption, ring-down decays measured by the CRDS technique become shorter and it is much more difficult to measure them accurately. This observation is also confirmed in Fig. 5 (a) in the paper [H3] by the non-physical pressure dependence of the CO line intensity (proportional to the drawn quantity A / p) in case of using the CRDS technique and analysis of the absorptive part of the spectrum. The low susceptibility of the CMDS technique to systematic errors was confirmed by the linear pressure dependence of both the integrated line area and the collisional linewidth. In addition, greater sensitivity of the dispersion spectrum than the absorption one to the choice of the theoretical line-shape model was demonstrated, also previously observed in the work of Wang et al.[26]. This is important information especially from the point of view of experimental verification of the collision theory and inter-molecular interactions.

The paper [H4] is an example of the only experiment so far, in which absolute values of molecular line positions and their pressure shifts were determined by means of three spectroscopic techniques, in this case CRDS, CMWS and CMDS. Moreover, realized in the work [H4] reference of both axes of the CMDS dispersion spectrum to the atomic frequency standard is an example of the first spectroscopic technique directly and completely linked to the atomic frequency standard. Previously, such links have been implemented only for one axis of the spectrum. It should be noted that such actions are highly desirable for future reference measurements of molecular spectra. The dispersive line shape recorded in [H4] with the signal-to-noise ratio better than 23000: 1 is the first

[25] A. Cygan et al., *Meas. Sci. Technol.* **22**, 115303 (2011)
[26] J. Y. Wang et al., *J. Quant. Spectrosc. Radiat. Transfer* **136**, 28 (2014)

as precise one which was demonstrated in dispersion optical spectroscopy. It is also shown for the first time that the analysis of the dispersive shape of the spectral line profile is better than the absorptive one. The positions of the two selected CO spectral lines were measured with uncertainty five times smaller than the most accurate available literature data. In relation to the HITRAN spectroscopic database our results for positions were characterized by uncertainties by more than two orders of magnitude smaller. It is noteworthy that the relative uncertainty of 10^{-10} for the line position was obtained by measuring the Doppler-broadened spectral line. Additionally, the values of self-induced pressure shifts of the CO spectral lines were for the first time determined with percentage accuracy. An important result of the work [H4] was also the first quantitative estimation and inclusion in the uncertainty budget of the systematic error of the measurement method, manifesting as a systematic distortion of the experimental profile of the spectral line. It should be mentioned that in the case of standard measurements, in which only one measuring technique is used, such identification of instrumental systematic errors is almost impossible.

The effect of incomplete laser beam shutdown at nearly resonant excitation of the cavity mode on the accuracy of measurement of the decay time constant in the CRDS method was examined in the paper [H5]. An experiment was carried out in which the response of the cavity to laser radiation switching on and off was examined under conditions of precise control of the frequency, intensity and phase of the laser radiation. The predictions of a simple analytical model were very well confirmed by experimental results. A systematic error of 0.5% in the decay time constant was found in the case of excitation of the cavity mode by the laser beam detuned by two cavity spectral widths (HWHM) from the cavity resonance and optical signal attenuation after switching off the laser beam at the level of 58 dB. The CRDS systems with a tight locking between the laser frequency and cavity mode, are particularly sensitive to such error if they do not have active error signal offset correction in the laser feedback loop and if they use commercial laser beam shutdown systems in the form of acoustooptics modulators with an extinction ratio of RF signal worse than 50 dB. The results presented in [H5] are of particular importance for the prevailing trend to the development of spectroscopic methods with sub-per-mille accuracy, necessary in many fields of modern science.

Importance of the achievement

The research results indicated in the main scientific achievements led to development of two new spectroscopic techniques with high resolution, sensitivity, precision and accuracy. These methods, in particular dedicated to advanced measurements of spectral line shapes, are able to meet the needs and constantly increasing requirements of modern molecular spectroscopy. The proposed detection of changes in concentration of the intracavity medium as a measurement of the cavity's mode parameters removes the fundamental problem of the bandwidth limitation of detectors and analog-digital converters used in the case of CRDS techniques. The purely frequency nature of the CMDS method allows the spectral measurement to be completely independent of any non-linearities associated with the detection of light intensity. Thanks to this CMDS method has a chance to be more accurate than all other known spectroscopic techniques and has the ability to easily reference the measured spectrum to the atomic frequency standard. In addition, unlike other dispersive techniques, including those with very high sensitivity, such as NICE-OHMS[27], CMDS spectroscopy does not require calibration of the cavity enhancement factor, as well as careful and precise control of the phase of the demodulated resulting signal. It is worth mentioning that in the case of the existing dispersion methods, these were the main factors limiting the accuracy of the determined line-shape parameters even up to several percent[26]. An important achievement was also demonstrating the potential of CMWS and CMDS methods to significantly extend the dynamic range of measurements towards the high concentrations of the medium, while maintaining high

[27] J. Ye et al., *J. Opt. Soc. Am. B* **15**, 6 (1998)

precision of measurement of small concentrations, comparable to the precision of the most sensitive spectroscopic techniques such as CRDS. The high dynamic range of measurements combined with the high accuracy offered by the spectroscopic method proves its high universality and convenience of use in numerous applications, especially when the wide range of pressure of the sample should cover both Doppler and collisional conditions. The largest area of application that imposes such requirements is modern atmosphere research, its interaction with solar radiation and climate variability. In these extremely important studies even small systematic errors of data used to interpret measurements may lead to contradictory conclusions. The developed methods of ultra-accurate frequency-based spectroscopy in the optical cavity have a chance to solve this problem by easily and directly referring measurements to primary frequency standards, which will greatly facilitate the comparison of data obtained in different laboratories around the world.

CMDS spectroscopy is dynamically developed at the Institute of Physics of the Nicolaus Copernicus University in Toruń. New design solutions implemented in the experimental system of the spectrometer enabled better spectral separation of the measuring beam and stabilizing the laser frequency to the cavity mode. This significantly influenced the reduction of the problem of disturbing the feedback loop response in the laser frequency stabilization system by means of absorption/dispersion measurement. In addition, the scanning range of the measuring beam has been significantly expanded from the previous few MHz up to 20 GHz and now has the possibility of convenient remote control using a programmable microwave generator. Preliminary results of measurements, carried out with the new system in a wide range of pressures from the Doppler up to collisional (atmospheric) regime, ultimately confirm the superiority of the ultra-accurate CMDS method over the intensity-dependent CRDS and CMWS absorption techniques. For the first time, analyzing the shape of the spectral line in such a wide range of absorption changes, sub-per-mille accuracy was obtained for measuring the intensity of the line. In addition, in the measurement of the Doppler-broadened spectral line, an accuracy of 20 kHz was obtained for the position of the line, comparable to the accuracy offered by sub-Doppler saturation spectroscopy. As a result, the scientific achievement presented for evaluation led to the development of the first spectroscopic technique with sub-per-mille accuracy. The presented research is also one of the first which set a new trend to switch from absorption spectroscopic techniques to dispersive ones. The results described above were sent recently for publication.

The CMWS and CMDS spectroscopic techniques developed as a part of the habilitation cycle presented here influenced also the direction of development of new broadband absorption and dispersion spectroscopic methods directly using the optical frequency comb as a source of laser radiation illuminating the sample. In these techniques, mainly developed in the group of O. Axner and A. Foltynowicz (Sweden)[28,29] and the group of R. S. Trawiński and P. Masłowski[30,31] from our research team, the optical frequency comb, stabilized to the optical cavity, is precisely tuned through the comb of the cavity modes in such a way as to obtain, in a relatively short time, a transmission spectrum of the cavity modes from the entire spectral range of the comb. In this way, full information about the wavelength dependence of both resonant and non-resonant parts of the refractive index of the investigated medium and the material of the mirrors forming the cavity is obtained. Ultraaccurate and ultraprecise spectroscopic measurements of whole molecular bands are crucial for detection and distinguishing of various chemical compounds in the investigated samples. Broadband measurements of loss and dispersion of mirrors are also used to test and develop new technologies for mirroring reflective coatings, important from the point of view of various fields of science, including construction of more stable resonators as short-term frequency standards for optical atomic clocks.

[28] L. Rutkowski et al., *Opt. Express* **25**, 21711 (2017)
[29] A. C. Johansson et al., *Opt. Express* **26**, 20633 (2018)
[30] D. Charczun et al., *Phot. Lett. Pol.* **10**, 48 (2018)
[31] G. Kowzan et al., in preparation (2018)

The high level of precision and frequency control of laser systems developed in works [H1-H3], for both metrological and spectroscopic applications, has been noticed in numerous works of other groups[32,33,34]. Additionally, the positions of CO lines, determined in the paper [H4], were included in the latest HITRAN2016[35] spectroscopic database update as data from ultra-precise experiments using the best calibration standards. The research results indicated in the main scientific achievement have also been awarded many times. For the contribution to the development of ultrasensitive spectroscopy in the optical cavity and HITRAN spectroscopic database, I received the international "James Brault Young Scientist Award" in 2014. Research in topics of CMWS spectroscopy were also honored with four awards of Rector of the Nicolaus Copernicus University, two scholarships Start of the Foundation for Polish Science (including one with distinction) and the scholarship of the Ministry of Science and Higher Education for an outstanding young scientist. The results of research presented at national and international conferences have always been highly rated and met with great interest. This was reflected in two invited lectures at the prestigious conferences "22nd International Conference on Spectral Line Shapes" in Tullahoma, Tennessee (USA) and "17th International Conference Laser Optics 2016" in St. St. Petersburg (Russia). It is worth noting that the presented scientific achievement has been fully developed and realized in Poland, at the National Laboratory FAMO in Toruń.

5. Other scientific achievements

In my previous scientific work, three main trends of research can be distinguished:

- experiments using optical cavities, including:
  - construction of spectrometers with high sensitivity,
  - development of new spectroscopic techniques in optical cavities,
  - construction of short-term frequency standards,
  - automation of measurements and remote control of the experiment,

- atomic and molecular spectral line shapes, including:
  - analysis of collisional effects in spectral line shapes,
  - new methods for calculating spectral line profiles,
  - providing precise line-shape parameters for spectroscopic databases,
  - precise gas metrology, that is, determining the concentration of the molecules based on the analysis of the spectral line shape,

- simulations and analysis of experimental data, including:
  - programs for multidimensional fits,
  - programs for complex analysis of spectral line shapes,
  - programs for determining the laser spectral width based on the laser noise power spectrum,
  - simulation of the interaction of laser radiation with the optical cavity,
  - testing the application ranges of spectral line shape models.

Experiments using optical cavities

[32] D. Świerad et al., *Sci. Rep.* **6**, 33973 (2016)
[33] H. I. Mohamad, F. Aflatouni, *Nat. Comm.* **8**, 1209 (2017)
[34] L. Yujia et al., *Opt. Express* **26**, 26896 (2018)
[35] I. E. Gordon et al., *J. Quant. Spectrosc. Radiat. Transfer* **203**, 3 (2017)

I started to experiment with optical cavities since 2008 when we started the construction of the first CRDS spectrometer in Toruń. In the initial phase of the project, the spectrometer was a copy of the system from NIST (USA) [36], built and automated at NIST with a significant participation of members of our research team[37,38]. It enabled the first precise measurements of the shapes of the spectral lines from the weak O_2 B band with a high at that time signal-to-noise ratio of 2000:1 [A2] (numbering in accordance with the Appendix No. 3 "Wykaz opublikowanych prac naukowych (...)", point II A). The second part of the project, constituting a technological novelty, consisted in implementing the Pound-Drever-Hall technique tightly locking the frequency of the measuring laser to the cavity mode in the CRDS spectrometer with a linear optical cavity (i.e. composed of two mirrors). The introduced changes significantly increased the sensitivity and precision of measurements with a CRDS spectrometer, and also accelerated the data acquisition process [A4]. Thanks to them, it was possible to record the absorption spectrum of the O_2 molecule with the highest achieved in optical spectroscopy signal-to-noise ratio of 220000:1 [A9]. In the paper [A6] we solved the problem of thermal drift of the error signal offset in the laser stabilizing loop, which in the case of CRDS spectrometers with linear cavities previously prevented their reliable and continuous operation. The precise and reliable high-resolution CRDS absorption measurement technology developed in Toruń has gained wide recognition in the world. It was used, among others at the National Metrology Institute of Japan, AIST (Japan) for ultra-precise CRDS hygrometry [A22, A28], developed directly for applications in the semiconductor industry and at NIST (USA) where, at the invitation of J. T. Hodges, I built a copy of the CRDS spectrometer for precise measurements of CO_2 spectral line shapes [A12]. In 2012, we realized in Toruń a first link of the frequency axis of the CRDS spectrometer to the optical frequency comb, which revolutionized the precision of measurements of transitions in molecules [A7]. A year later, the link between the CRDS spectrometer and the comb was also implemented at NIST (USA) thanks to which it was possible to demonstrate the world's first Doppler spectroscopy, in which the position of the line was determined with a precision of several kHz [A12]. The research results described above became the basis of my doctoral dissertation. In a compact form, they were also described in short review papers [A10, A17].

In years 2008-2014 I was a contractor in two projects of the Ministry of Science and Higher Education realized as part of a consortium of three Universities: Warsaw, Jagiellonian and Nicolaus Copernicus, established to build the Polish Optical Atomic Clock at the National Laboratory FAMO in Toruń [A29]. My research work was mainly related to the construction of short-time clock frequency standards, i.e. ultra-stable and spectrally narrow lasers operating at 689 nm [A8, A11] and 698 nm [A20, A24] for detection of $^3P_1$-$^1S_0$ and $^3P_0$-$^1S_0$ transitions in strontium atoms. Having two optical atomic clocks in Toruń enabled a series of interesting and important experiments. In the work [A33], the first in the world measurements of molecular spectroscopy with reference of the frequency axis of the absorption spectrum to the optical frequency standard were made. The first remote synchronization of observations of the VLBI radio telescope network using a fiber optical link providing an optical time and frequency reference to the radio telescope antenna is described in the paper [A32]. Observation that the atoms and optical cavity have different susceptibility to changes in the fine structure constant became the basis for development of a new method for detecting topological defects of dark matter using a single optical atomic clock [A30]. Finally, the design of a system of two phase-locked lasers, in which the stability of the clock laser can be transferred to a second laser tunable in the 20 GHz range, was used in the first demonstration of the CMWS method to measure the optical cavity mode widths, within the weak molecular oxygen spectrum line, described in the paper [H1] from the habilitation cycle.

Since 2012, I have been involved in the development of new spectroscopic techniques in optical cavities. The main goal that guides this research is the invention of a precise method, free

[36] J. T. Hodges et al., *Rev. Sci. Instr.* **75**, 849 (2004)
[37] J. T. Hodges, R. Ciuryło, *Rev. Sci. Instr.* **76**, 023112 (2005)
[38] J. T. Hodges, D. Lisak, *Appl. Phys. B* **85**, 375 (2006)

from instrumental distortions, which in the most exact way will reflect the shape of the investigated spectral line and, consequently, physics of molecular collisions. These studies have been indicated as the main scientific achievement and are described in point 4.3 of the self-presentation.

An integral part of the experiment is the measurement procedure and efficient management of all components of the system. I devoted a lot of effort and time for preparing the software controlling CRDS, CMWS and CMDS experiments, which not only allows remote control of measurements, but also is insensitive to random effects interfering with the course of research (such as unexpected break of the laser lock to the cavity or loss of stabilization of the comb of cavity mods). The software was also used to handle experiments at NIST (USA) [A12] and partly at AIST-MNIJ (Japan) [A22,A28]. I was also involved in the development of fast data acquisition methods, thanks to which it is possible to more efficiently average the measurement data under conditions of slow drift of physical quantities, which always accompanies measurements.

Atomic and molecular spectral line shapes

In the years 2006-2008, as part of the preparation of my master's thesis, I participated in studies on the impact of optical collisions on the shape of the spectral line of cadmium isotope 113 by means of laser induced fluorescence. Conducted systematic numerical tests of cadmium line shifts for the ^{113}Cd-Ne system led to a change in the existing assumptions as to its isotopic structure. The determined new isotopic structure applied to the ^{113}Cd-Xe and ^{113}Cd-Ar systems significantly reduced the previously observed systematic error of the pressure shift of ^{113}Cd line and enabled precise determination of split of hyperfine 5p $^3P_1$ state [A1]. The obtained result was the first one from a direct analysis of the registered shape of the spectral line.

Since 2008 I have been measuring and analyzing the shape of molecular spectral lines important from the point of view of providing accurate reference data necessary to interpret atmospheric spectra (study of molecules: O_2, CO, CO_2, H_2O) as well as basic research due to testing of quantum and relativistic calculations or searching for a new physics (study of D_2 molecule). Proper analysis of the shape of the spectral line is also the basis for the exact metrology of the amount of gases and the development of accurate methods of Doppler thermometry. Typical parameters determined in the spectral line analysis are its position, Doppler and collisional width, pressure shift, intensity and background parameters. There are also a number of subtle effects contributing to the line shape, such as Dicke narrowing, dependence of the line width and shift from the absorber speed, correlations between phase and state changing collisions, or line mixing effect, the observation of which requires high accuracy and precision of measurements. The very high signal-to-noise ratio of the O_2 spectrum demonstrated in [A9] made it possible to observe the subtle asymmetry in the shape of this line, the smallest that has ever been observed in the case of self-broadened lines. An important result of the work [A14] was the presentation of a novel method of calculating the line shape, using a new approach to the perturbation series in solving the Boltzmann transport/relaxation equation. This work is a good example of how experiment and theory can influence each other. High quality experimental data from work [A9] proved necessary to test the accuracy and convergence of the method. On the other hand, the developed technique enabled the use of more complex theoretical profiles in the line-shape analysis, such as Billiard-ball profile, which in turn influenced the further increase in the accuracy of obtained line-shape parameters. In the work [A35] we examined the influence of the speed-dependent effects on the Lamb dip shapes measured by the Doppler-free spectroscopy. A new approach to direct determination of the speed-dependent functions of the line collisional width and shift based on the measurement of saturation dips for selected velocity components from the Maxwell-Boltzmann speed distribution was also proposed.

In systematic studies of the shape of spectral lines, we show that the use of simplified models such as the Voigt profile is usually insufficient to properly interpret experimental data. For example, in the work [A27] we demonstrated that the analysis of spectral lines in the B band of molecular oxygen with the Voigt profile can result in a systematic error of up to 5% in the determined line-shape parameters. As a result of the joint efforts undertaken by various research groups in the world, including ours, a new standard for the description of the shape of the spectral lines for atmospheric applications was developed - Hartmann-Tran profile (HTP)[39] taking into account the subtle line-shape effects mentioned above. In cooperation with scientists from UMR CNRS (France), NIST (USA) and IEM-CSIC (Spain), in the work [A26] tests of the HTP profile were carried out in a wide range of pressures up to atmospheric conditions, which proved its sub-per-mille accuracy in reconstruction of both simulated and experimental molecular spectra. In the paper [A25] we presented a theoretical description of the temperature dependence of collisional line width and shift parameters under conditions of, commonly used in atmospheric studies, the quadratic dependence of these parameters on the absorber speed. In the work [A3] we showed, that also at very low pressures, in which the shape of the line is determined mainly by the Doppler part, simultaneous consideration of the occurrence of velocity-changing collisions as well as speed dependence of collisional line width and shift is necessary to determine the Boltzmann constant from the Doppler linewidth with relative accuracy better than 10^{-6}. The research presented in the work [A3] significantly influenced the development of the areas of optical measurement of the Boltzmann constant and gas thermometry, in which the analysis of Voigt and even Gauss was previously considered to be sufficient.

The results of systematic analyzes of the shapes of molecular oxygen spectral lines were included in the works [A2, A5, A7, A13, A18, A21, A23, A27, A33] and the CO spectral lines in the works [A15, A31] and [H4]. In most cases, the absolute positions of the lines were determined with 150 kHz standard uncertainty, i.e. more than three orders of magnitude smaller than the uncertainties offered by the HITRAN spectroscopic database. In the paper [A33] we also demonstrated that under conditions of high precision of experimental data the position of the Doppler-broadened O_2 line can be determined with standard uncertainty of up to several kHz. Relative standard uncertainties obtained for line intensities are within 0.3-0.5%, and for the collisional linewidth within 0.1-0.5%. In addition, pressure line shifts are determined with sub-percent accuracy. It should be noted that results obtained for O_2 and CO spectral lines are the most precise that has been obtained so far. In cooperation with scientists from CalTech (USA) and NIST (USA), in the work [A19] we measured and analyzed the shape of the CO_2 spectral line important from the point of view of monitoring of CO_2 concentration in the ASCENDS mission. We have again shown that advanced analysis of the spectral line shape is necessary to obtain reference data of sub-percent accuracy. A well-physically justified model of the shape of the spectral line can also be used, in basic research, to precisely measure the energy of transitions in the D_2 molecule. In the paper [A34] we showed that even under atmospheric pressure conditions, which require to take into account a series of collisional effects to describe the shape of the spectral line, the use of a complex line profile allows us to reproduce the experimental spectrum of the D_2 line with high accuracy and achieve high precision of 400 kHz for the line position. Such precision is sufficient enough for testing with high accuracy quantum and relativistic calculations for the D_2-D_2 system.

The basis for the exact optical metrology of gases amount is the correct modeling of the spectral line shape. In the work [A22], carried out in cooperation with AIST-MNIJ (Japan), ultra-precise CRDS hygrometry was demonstrated, which in combination with advanced spectral line shape analysis enabled the detection of H_2O molecules at the level of 5 ppt. In the paper [A16], however, the influence of argon fluctuations in synthetic air on the accuracy of CO_2 concentration measurement by commercial CRDS spectrometer was investigated. Conducted, using a CRDS laboratory spectrometer at NIST (USA), tests showed systematic errors in the calibration of the CO_2 sensor by an order of magnitude greater than its precision. This was related to the method of determining the concentration of CO_2 in the sensors, based on the measurement of the absorption coefficient at the maximum of the spectral line instead of on a thorough analysis of the shape of the line.

[39] J. Tennyson et al., *Pure Appl. Chem.* **86**, 1931 (2014)

Simulations and analysis of experimental data

My scientific achievements include many programs for simulation and processing and analysis of experimental data written in LabView, Mathematica and Fortan. In 2012, I created an advanced software enabling global, multidimensional analysis of molecular spectra recorded in a wide range of pressures [B21] (numbering in accordance with the Appendix No. 3 "Wykaz opublikowanych prac naukowych (...)", point II C). The wide range of analytical and semi-analytical line-shape models available in the program enables a convenient and accurate interpretation of the physical effects influencing the formation of the shape of the spectral line. Implemented algorithm for simultaneous fitting of the spectra corresponding to different gas pressures, so-called multi-spectrum fit[40], reduces the numerical correlation between the fitted line-shape parameters. This is especially important in the case of using physically well-justified, multi-parameter line profiles such as the HTP. The software is still being developed. Depending on the needs, further improvements are introduced. Currently, it enables the analysis of both absorption and dispersion spectra obtained using techniques of direct measurement of the absorption/dispersion coefficient as well as the measurement of the intensity of light transmitted through the medium. It is a technology irreplaceable in the treatment of a large amount of experimental data clearly indicating its usefulness for creating a new generation of spectroscopic databases with sub-percent accuracy. In our team, it is used to analyze practically the majority of data obtained from various experiments. Other research teams are also interested in the software and cooperation in the field of data analysis. Currently, the software developed in Toruń is used, among others in such institutions as NIST (USA), CalTech (USA), AIST-NMIJ (Japan), Umea Universitet (Sweden), or University of Lethbridge (Canada).

I also wrote a software for complex analysis of the shapes of spectral lines, which were used, among others, in the work [H3] to interpret simultaneously measured absorption CRDS and dispersive CMDS spectra. As shown in [H3], complex analysis of experimental data can be a very convenient tool for detecting systematic errors of measurement methods. For the purpose of my work [H4] I wrote the software that allows me to determine the spectral width of a laser based on measuring the power spectrum of its noise. The software used the algorithm described in paper of Bucalovic et al.[41]. In the work [A3], I tested ranges of applicability of spectral line shape models for ultra-accurate measurements of the Boltzmann constant determined from the width of the Doppler-broadened spectral line. I was also involved in simulating various phenomena and processes such as propagation of a Gaussian laser beam in the optical system, FEM simulation of thermal conditions in a chamber that isolates the optical cavity from the environment, or characterization of the error signal in the Pound-Drever-Hall method used to stabilize the laser frequency to the optical cavity mode. These simulations served both better understanding of physical processes as well as improved and accelerated an experimental work. In addition, the model of precision of CRDS and CMWS spectroscopic methods, developed and simulated in the work [H1], enables determination of the applicability range of these methods. On the other hand, presented in [H5], the simulation of the electromagnetic radiation interaction with the optical cavity served to explain the characteristic response of the optical cavity under conditions of nearly resonant excitation of its modes.

A. Cygan

[40] D. C. Benner et al., *J. Quant. Spectrosc. Radiat. Transfer* **53**, 705 (1995)
[41] N. Bucalovic et al., *Appl. Opt.* **51**, 4582 (2012)