Self-presentation

1. Name and Surname:

Daniel Lisak

2. Owned diplomas, degrees - with the name, place and year of obtaining:

1998 Nicolaus Copernicus University (NCU) in Toruń, Master of Physics 2003 Nicolaus Copernicus University in Toruń, Doctor of Physical Sciences in Physics

3. Information on previous employment in scientific institutions:

2002 – 2004	Assistant in the Department of Gas Phase Spectroscopy of the Institute of Physics, NCU
2003	1.5-month research trip to the Universita di Napoli "Federico II", Dipartimento di Scienze Fisiche (Naples, Italy), working in the group of prof. Antonio Sasso
2004 – present	Assistant Professor in the Department of Atomic, Molecular and Optical Physics of the Institute of Physics, NCU
2005 – 2008	Postdoctoral research associate - three research trips (a total of 19 months) to the National Institute of Standards and Technology - NIST, Process Measurements Division (Gaithersburg, MD, USA). Working in a group of Dr. Joseph T. Hodges

4. Display of achievements* under art. 16 ust. 2 of the act of 14 March 2003 on Academic Degrees and Title and on Degrees and Title in the field of art (Dz. U. nr 65, poz. 595 ze zm.):

As indicated above under the Act for a scientific achievement I chose monothematic cycle of 6 publications on the cavity ring-down spectroscopy - CRDS) used to study H_2O spectra in the near infrared. Impact factor of journals from the year of publication, number of citations (according to the base Web of Science) and estimated by me percentage of my contribution is given for each of the publications below.

1. **D. Lisak**, J. T. Hodges, R. Ciuryło, "Comparison of semiclassical line-shape models to rovibrational H_2O spectra measured by frequency-stabilized cavity ring-down spectroscopy",

Phys. Rev. A **73**, 012507 (2006) impact factor 3.047, number of citations 35, my contribution 70%

In the paper for the first time was shown that the CRDS technique is suitable to study subtle effects influencing the shape of the spectral lines. The single-mode frequency-stabilized cavity ring-down spectroscopy – FS-CRDS was used for systematic studies of the shapes of spectral lines. FS-CRDS spectroscopy developed by Joseph T. Hodges uses an optical cavity with frequencies of resonant modes actively stabilized to a stable frequency of the reference laser. A spectrally narrow continuous wave probe laser is used with its beam shape and frequency matched to a single TEM₀₀ mode of the cavity. This approach allows to obtain a pure exponential decay signal from the cavity, provided a suitable rapid switching off the laser. In addition, the stabilized comb of longitudinal cavity modes, to which the probe laser is consecutively locked, provides very accurate relative frequency axis of measured spectrum. It is worth noting that in CRDS spectroscopy the absorption coefficient of the investigated gas is obtained directly from the measured decay time of light, so that fluctuations of the probe laser power does not affect the measured spectrum.

As part of this work FS-CRDS spectrometer was built and a control and data analysis software was written. The applicability of this method for very precise measurements of spectral line shapes in the gas was demonstrated. On example of the rotation-vibration lines of H_2O in the near-infrared the applicability of model profiles of spectral lines was tested. On example of three perturbing gases He, N_2 and SF_6 the influence of collisional narrowing of spectral lines and dependence of pressure broadening and shifting on velocity of the absorber molecules, the so-called speed-dependent effects, on resulting line shape was demonstrated. Both these effects are often difficult to distinguish although the physical cause is quite different. Additionally, speed-dependent effects can cause asymmetry of the line. The study demonstrated that with sufficiently high signal to noise ratio of the experimental spectra it is necessary to simultaneously take into account the above mentioned effects in order to get the agreement of model line profiles with the results of the measurements. Also a very high spectral resolution of 50 kHz and agreement of the Doppler line width with the value resulting from the gas temperature at the level of 0.2% was demonstrated.

My contribution to the paper: planning the experiment, selection of physical conditions, partly construction of the experimental setup (together with J.T. Hodges), writing about a half of the software that controls the measurement process, selection of physical models (except model of billiard-ball collisions proposed by R. Ciuryło) taking measurements contained in the paper, selection of methods of data analysis, writing software to analyze data, collecting results and preparing most of the text publication.

2. J. T. Hodges, **D. Lisak**, "Frequency-stabilized cavity ring-down spectrometer for high-sensitivity measurements of water vapor concentration", Appl. Phys. B **85**, 375-382 (2006) impact factor 2.023, number of citations 16, my contribution 50%

A portable FS-CRDS spectrometer working at 1.4 microns spectral region was built and used for detection of trace amounts of water in a carrier gas. Spectroscopic and thermodynamic method for the detection of water vapor was compared. The accuracy of the FS-CRDS method has been compared to other CRDS methods based on unstabilized laser or optical cavities. Obtained ratio of signal to noise of measured spectra was about 2500:1. Spectrometer's detection limit of absorption was determined as about 1.2 x 10^{-10} cm⁻¹ Hz^{-1/2} and the minimum detectable mole fraction of H₂O was 0.7 x 10^{-9} . In contrast to conventional hygrometers, which are based on accurate temperature measurement of the optical condensation the hygrometer based on CRDS spectroscopy does not require periodic calibration except of a single measurement of the intensity of the used spectral line.

My contribution to the paper: partly construction equipment (together with J.T. Hodges), selection of methods of spectroscopic data analysis and development of software for automated data analysis, taking measurements contained in the paper, data analysis and preparation of results for publication, participation in the final text editing work.

3. **D. Lisak**, J. T. Hodges, "High-resolution cavity ring-down spectroscopy measurements of blended H₂O transitions", Appl. Phys. B, **88**, 317-325 (2007) impact factor 2.280, number of citations 20, my contribution 70%

In this paper the stability of the frequency axis and a high resolution of the FS-CRDS spectrometer was exploited to accurately determine the relative positions, intensities and line-shape parameters of the four weakly separated lines of H_2O broadened by N_2 . Using saturation Doppler-free spectroscopy with resolution of 50 kHz relative line position were precisely determined. Then they were used in full analysis of Doppler- and pressure broadened lines. Using this approach, combined with an advanced model of the spectral line shape we obtained uncertainties of the measured intensities of about 0.6%. The systematic errors of determined pressure widths and line intensities in the system under study resulting from the use of simplified models of the line shape, in particular the Voigt profile, were quantified. These errors may even be over a dozen percent of the measured values.

My contribution to the paper: planning the experiment, partly construction equipment (together with J.T. Hodges), selection of methods of spectroscopic data analysis, taking measurements contained in the paper, data analysis and preparation of results for publication, writing most of the text of publication.

4. **D. Lisak**, J. T. Hodges, "Low-uncertainty H₂O line intensities for the 930-nm region", J. Molec. Spectrosc., **249**, 6–13 (2008)

impact factor 1.636, number of citations 6, my contribution 70%

FS-CRDS method was used to measure the intensities of more than 70 spectral lines of H_2O in the near infrared. For relatively strong spectral lines we obtained agreement with data

obtained in other laboratories at 1% level, but in the case of lines having very weak intensities our results were systematically higher by about 20% from commonly used data. It should be noted that the earlier data were obtained by the Fourier-transform spectroscopy – FTS, which is not as sensitive as the CRDS technique. For this reason, the intensity of investigated lines were close to detection limit of FTS spectroscopy, while the spectra obtained by the FS-CRDS achieved signal to noise ratio of up to 450:1. The intensity of the weakest measured spectral line of H_2O was equal 1.4×10^{-27} cm² cm⁻¹ molecule⁻¹.

My contribution to the paper: partly planning the experiment (with J.T. Hodges), making the necessary modifications to the experimental setup and software for data analysis, spectroscopic measurements and their analysis, comparing the results with literature data, writing the majority of the text of publication.

5. J.T. Hodges, **D. Lisak**, N. Lavrentieva, A. Bykov, L. Sinitsa, J. Tennyson, R.J. Barber, R.N. Tolchenov, "Comparison between theoretical calculations and high-resolution measurements of pressure broadening for near-infrared water spectra", J. Molec. Spectrosc. **249**, 86–94 (2008)

impact factor 1.636, number of citations 7, my contribution 50%

In this paper profiles were measured of over 20 rotational-vibrational spectral lines of H_2O , in the wavelength region around 935 nm, perturbed by nitrogen and by air. Pressure broadening coefficients were determined and the observed effect of line narrowing was analyzed. Interpretations of this effect as the Dicke narrowing or as the dependence of pressure broadening on the velocity of molecules significantly affects determined pressure broadening coefficient of lines, what should be taken into account when comparing the experimental values. In addition, theoretical calculations were made of pressure broadening coefficients of investigated H_2O lines using the newest available data on energy levels and transition dipole moments. We obtained good agreement of theoretical results with experimental at level of around 4%.

My contribution to the paper: partly planning the experiment (with J.T. Hodges), adaptation of software for data analysis, spectroscopic measurements and their analysis, the comparison of experimental results with theoretical (theoretical calculations were made by the other coauthors), writing about half the text of the publication.

 D. Lisak, D. K. Havey and J. T. Hodges "Spectroscopic line parameters of water vapor for rotation-vibration transitions near 7180 cm⁻¹", Phys. Rev. A 79, 052507 (2009) impact factor 2.866, number of citations 14, my contribution 70%

Aim of this study was to determine the intensities of spectral lines and line shape parameters of 15 H_2O lines from the region of 1.39 microns which may be used as a reference data in the optical hygrometry. As a source of gas having a well-known molar faction of H_2O we used the NIST primary standard humidity generator, which provided the world's lowest possible

uncertainty of H_2O content in the sample. Using the FS-CRDS spectroscopy and improved data analysis procedure involving the simultaneous fitting of spectra corresponding to different gas pressures (multi-spectrum fit) we obtained intensities of the spectral lines with uncertainty below 0.4%. The multi-spectrum fit data analysis method has allowed to distinguish between the effects of line narrowing due to velocity changing collisions (Dicke narrowing) and dependence of collisional width on absorber velocity, by using the so-called Speed-Dependent Nelkin-Ghatak Profile – SDNGP. We discuss the systematic errors of line intensities caused by use of simplified models of line shapes as well as by the range of the measured spectrum with respect to the spectral line width.

My contribution to the paper: partly planning the experiment (with J.T. Hodges), partly construction of equipment (with J.T. Hodges), writing most of the measurement automation and control software and all software for data analysis methods with multi-spectrum fit, the selection of physical models for data analysis, taking data contained in the paper, collecting the results and writing the majority of the text of publication.

The above-described series of publications is the first application of the Frequency-Stabilized Cavity Ring-Down Spectroscopy — FS-CRDS for systematic studies of the shapes of spectral lines. For the first time a reliable measurements and analysis of spectral line shapes taking into account the subtle effects was made with use of CRDS spectroscopy. This work demonstrated that CRDS can be not only very sensitive spectroscopic method, but also precise and accurate. Demonstrated excellent linearity of the frequency axis, defined by the comb of stabilized resonant cavity modes, connected with very high spectral resolution resulting from the excitation of one cavity TEM mode and independence of the decay time from the power of the probe laser light makes FS-CRDS ideal technique for the study of weak molecular spectra. The obtained spectra of H₂O lines were characterized by very high signal-to-noise ratio of up to 2500:1 and submegahertz resolution while the Doppler width of studied spectral lines was in the order of 1 GHz. This make possible to study a subtle line shape effects such as collisional line narrowing and speed-dependent effects for spectral lines with very low intensities.

Precise quantitative measurements of water vapor spectra are quite difficult, especially in the case of small concentration of H_2O molecules. This is due to unstable H_2O content in the absorption cell due to the ongoing process of absorption and desorption of water from the cell walls. In the case of cavity enhanced methods additional difficulty is the condensation of water on the resonant cavity mirrors. For this reason, the experiment must be conducted under conditions of continuous flow of gas of known molar fraction of H_2O and stable pressure and temperature. For the generation of the gas stream we used precise saturator and hygrometer based on measured of dew point temperature and calibrated in the hygrometric laboratory at NIST. In a subsequent measurements of intensities and shapes of spectral lines of H_2O as the source of gas stream the NIST primary standard humidity generator was used directly. The resulting spectroscopic data set is characterized by accuracy unattainable by other laboratories in

the world and can serve as reference data in both basic and applied research, in particular in the precision optical hygrometry. The obtained parameters of the intensity and shape of the spectral lines were used in the group of Prof. J. Tennyson (UCL, London) for testing theoretical methods of spectra calculation and for verification of spectroscopic parameters of the ESA database obtained by Fourier-transform spectroscopy.

The potential of the FS-CRDS spectroscopy and advanced methods of the spectral line shapes analysis developed in the course of these papers were used by groups engaged in satellite measurements of the Earth's atmosphere composition from NASA-JPL and California Institute of Technology, with whom I collaborate. Using technology and data analysis methods developed in for measurements of H₂O spectra a series of studies of spectral lines of oxygen and carbon dioxide were performed to serve as a reference data in the analysis of satellite spectra. FS-CRDS spectroscopy is currently being developed at NIST (the group of Dr. J.T. Hodges), the Nicolaus Copernicus University in Torun (the group where I work) and in California Institute of Technology (group of Prof. M. Okumura). In addition, a group of Dr. H. Abe of the National Metrology Institute of Japan is preparing to build a similar unit. The spectrometer is to be used for the detection of trace amounts of water vapor in technical gases used in the semiconductor industry.

5. Description of other scientific achievements.

My research interests are focused around three main themes:

- Methods of experimental spectroscopy (spectrometers design, automation of measurements)
- Analysis of experimental data (multidimensional fitting, the method of calculating the profiles of spectral lines)
- Shapes of atomic and molecular spectral lines (the impact of the collisional effects on the shapes of spectral lines in different systems, providing precision spectroscopic parameters to the databases, the application of analysis of spectral line shapes in metrology and detection of gases)

These issues are complementary, and the development of experimental methods and data analysis are the means to realization of the third of these points.

Methods of experimental spectroscopy

In order to study the collisional effects on spectral line shapes of the intercombination cadmium line in 1999 we built spectrometer for precise measurements using laser-induced fluorescence – LIF method with high resolution, of the order of 1 MHz, in the ultraviolet (wavelength 326.1 nm) . Fluorescence spectrum was induced by a ring laser with intracavity frequency doubler, and detection realized by photomultiplier operating in photon counting mode, provided a high

sensitivity of the spectrometer. The absolute frequency axis of measured spectra was calibrated against the well-known line of lodine molecules I₂. Spectrometer allows for fully automatic measurements of spectra with a signal-to-noise ratio of up to 300:1, and has been used in studies of subtle effects of the shape of ¹¹⁴Cd and ¹¹³Cd lines described later in this presentation. The temperature of fluorescent cell was regulated at several points what allowed for selection of the optimal concentration of Cd atoms independently from the temperature of the investigated gas. The spectrometer has been described in [3] (numbering according to Annex 3 - List of publications, Part A - publications in journals from JCR list). In 2008, modifications to the spectrometer provided improved linearity and stability of the frequency axis controlled with the reference frequency stabilized HeNe laser. Details of the upgraded version of the spectrometer have been published in [24].

In collaboration with the group of prof. A. Sasso from *Universita di Napoli "Federico II"* (Naples, Italy) we planned study of the impact of optical collisions on the shapes of spectral lines of H_2O , and C_2H_2 in the wavelength region of about 3 microns. For this task a Difference Frequency Generation (DFG) laser absorption spectrometer with a high spectral resolution was built. Spectrally narrow radiation in the infrared was obtained by a nonlinear effect of the difference frequency generation of waves from two lasers (Nd-YAG and tunable diode laser) operating in the near infrared, on the PPLN crystal (periodically poled LiNbO3). A system of two absorptive cells with fixed and floating gas pressures allowed for precise measurements of the pressure shift of spectral lines, and the frequency axis of the spectrum was calibrated relative to a stable Fabry-Perot interferometer (IFP) and to the Michelson interferometer designating the absolute wavelength. The spectrometer has been described in [15].

As a postdoc in the group of Dr. J.T. Hodges at the National Institute of Standards and Technology - NIST (Gaithersburg, MD, USA), I began using Cavity Ring-Down Spectroscopy – CRDS) for precise quantitative measurements of molecular spectra. CRDS spectrometer was built with active stabilization of the optical cavity mode's frequencies to the laser frequency reference (Frequency-Stabilized CRDS - FS-CRDS). This is one of the most precise and accurate spectroscopic method and is also characterized by very high sensitivity. Studies on H₂O molecules, described in 6 publications from the JCR list were chosen as a habilitation scientific achievement, and therefore they were described in an earlier section of this presentation. Using this technique a number of other precision studies of molecular spectra with a variety of applications were made, and they will be described later in this presentation.

The idea of the FS-CRDS^{1,2} method is to use a comb of TEM_{00} modes of an optical cavity to achieve very high spectral resolution and excellent linearity of the frequency axis of the measured spectrum. To eliminate the frequency drift of the cavity modes, caused by e.g. temperature or pressure change inside the cavity, the optical path length between the mirrors forming the cavity

¹ J. T. Hodges, H. P. Layer, W. W. Miller, and G. E. Scace, Rev. Sci. Instrum. **75**, 849 (2004)

² J. T. Hodges and R. Ciuryło, Rev. Sci. Instrum. 76, 023112 (2005)

is actively stabilized to a stable external optical reference – in this case to a frequency-stabilized HeNe laser. This solution allows one to simultaneously move the whole comb of the optical cavity modes by tuning the reference laser, what enables densification of the measurement points of the spectrum compared to the interval defined by the cavity free spectral range. In practice, resolution of 50 kHz was demonstrated [19]. In addition, by mode matching the beam profile and locking the frequency of the laser to cavity TEM₀₀ mode a very pure single-exponential decay of light from the cavity output is achieved, which results in accurate determination of light absorption coefficients. In collaboration with NIST four FS-CRDS spectrometers (3 in the NIST and one at Nicolaus Copernicus University in Torun) were built, including a portable one. They were used in the wavelength range from 0.69 microns to 1.65 microns for both basic research on the subtle effects of the spectral line shapes, and testing theoretical methods of molecular physics, as well as for applied research, particularly metrology and detection of trace gases.

A precise method for measuring the pressure shift of weak molecular lines was developed. The method is based on the FS-CRDS spectroscopy and does not require an optical frequency reference close to the frequency of measured spectral lines. Instead it benefits from stability of the optical cavity modes and knowledge of the dispersion of the cavity modes as a function of pressure. The method is described and applied to the spectra of O_2 in Ref. [20].

A detailed description of the spectrometer, built at NCU in Toruń, in the version used until 2010 can be found in Ref. [27]. In 2010, we made significant modifications to the FS-CRDS spectrometer consisting of a probe laser locking to the cavity mode using fast Pound-Drever-Hall (PDH) method. This allowed the narrow spectral line width of the probe laser to less than the width of the TEM₀₀ mode of the cavity (about 20 kHz). This caused a huge increase in the speed of light decay acquisition, due to the elimination of the accidental nature of the laser wave frequency coincidence with the narrow cavity mode, and thus increase the speed of the spectrum measurement. Moreover, the new method has enabled a significant increase in signal-to-noise ratio of the measured spectra due to higher power of light matched to the cavity mode and it allowed for fast averaging a large number of decays. Practical measurements using this method required a precision correction of the PDH error signal due to a difficult to eliminate DC offset associated with a small amplitude modulation of the light wave by the phase modulator, and the imperfections of electronics in the control feedback loop controlling the laser diode current. Obtained O₂ spectra are characterized by signal to noise ratio of the order of 8000:1. The new system is described in [31, 34]. Recently as a result of averaging 3000 spectra we obtained experimental spectral line shape with a signal-to-noise ratio higher than 200000:1, which is the highest value ever achieved in optical spectroscopy and opens new possibilities for metrological research. These results were sent for publication in Phys. Rev. A in 2011.

In 2011, the FS-CRDS spectrometer was linked with a femtosecond optical frequency comb in order to obtain an accurate measurement of absolute probe laser frequency with submegahertz accuracy at each point of the measured spectrum. It is the world's only such a spectrometer which allows precise measurements of the frequency of transitions, the intensity

and line shape parameters of very weak molecular spectra. The results may serve as a reference data for other methods of measurement and calculation. The results were sent for publication in J. Chem. Phys. in 2011.

In 2009 construction of optical atomic clock based on the Sr atom started in KL-FAMO laboratory in Toruń. As a part of this project a tunable laser system for ultra-narrow spectral width, below 10 Hz was designed and built, in order to serve as local oscillator of the clock based on optical transition in Sr. Two identical laser systems were built, which allowed to determine their spectral width. Each of them consists of a diode laser using PDH-locked to an ultra stable optical cavity having high finesse, of the order of 70000, isolated mechanically, acoustically and thermally from the environment. In addition, a tunable system was built, which uses two lasers phase phase-locked using optical beat note signal. Achieved relative spectral width of lasers of about 150 mHz while relative detuning of lasers was several GHz. The laser system coupled with the strontium atomic trap and an optical frequency comb will create an optical clock. The results are being prepared for publication.

Analysis of experimental data

Precise analysis of spectroscopic data with high resolution and high signal-to-noise ratio requires consideration of many physical effects, which in varying degrees, affect the observed spectral line profile. In order to analyze the data obtained using the spectrometers described above, as well as other devices which I did not construct, I wrote software for fitting theoretical models of spectral line shapes to experimental data. The software is continuously developed since the beginning of my MA thesis, until now. It allows inclusion of many physical effects to the line shape analysis. The Doppler- and pressure broadening and shifting of line describes the well known Voigt profile. It assumes statistical independence between the Doppler and pressure line broadening. Taking into account the dependence of pressure dependence of broadening and shifting on the speed of absorber (or emitter) leads to the so-called speed-dependent Voigt profile³. Another physical effect which had to be taken into account in the analysis of many studied spectra are velocitychanging collisions leading to Dicke narrowing of the line. It was analyzed in both the so-called soft- and hard-collision approximation, leading to the Galatry profile⁴ and Nelkin-Ghatak profile⁵ (also called Rautian profile in the literature), respectively. In addition, a more realistic approximation is implemented - the billiard-ball collision model, leading to the Billiard-Ball profile⁶. An additional effect influencing the shape of analyzed spectral lines is correlation between velocity-changing and state-changing (dephasing) collisions. It can lead to line

³ P. R. Berman, J. Quant. Spectrosc. Radiat. Transf. **12**, 1331 (1972)

⁴ L. Galatry, Phys. Rev. **122**, 1218 (1961)

⁵ M. Nelkin, A. Ghatak, Phys. Rev. **135**, A4 (1964)

⁶ R. Blackmore, J. Chem. Phys. **87**, 791 (1987)

asymmetry as well as difficulties in analyzing the collision narrowing of the line. This effect can be included in the analysis using the so-called correlated profiles, such as correlated Galatry profile or correlated Nelkin-Ghatak profile. Other factors that may cause asymmetry of the spectral line is the finite duration of the absorber – perturber collision leading to the collision-time asymmetry and effect of line mixing. The so-called asymmetric line shape models allow to analyze such effects⁷.

During the analysis of spectral lines with high signal-to-noise ratio it is often necessary to take into account many of these physical effects simultaneously in the data analysis. The parameters describing them are often highly correlated with each other. I programmed and used in several papers [27,32,33] a data analysis procedure involving the simultaneous fitting of the model profile of spectral lines to the spectra obtained for different perturbing gas pressures (so-called multi-spectrum fit). This method allows to cope with the numerical correlation between the fitted parameters of the line profile. For example, the Dicke narrowing parameter and parameter describing the speed dependence of the collisional width in the Speed-Dependent Nelkin Ghatak Profile⁸, even though they describe different physical effects, however, have quite similar effect on the observed spectral line shape in a given pressure. However, the pressure dependence of these two parameters are quite different. The method of multi-spectrum fit captures these differences in the data analysis and allows to obtain data on the contribution of each effect to the observed spectral line narrowing.

Methods of data analysis are essential to eliminate systematic errors when calculating the spectroscopic data obtained with high precision, including physical constants. In [28] we analyzed the problem of the impact of the line shape effects on systematic error in the optical measurement of the Boltzmann constant determined form the Doppler width of spectral line. Due to the precision of this analysis advanced numerical methods were adapted for calculating profiles of spectral lines to achieve a relative accuracy of the order of 10⁻¹⁰. On example of molecular oxygen line with a wavelength of 687 nm, we analyzed the impact of the speed-dependent effects and the collision narrowing on the Doppler line width determined from fitting different model profiles of the line.

Shapes of atomic and molecular spectral lines

During the preparation of my master thesis I began experimental studies on the impact of speed-dependence of pressure broadening and shifting of spectral lines on observed line profile, on example of argon and neon lines in a glow discharge in gas phase. The processes of atom excitation, in particular dissociative recombination was also investigated with respect to its

⁷ R. Ciuryło, J. Szudy, R. S. Trawiński, J. Quant. Spectrosc. Radiat. Transf. **57**, 551 (1997).

⁸ B. Lance, G. Blanquet, J. Walrand, and J.-P. Bouanich, J. Molec. Spectrosc. **185**, 262 (1997)

impact on formation of the emission profile of spectral lines. It was shown that at low gas pressure dissociative recombination leads to non-thermal velocity distribution of atoms, what is the main factor causing the observed line shape distortion from the Voigt profile. The studies used a pressure-tuned Fabry-Perot interferometer. The results of these studies have been published in two articles [1, 2]. Continuing the post-doctoral basic research on the impact of the optical collisions effects on atomic emission profiles, we measured shapes of the 748.8 nm line of neon in the glow discharge lamp. Particular attention was paid to the temperature dependence (temperature range 150 K - 650 K) of collisional broadening and shifting of the line, as well as of collision-time asymmetry and effect of dissociative recombination. The results were published in papers [26, 29, 30].

The main topic of research during doctoral studies, also continued later, was a highresolution spectroscopy of cadmium atoms by laser-induced fluorescence (LIF). Experimental studies included the measurement of the influence of the collisional effects on the profiles of spectral lines. The impact of such effects as Dicke narrowing, the speed-dependence of pressure broadening and shifting and the subtle effect of collision-time asymmetry was observed. We performed systematic measurements of the ³P₁ - ¹S₀ intercombination line of ¹¹⁴Cd isotope. Line shape dependence of on perturbing gas pressure, for atomic Xe, Kr, Ar, Ne, He [4-7, 10] and molecular H2, D2, N2, CH4 perturbers was analysed [3, 9]. The obtained experimental results concerning the collisional broadening, the collision shift and asymmetry of the line were compared with the results of calculations which assume semiclassical, analytical and numerically calculated interaction potentials of the emitter – perturber system. We demonstrated that in the case of Cd - Xe system taking into account simultaneously the speed-dependent effects and collision-time asymmetry allows for correct interpretation of experimental data [4]. In addition, for the system Cd – Xe the possibility of observing The Dicke narrowing effect in the optical range of atomic spectra was analysed [11]. Data analysis using a more advanced theoretical spectral line profile, which take into account the simultaneous occurrence of speed-dependence effects, collision-time asymmetry and velocity-changing collisions of atoms, showed no evidence of Dicke narrowing. This result was explained in terms of correlation between the occurrence of collisions changing the phase and velocity of atoms. Also calculations were made of pressure broadening, shift and asymmetry parameters of the of 114 Cd 3 P₁ - 1 S₀ line perturbed by all the noble gases, in the framework of the non-adiabatic impact theory, and compared with our experimental data. The results were published in article [12].

In another series of experiments [14, 29] the shapes of two hyperfine components of the intercombination line of even-odd isotope ¹¹³Cd, perturbed by argon was investigated. The main objective of this study was seeking the line mixing effect in the atomic system. Line asymmetry of the two components of the line have been observed, which could not be explained by collision-time asymmetry itself. Further precise studies led to improvement of the isotopic and hyperfine structure determination of this line. Also it was shown that the observed asymmetry of the line

can be explained by simultaneous occurrence of dependence of collisional shifting on emitter velocity and collision-time asymmetry.

Another study in which I took part was experimental investigation of highly excited states of Ca atoms using three-photon ionization process. The work discussed the dynamics of multiphoton excitation and parameters of auto-ionizing lines described with Fano profile were measured. Lifetimes of auto-ionizing states of Ca were determined. The results were published in publication [13].

In collaboration with the group of prof. A. Sasso of universitet di Napoli "Federico II" (Naples, Italy) I studied the impact of optical collisions on the shapes of spectral lines of H₂O, and C₂H₂ for the wavelength of about 3 microns, perturbed by Xe. The choice of heavy perturbing gas allowed to study strong speed-dependent effects. Laser spectrometer based on difference frequency generation (DFG) process was built. Analysis of the shapes of spectral lines provided information on the collisional broadening and shifting of lines and their dependences on velocity of molecules, and also contribution of Dicke narrowing and correlation between the phase-changing and velocity-changing collisions was analyzed. The effect of the choice of model spectral line profile on systematic errors in determined line shape parameters was studied. The results were published in [15, 16].

Using the apparatus and methods of data analysis developed during the study spectra of H₂O by FS-CRDS, we measured the relative positions of the oxygen 16O2 line of band A with an accuracy of 70 kHz. This research was done in cooperation with NIST, California Institute of Technology and the Jet Propulsion Laboratory - JPL (Pasadena, CA, USA). We obtained five times more accurate measurements of the pressure shift coefficients comparing to the previously available data. Using the above-mentioned measuring system we performed a systematic study of spectral lines of the O₂ A-band and CO₂ lines in the near infrared region. Parameters of shape and intensity of these spectral lines were determined. Accuracy of parameters available in HITRAN database were improved significantly. The study was motivated by high requirements for precision and accuracy of line parameters for satellite-based measurements of oxygen in Earth's atmospheric composition, in particular NASA's Orbiting Carbon Observatory Project - OCO. The research was published in the papers [20, 21, 32].

In 2009 I began the study of molecular spectra using the FS-CRDS at the Nicolaus Copernicus University in Toruń. A study of weak spectra of molecular oxygen band $b^1\Sigma_g^+$ (v=1) \leftarrow $X^3\Sigma_g^-$ (v=0), so called B-band (wavelength about 687 nm) was performed. We btained very high signal-to-noise ratio of the measured spectra, of the order of several thousands, which allowed to determine the line intensities and line shape parameters of O_2 spectra with an accuracy exceeding even by two orders of magnitude the previously available data. Using the aforementioned method of multi-spectrum fit the observed effects of line narrowing were interpreted as simultaneous occurring of Dicke-narrowing and strong speed-dependent effects. Using a model of the speed-dependent Nelkin-Ghatak profile, the impact of both these effects on

the observed line narrowing of the oxygen lines was determined. Moreover, a systematic difference was observed between the measured intensities of spectral lines of oxygen in the B-band relative to data from the HITRAN database, probably resulting from systematic errors in the database. The results were published in [27, 33].

Using the FS-CRDS technique the saturation vapor pressure of H_2O in a wide temperature range from -70 to 0 °C was measured. For generation of saturated steam a very precise saturator was used, the one which serves to calibrate hygrometers at NIST (NIST Primary Standard Humidity Generator). The method does not require knowledge of the intensities of spectral lines used and the results of experimental saturated vapor pressure of H_2O are linked to the well known value at the triple-state point of water. We obtained the first experimental data with the relative accuracy of about 0.5%, enabling the most accurate verification of the results of thermodynamic calculations that are commonly used for example in studies of Earth's atmosphere. The results were published in [35] (accepted for publication).

Leadership and participation in research projects

- Grant KBN: "Influence of the optical collisions on spectra line shapes" nr: 1 P03B 065 29 (Contract No. 0382/P03/2005/29), realization in the Institute of Physics NCU, Toruń, investigator,
- Grant NCU: "Spectral line shape analysis of the C_2H_2 molecule perturbed by xenon", project leader,
- Grant for investment in equipment "Purchase of parts to construct spectrometer CRDS (cavity ring-down spectroscopy) in the Institute od Physics, NCU in Toruń." (decision MNiSW No. 104/03/E-337/S/2006-4), realization in the Institute of Physics NCU, Toruń, team member
- Grant NCU: "Saturation effects in precise cavity ring-down spectroscopy", project leader,
- Grant MNiSW "Ultraprecise measurements with methods of optics and atomic physics" no: N N202 1489 33 (Contract No. 1489/B/H03/2007/33), realization in the KL FAMO laboratory, NCU in Toruń, investigator,
- Grant NCU: "Construction of actively stabilized, tunable optical cavity", project leader
- Grant MNiSW "Ultraprecise spectroscopy of molecular oxygen with CRDS method (cavity ring-down spectroscopy)", no: 1255/B/H03/2008/35 N N202 125535, realization in the Institute of Physics NCU, Toruń, main investigator,
- Grant NCU: "Precise spectroscopy of H2O in 1.39 um region with CRDS", project leader,
- Grant NCN: "Frequency-stabilized cavity ring-down spectroscopy as a new tool in ultraprecise research of gas-phase systems" nr: UMO-2011/01/B/ST2/00491, realization in the Institute of Physics NCU, Toruń, project leader.

Conferences and talks

Organization of conferences:

- XXXVI Meeting of Polish Physicists, Toruń 2001, secretary of the organizing committee
- Il Scientific Workshop of the National Laboratory, Toruń 2006, member of the organizing committee

Participation in conferences:

- 15th International Conference on Spectral Line Shapes, Berlin, Germany 2000, poster Pressure broadening and shift of the 326.1 nm Cd line perturbed by H₂ and D₂
- 35th European Group on Atomic Systems Conference, Brussels, Belgium 2003 poster Reduction of Dicke narrowing of cadmium line perturbed by Xe
- High Resolution Molecular Spectroscopy 19th Colloquium, Salamanca, Spain 2005 poster Cavity Ring-Down Lineshape Study of Water Lines Near 936 nm
- 38th European Group on Atomic Systems Conference, Ischia, Italy 2006 poster *Precise* line intensity and line shape measurements using single-mode frequency-stabilized cavity ring-down spectroscopy
- International School of Physics "Enrico Fermi", Course CVXVIII "Atom Optics and Space Physics", Varenna, Włochy 2007
- Information Day of the IDEAS 7 Framework Programof EU, Warszawa 2007
- 21st Colloquium on High Resolution Molecular Spectroscopy, Castellamare di Stabia, Italy 2009 - poster Frequency-stabilized cavity ring-down spectroscopy of water transitions near 1.39 μm
- Cavity enhanced spectroscopy Recent developments and new challenges, Leiden,
 Holandia 2009 talk Cavity ring down measurements of the line parameters of water rotation-vibration transitions
- 41st European Group on Atomic Systems Conference, Gdańsk 2009 poster Cavity ring-down measurements of the line parameters of water rotation-vibration transitions near 1.39 μm
- 20th International Conference on Spectral Line Shapes, St. John's, Kanada 2010 talk CRDS investigation of line shapes and intensities of the oxygen B-band transitions at low pressures
- Workshop NLTK: Modern Spectroscopic and Optical, Toruń 2010 invited talk Application of cavity ring-down spectroscopy in H₂O metrology

- 22nd Colloquium on High Resolution Molecular Spectroscopy, Dijon, France 2011 poster Measurement of the saturation vapor pressure of ice using cavity ring-down spectroscopy
- Polish Optical Conference, Międzyzdroje 2011
- International Symposium Quantum Metrology with Photons and Atoms, Toruń 2011 poster High signal-to-noise ratio line-shape measurements by PDH-locked FS-CRDS technique

Talks in other research institutions:

- Institute of Experimental Physics, Warcaw University, Warszawa 7.12.2006 talk Frequency-stabilized cavity ring-down
- Department of Photonics, Institute of Physics, Jagiellonian Uniwersity, Kraków 15.6.2011 talk *Frequency stabilization of diode lasers*

Daniel Lisak