Załącznik 3.

Self-presentation

1. Name:

Jolanta Domysławska

2. Scientific degrees (including name, place, year and title of thesis):

- 1992 r.: Nicolaus Copernicus University in Toruń, MSc degree, experimental physics, supervisor – prof. dr hab. Andrzej Bielski, title of thesis: Heating system for the absorption cells and a search of the collisional asymmetry of the cadmium $\lambda = 326.1$ nm spectral line shape.
- 1998 r.: Nicolaus Copernicus University in Toruń, PhD in physics, supervisor – prof. dr hab. Andrzej Bielski, title of thesis: Pressure broadening of the Cd $\lambda = 326.1$ nm line perturbed by Kr.

3. Employment:

- 1996–1999 assistant at the Gas Phase Spectroscopy Division, Institute of Physics, Nicolaus Copernicus University in Toruń
- 01.09.1999–2011 adjunct at the Gas Phase Spectroscopy Division/Department of Atomic, Molecular and Optical Physics, Institute of Physics, Nicolaus Copernicus University in Toruń
- X 1999–IX 2001 *research associate (post-doc)* - University of Windsor, Ontario, Canada, group of prof. William McConkey
- from 2011 senior scientific–technical specialist at the Laboratory of Physical Demonstrations, Institute of Physics, Nicolaus Copernicus University in Toruń
- XI 2015–II 2016 - *visiting scientist* - PTB, Braunschweig, Germany - working group 3.22 Metrology in Molecular Spectroscopy

4. The scientific achievement: title of the scientific achievement – series of publications: *Determination of the absolute frequencies and the spectral line shape parameters of the molecular oxygen B-band transitions based on the optical frequency comb.*

4.1. List of publications accounting for the achievement:
(Detailed contributions are given in separate Appendices, including statements of coauthors – Załącznik 4, Załącznik 6)

H1. J. Domysławska, S. Wójtewicz, D. Lisak, A. Cygan, F. Ozimek, K. Stec, Cz. Radzewicz, R. S. Trawiński, R. Ciuryło, *Cavity ring-down spectroscopy of the oxygen B-band with absolute frequency reference to the optical frequency comb.* J. Chem. Phys. **136**, 024201 (2012).
Citations: 33. IF 3.164

H2. J. Domysławska, S. Wójtewicz, A. Cygan, K. Bielska, D. Lisak, P. Masłowski, R. S. Trawiński, R. Ciuryło, *Low-pressure line-shape study in molecular oxygen with absolute frequency reference.* J. Chem. Phys. **139**, 194312 (2013).
Citations: 13. IF 3.122

H3. S. Wójtewicz, A. Cygan, P. Masłowski, J. Domysławska, D. Lisak, R. S. Trawiński, R. Ciuryło, *Spectral line shapes of self-broadened P-branch transitions of oxygen B band.* J. Quant. Spectrosc. Radiat. Transfer **144**, 36–48 (2014).
Citations: 11. IF 2.645

H4. J. Domysławska, S. Wójtewicz, P. Masłowski, A. Cygan, K. Bielska, R. S. Trawiński, R.Ciuryło, D. Lisak, *Spectral line shapes and frequencies of molecular oxygen B-band R-branch transitions*. J. Quant. Spectrosc. Radiat. Transfer **155**, 22–31 (2015).
Citations: 5. IF 2.859

H5. J. Domysławska, S. Wójtewicz, P. Masłowski, A. Cygan, K. Bielska, R. S. Trawiński, R. Ciuryło, D. Lisak, *A new approach to spectral line shapes of the weak oxygen transitions for atmospheric applications.* J. Quant. Spectrosc. Radiat. Transfer **169**, 111–121 (2016).
Citations: 3. IF 2.859 (2015)

4.2. Presentation of research goals, results and resulting publications, implication for future work and application:

4.2a. Motivation

Oxygen is one of the two most abundant molecular gases in the terrestrial atmosphere, its content in the dry air (20.9476% [1]) is invariable. The solar radiation recorded at the Earth's surface is affected by the atmospheric oxygen absorption giving reason to some of the Fraunhofer lines in the optical spectrum of the Sun. The A, B and γ bands at the red part of this spectrum are due to $b^1\Sigma_g^+ - X^3\Sigma_g^-(0 \leftarrow 0)$, $b^1\Sigma_g^+ - X^3\Sigma_g^-(1 \leftarrow 0)$ and $b^1\Sigma_g^+ - X^3\Sigma_g^-(2 \leftarrow 0)$ intercombination magnetic dipole transitions, respectively. They are centered at around 0.76 μm (A band), 0.69 μm (B band) and 0.63 μm (γ band) respectively and their Franck-Condon factors ratio is 0.931 : 0.066 : 0.003 [2]. Despite the low intensity those lines are observable because of the high oxygen content in the atmosphere. The A-band lines are used extensively in the remote sensing of the atmosphere for ground level measurements as well as extraterrestrial i.e. from aircraft or satellite [3–5]. The subject of this investigation is oxygen B band, which is approximately 15 times weaker than the A band. The strongest B-band line do not exceed $6 \times 10^{-25}\text{cm}^{-1}/(\text{molecule/cm}^2)$. Use of the B band for remote sensing of the atmosphere has been less common mainly because of the insufficient laboratory data and low B-band intensity. However, the B band can give the advantage because its intensity is similar to the green-house-gases intensities leading to minimize the impact of common systematic error. It is also worth noting that in the case of atmospheric measurements when the recorded light is traveling a very long optical path (high air mass) line centers are entirely saturated so line-wing shape becomes more important [6]. In this situation it is necessary to use the line wings or the weaker lines of the same band. It seems that the reference data of the same quality would give a lower systematic errors for the weaker lines, in favor of the B band over the A band.

4.2b. B-band data available in the literature

Before 2010 only a few experimental papers containing spectroscopic data of individual B-band spectral lines were published. The first investigations of the oxygen B band were performed by observation of the solar spectra by Babcock and coworkers [7, 8]. Spectral lines due to $b^1\Sigma_g^+ - X^3\Sigma_g^-$ transitions have been identified for different molecular oxygen isotopologues in the absorption spectrum. Transition frequencies and rotational and vibrational constants were determined.

The intensities and self-broadening coefficients for the individual rotational lines of the B band were published in 1974 by Giver [9], and subsequently pressure shifts by Phillips *at al.* [10] in 1995, line positions and intensities by Cheah *et al.* [11] in 2000, shifts and broadening by Barnes and Hayes [12] in 2002. Above measurements were focused mainly on the P branch and only first few lines of the R branch were measured. P branch consist of a isolated lines distant by 50 GHz (1.7 cm^{-1}) or more while R-branch transitions with higher J'' are very close or even overlapping with stronger ones due to the band turn. The above results were obtained by absorption measurements in the multipass cell with grating spectrometer [9] and Fourier transform spectrometers [10, 11] or by photoacoustic spectroscopy [12].

The research reported here was aimed at measuring the oxygen B-band with very high resolution, the determination of the line positions with reference to absolute frequency standard and the determination of the line shape parameters with subpercent accuracy. Measurements described in Refs. [H1-H5] are the first to determine simultaneously the line intensities and broadening coefficients along with their positions and shifts, and other line shape parameters. Depending on the model used for fitting the measured spectra the other parameters were determined including the Dicke narrowing, the speed-dependence of the width and shift parameters, the correlation coefficient between the velocity- and phase-changing collisions.

4.2c. B band in the HITRAN database

HITRAN is an acronym for *hi*gh-resolution *tran*smission molecular absorption database. It is a self-consistent set of parameters due to direct observations, theoretical calculations and semi-empirical values which can be used as input to modeling codes for molecular spectra line-by-line. The database was established by Air Force Cambridge Research Laboratories (AFCRL) in the late 1960s to predict and simulate the transmission and emission of light in the atmosphere. The first publicly available version released in 1973 [13] contained 7 most important atmospheric molecules including oxygen. The current version includes 47 molecules with different isotopic composition an is the most valuable data for atmospheric research.

When our experiment was at the design stage the available database version was HITRAN 2008 [14] which contained oxygen B-band data not refreshed from 1998 (HITRAN 1996 [15]). Due to the increasing consideration of the B band for remote atmospheric sensing in 2011 Gordon at al. [16] derived new set of spectral parameters based on the careful review of available data which was then included in the HITRAN 2012 [17]. Accuracy of the line positions is claim to be between 0.00001 and 0.0001 cm^1 (between 0.3 and 3 MHz), line intensities accuracy is in the range of 5-10%. The B band line lists have been validated against atmospheric spectra recorded with solar-pointing Fourier transform spectrometer at the Total Column Carbon Observing Network (TCCON) site in Park Falls, Wisconsin, USA. Precision requirement for the laboratory data used in the atmospheric measurements analysis is much lower and it is 1% or lower [18, 19].

4.2d. The significance of the oxygen spectrum for atmospheric research

The most common are applications where the oxygen spectrum is used for the atmosphere diagnosis directly. There are also applications exploiting the fact that the mixing ratio of O_2 in the atmosphere is uniform and relatively constant so it is suitable for an accurate determination of the atmospheric air mass or column density on the measured light path to the detector. It may be direct sunlight or reflected from the Moon and registered by the detectors on the satellite, aircraft or on the ground, but also a light from other sources affected by atmosphere. In the following few application of the B band for the atmosphere study are listed. The stratospheric wind determination by measuring the Doppler shift of the individual rotational lines in the O_2 B and γ bands is reported in Ref. [20]. It has been performed from UARS (Upper Atmosphere Research Satellite) with the use of the HRDI (High Resolution Doppler Imager) on the absorption spectra in sunlight scattered from the stratosphere. An important application of the oxygen absorption lines is the cloud parameters determination. In Ref. [21] the method for determination of cloud top height and related parameters using the O_2 A and B bands has been proposed as a contribution to the development of the GOME (Global Ozone Monitoring Experiment) and SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric ChartographY) on the ESR-2 (1995-2011) and Envisat (2002-2012) European Space Agency (ESA) satelites, respectively. So far only the A band was used for cloud diagnosis in GOME [22] and SCIAMACHY [5]. However, Sanghavi *et al.* [23] used absorption spectra around A and B bands from SCIAMACHY to retrieve aerosol optical depth and vertical distribution of aerosols over Kanpur, India. Daniel *et al.* [24] analyzed the fractional absorption of scattered solar radiation from the above cloud measurements in order to retrieve information of cloud optical depth, cloud base and top heights. They demonstrated through theoretical calculations that the addition of the B-band and O_2–O_2 477 nm band absorption information to the A-band measurements can decrease the uncertainty in cloud parameter estimates by more than 50% compared to using only the A band. Another method to retrieve cloud top height and cloud geometrical thickness simultaneously was presented by Yang at al. [25] for Deep Space Climate Observatory (DSCOVR) mission. Due to the different absorption and the different effective depth of light penetration into a cloud, retrievals from either O_2 A- or B-band channels alone gives the corresponding cloud centroid inconsistent. Authors showed that the sum and the difference between the retrieved cloud centroid heights in the A and B bands are functions of cloud top height and cloud geometrical thickness. The evaluation of using the O_2 B band to determine pressure and temperature profiles from occultation instruments was presented by Nowlan *et al.* [26] using the data from ACE-MAESTRO (Atmospheric Chemistry Experiment–Measurement of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation) apparatus on SciSat satellite. SciSat uses solar occultation technique (15 times per day) to observe the upper part atmosphere that is too high to be reached by balloons and airplanes and too low for orbiting satellites. Authors proved that the uncertainty of pressure and temperature profiles determined from measurements of solar absorption in the A and B band together show an improvement over the A band using only.

The calibration usefulness of the oxygen spectra relies on the determination of the effective oxygen column which is necessary to obtain an accurate air mass parameter. Data is crucial for high precision measurements of greenhouse gases like CO_2, aerosols and other pollutants. The Orbiting Carbon Observatory (OCO) [4] was the first instrument invented for global measurements to understand nature and geographic distribution of CO_2 in the atmosphere. To improve accuracy of the atmospheric CO_2 mole fraction determination the simultaneous CO_2 and O_2 measurement was intended. The O_2 A-band measurements were meant to characterize the vertical distribution of clouds and aerosols in each measurement and make decision whether it can be accepted or rejected. Only the A-band line-shape parameters with high precision necessary to achieve this goal were available, while the high accuracy B-band parameters were unavailable at that time. The Greenhouse Gases Observing Satellite (GOSAT) is the world's first satellite dedicated specifically to measure from space the concentrations of carbon dioxide and methane, the two major greenhouse gases [27]. The observation instrument onboard the satellite includes the Fourier Transform Spectrometer (FTS) and the Cloud and Aerosol Imager (CAI). FTS records sunlight reflected from the earth's surface and light emitted from the atmosphere and the surface to retrieve column abundances of CO_2 and CH_4. Information from CAI are used to resolve whether the sky is clear or to determine the amount of aerosols and clouds and to correct the effect of those on the FTS spectra. CAI measurements covers 4 spectral ranges from UV to NIR and the Band 2 of this instrument is for range around 0.67 μm (O_2 B-band) [27].

Chlorophyll fluorescence induced by sunlight may be used for large scale monitoring of plant status and functioning by reason of its dependence on the efficiency of the photosynthesis. It may allow a more accurate carbon assimilation estimate and earlier stress detection than it is possible from reflectance data alone. The paper by Meroni *et al.* [28] presents a profound review of the current methods and devices used to evaluate solar induced chlorophyll fluorescence over terrestrial vegetation together with their application at different observation scales, from ground to airborne and spaceborne measurements. Based on the Fraunhofer line discrimination method the region of the oxygen A and B bands can be used for monitoring the chlorophyll fluorescence spectrum as they overlap as a result the chlorophyll fluorescence is relatively stronger at the dark parts of the atmospheric spectrum. Recent developments for fluorescence retrieval from passive high spectral resolution spaceborne measurements has been performed in preparation of the FLuorescence EXplorer (FLEX) mission developed by the European Space Agency and are presented in Refs. [29] and [30]. In conclusion of the latter paper the better performance in the O_2 B band is explained by the relatively higher contribution of fluorescence to the reflected radiance. FLEX aims to quantify photosynthetic activity and plant stress by mapping vegetation fluorescence. FLEX will give a better understanding of an important part of the carbon cycle and provide important information about the health and stress of the planet's vegetation. The FLEX mission will not be launched before 2022.

4.2e. Experimental setup

CRDS – cavity ring-down spectroscopy is widely recognized method for study the weak spectra and trace gas detection. In 1988 O'Keefe and Deacon [31] published first absorption spectra obtained by this technique with pulsed laser. Weak spectra of the oxygen B (689 nm) and γ (628 nm) bands due to $b^1\Sigma_g^+ - X^3\Sigma_g^-(1 \leftarrow 0)$ and $b^1\Sigma_g^+ - X^3\Sigma_g^-(2 \leftarrow 0)$ transitions were first registered. Absorption measurements relies on the determination of the light decay time constant after switching off the probe light. This method is insensitive to the probe light intensity fluctuation and background light on the quality of the measured spectra.

For the purpose of this research the frequency stabilized CRDS (FS-CRDS) with active stabilization of the cavity mode frequency to the frequency standard was chosen, as a very high resolution and high sensitivity technique. As it was shown before this method proved itself to high precision line shape measurements of the weak line of H_2O [32]. The cavity is made of two concave mirrors with 1 m curvature within the distance of about 73 cm, which results in the free spectral range close to 203 MHz. One of the mirrors mounted on the piezoelectric transducer let the optical pathlength to be changed up to 12 μm. Cavity length is actively stabilized by locking the cavity mode comb to the frequency of the HeNe reference laser thermally stabilized. Probe laser is actively stabilized to the cavity TEM_{00} mode using the Pound-Drever-Hall (PDH) method, which allows for a tight lock to the cavity resulting in the significant decreasing of the laser width and coupling more power into the cavity. The optical frequency comb (OFC) allows for the determination of the optical frequencies with extremely high accuracy by direct measuring the radio frequencies. The instrument FC1500 from Menlo Systems was used in this setup. The pulse train emitted by the femtosecond Er doped mode-locked fiber laser in the time domain is equivalent to the spectrum of thousands of very narrow equidistant spectral lines, so called frequency comb, in the frequency domain. The frequency of every mode (comb tooth) is defined by two radio frequencies: femtosecond laser repetition rate f_{rep} (mode distance) and offset frequency f_0 due to the difference between the phase and group velocity inside the femtosecond laser cavity. In order to determine the unknown frequency it is necessary to beat the laser beam with the OFC beam and measure the frequecies f_{rep} and f_0 and the beat note frequency (f_{beat}) between the measured laser and the nearest adjacent comb mode. Since the primary source of light emits in the infrared (1.5 μm), its frequency has to be doubled before a beat note with the probe laser operating at 687 nm can be measured. The unknown frequency is then calculated using simple formula $f = 2f_0 + n \cdot f_{rep} \pm f_{beat}$, where factor 2 is the effect of the frequency doubling and n is the number of the comb mode contributing to f_{beat}. To determine the absolute number of the comb mode n the independent wavemeter is necessary, required accuracy of which is better than the half of the distance between the comb teeth, $f_{rep}/2$. In our setup $f_0 = 20$ MHz, $f_{rep} = 250$ MHz, and the wavemeter accuracy was 60 MHz. In general, f_{beat} spans between 0 and $f_{rep}/2$. In practice, the beatnote detection channel is optimized for much narrower frequency range due to low intensity of the beat note signal – in out setup from 25 to 35 MHz. In order to maintain the high comb accuracy the appropriate frequency standard is necessary. For this purpose the Cs or Rb atomic frequency standards are used often disciplined by the GPS signal for the long time stability. For the best performance the hydrogen maser or atomic optical clock is used.

4.2f. Data analysis

Spectral line profiles

All data concerning the oxygen B band line shape parameters published before our study were obtained assuming the Lorentzian profile or the Voigt profile (VP). With a development of measurement techniques, numerical methods and increase in signal-to-noise ratios (SNR) for acquired spectra it was observed that VP does not describe the obtained spectra properly. Moreover, the HITRAN 2012 database [17] includes parameters allowing only for the VP modeling. The VP which is a convolution of the Gaussian and Lorentzian profiles assumes statistical independence of Doppler and pressure broadening. In general, it should be assumed that the line-shape parameters may depend on the speed of the absorber, so the pressure and Doppler broadening can not be considered as statistically independent. It is also necessary to include the velocity-changing collisions as well as the correlations between the velocity- and phase-changing collisions. The resulting line profile depends on the model describing collisions.

The most advanced profile used in analysis of the measured oxygen B band lines is the partially correlated speed-dependent Nelkin-Ghatak profile (pCSDNGP) introduced by Pine [33]. Using notation from Ref. [34] this profile can be given in the following form:

$$I_{\mathrm{pCSDNGP}}(\nu) = \mathrm{Re}\frac{\mathcal{I}_{\mathrm{SDVP}^*}(\nu)}{1 - \pi\nu_{\mathrm{opt}}\mathcal{I}_{\mathrm{SDVP}^*}(\nu)}, \tag{1}$$

where the collisional narrowing parameter, ν_{opt}, can be complex number [35–38]. Here ν_{opt} is assumed to be independent of the absorber speed, v_A, in contrast to the original paper by Pine

[33] where this quantity was speed dependent. The complex function $\mathcal{I}_{\mathrm{SDVP}^*}(\nu)$ is defined like in Ref. [34]:

$$\mathcal{I}_{\mathrm{SDVP}}(\nu) = \frac{1}{\pi}\int \mathrm{d}^3\vec{v}_A\, f_{m_A}(\vec{v}_A) \times \frac{1}{\Gamma(v_A) - \mathrm{i}[\nu - \nu_0 - \Delta(v_A) - \vec{k}\cdot\vec{v}_A]}, \tag{2}$$

where $f_{m_A}(\vec{v}_A) = (\sqrt{\pi}v_{m_A})^{-3}\exp(v_A^2/v_{m_A}^2)$ is the Maxwellian distribution of the absorber velocity $\vec{v}_A$, $\Gamma(v_A)$ and $\Delta(v_A)$ are the speed-dependent collisional width (HWHM - half width at half maximum) and shift, respectively, ν_0 is the unperturbed line frequency, $\vec{k}$ is the wave vector of the absorbed light, $v_{m_A} = \sqrt{2k_BT/m_A}$ is the most probable absorber velocity, where m_A is the absorber mass, T is the gas temperature, and k_B is the Boltzmann constant. Asterisk in (1) denotes that $\Gamma(v_A)$ in formula (2) was substituted by $\Gamma(v_A) + \nu_{\mathrm{opt}}$.

This kind of profile (pCSDNGP) which incorporates speed-dependent effects as well as Dicke narrowing can be reduced to several simpler profiles [33, 34, 39]. Equation (1) reduces to the ordinary VP [40] if Dicke narrowing is neglected ($\nu_{\mathrm{opt}} = 0$) and only Doppler broadening and speed-independent collisional broadening and shifting are taken into account.

Velocity changing collisions lead to the collisional narrowing of the line [41, 42] as was first predicted by Dicke [43]. In the case when velocity changing collisions are described by the hard collision model [35, 44] the Dicke narrowed spectral line shape is given by the Nelkin-Ghatak profile (NGP) which can be obtained from Eqs. (1) and (2) assuming speed-independent collisional width Γ and shift Δ. The other popular description of velocity changing collisions is based on the soft collision model which leads to the Galatry profile (GP) [45]:

$$I_{\mathrm{GP}}(\nu) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty \mathrm{dt}\ \exp\left\{[\mathrm{i}(\nu - \nu_0 - \Delta) - \Gamma]\mathrm{t} - \frac{\nu_{\mathrm{D}}^2}{\nu_{\mathrm{opt}}^2}[\nu_{\mathrm{opt}}\mathrm{t} - 1 + \exp(-\nu_{\mathrm{opt}}\mathrm{t})]\right\}, \tag{3}$$

where $\nu_D = \nu_0 v_{m_A}/c$ is the Doppler width.

It was shown by Berman [46] that the speed dependence of collisional broadening and shifting must be included to properly describe spectral line shapes. When the Dicke narrowing is neglected but the speed-dependent collisional broadening is taken into account the speed-dependent Voight profile (SDVP) is given by the real part of Eq. (2) or by Eq. (1) with ν_{opt} set to zero. To describe the speed-dependent effects it is convenient to introduce the dimensionless functions $B_W(x)$ and $B_S(x)$ of the reduced speed $x = v_A/v_{m_A}$:

$$B_W(x) = \frac{\Gamma(xv_{m_A})}{\Gamma}, \tag{4}$$

$$B_S(x) = \frac{\Delta(xv_{m_A})}{\Delta}, \tag{5}$$

where $\Gamma = \int \mathrm{d}^3\vec{v}_A\, f_{m_A}(\vec{v}_A)\Gamma(v_A)$ and $\Delta = \int \mathrm{d}^3\vec{v}_A\, f_{m_A}(\vec{v}_A)\Delta(v_A)$ are thermally averaged collisional width and shift, respectively. When the absorber-perturber interaction is described by inverse power potential C_q/r^q both functions should be the same and can be expressed in terms of confluent hypergeometric function $M(a, b, z)$:

$$B(x) = (1+\alpha)^{-(q-3)/(2q-2)} M\left(-\frac{q-3}{2q-2}, \frac{3}{2}, -\alpha x^2\right), \tag{6}$$

where α is the perturber to absorber mass ratio.
At some level of accuracy the function $B(x)$ can be approximated by the quadratic formula in the way proposed by Priem *et al.* [47]:

$$B(x) = 1 + a(x^2 - 3/2). \tag{7}$$

A careful test of the limitation of this approximation is presented by De Vizia *et al.* [48].

For all models fitted to experimental profiles the Doppler width (HWHM) $\Gamma_D = \sqrt{\ln 2}\ \nu_D$ was set to the value corresponding to the gas temperature.

The SDNG profile with quadratic approximation of the speed dependence was recently recommended for use to describe the molecular line shapes by IUPAC [49] and is called the Hartmann-Tran Profile (HTP) for simplicity. It is also considered as a basis for expanding existing spectroscopic databases or constructing new ones for molecules essential for atmospheric applications [50].

Multispectrum fitting technique

The multispectrum fitting technique [51] was developed for simultaneous fitting of multiple spectra measured in a range of parameters, such as pressure or temperature. The main advantages of this technique are less parameters and constrains, reduced parameters correlation and automatic averaging of the coefficients [52, 53]. It requires the parameters to be consistent throughout the range of application. Moreover, this approach makes it possible to find parameters that are not determinable from a single spectrum fit.

For the B-band investigation all spectra acquired in different pressures were analyzed simultaneously instead of the separate fits of each recorded line shape. The values of the collisional width, γ_L, and the frequency of optical collisions, ν_{opt}, were assumed to be the linear function of the molecule concentration, N, so one collisional broadening coefficient, γ_L/N, and one narrowing coefficient, ν_{opt}/N, were fitted instead of single line parameters. Speed-dependence functions of the width and shift parameters, a_W and a_S, were assumed constant with pressure so only one value for either parameter was fitted to all spectra in the whole pressure range. Moreover, fitting all the measured spectra simultaneously enables to extract the collisional shifting coefficient, Δ/N, which is assumed to be a linear function of concentration and the unperturbed line position, ν_0, which is not possible to achieve with a single pressure fit.

Quality of the fit evaluation

In order to apprise the goodness of the fit a quantity called the quality-of-the-fit (QF) was introduced. QF is defined as the ratio of the peak absorption signal to the standard deviation of the fit residuals, $\widetilde{S}_R$, calculated from the whole spectrum [P22,[54], as follows:

$$QF = (\alpha_{max} - \alpha_{min})/\widetilde{S}_R, \tag{8}$$

were the standard deviation of the fit residuals has the form:

$$\widetilde{S}_R = \sqrt{\frac{1}{M-k}\sum_{i=1}^{M}[\alpha_{exp}(\nu_i) - \alpha_{fit}(\nu_i)]^2}. \tag{9}$$

Terms $\alpha_{exp}(\nu_i)$ and $\alpha_{fit}(\nu_i)$ are experimental and fitted absorption coefficients, respectively, for a given measurement point of the spectrum, i. M is the number of measurement points in a single spectrum k is the number of fitted parameters for a given theoretical model. In order to find QF for the multispectrum procedure the maximum absorption of all spectra is taken and the standard deviation of the fit residuals is a sum over the all measured spectra. It is worth to notice that the above definition of QF takes into account not only random noise in the experimental spectrum, but also systematic distortions of the line shape, which for example may be caused by unwanted interference in the optical setup, so called *etaloning effects* or limitations in the line-shape model.

4.3. Overview of the results

[H1] J. Domysławska, S. Wójtewicz, D. Lisak, A. Cygan, F. Ozimek, K. Stec, Cz. Radzewicz, R. S. Trawiński, R. Ciuryło, *Cavity ring-down spectroscopy of the oxygen B-band with absolute frequency reference to the optical frequency comb.* J. Chem. Phys. **136**, 024201 (2012).

For the first time the frequency-stabilized cavity ring-down spectrometer (PDH-locked FS-CRDS) linked to the optical frequency comb (OFC) was used to measure the positions of the weak molecular transitions. The investigation of the transition frequencies for the oxygen B-band (due to $b^1\Sigma_g^+ - X^3\Sigma_g^-(1 \leftarrow 0)$) is presented. For the first time the oxygen lines were measured on the absolute frequency scale with reference the optical frequency comb, which was used as a very precise wavemeter for the probe laser. The length of the cavity was actively locked to the mode of the thermally-stabilized HeNe laser to eliminate the slow thermal drift. Pound-Drever-Hall (PDH) method was used to lock the probe laser to the high-finesse ring-down cavity. As a result the narrowing of the probe laser line width below the cavity mode width and the increase the light power pumping up the optical cavity is achieved, as well as the higher repeatability of the ring-down signals and the increased ringdown event acquisition rate. FS-CRD spectrometer was connected through 200 meters long single mode optical fibre to the Menlo Systems OFC based on femtosecond erbium-doped fiber laser. As a 10 MHz standard frequency for comb stabilization (f_0 and f_{rep}) Stanford Research FS725 Rubidium Frequency Standard was used. In this work the comb was used to perform the probing frequency absolute measurements at the beginning and at the end of the subsequent eleven scan series, corresponding to the first and the last measured spectrum point, respectively, while the probe laser was PDH-locked to the cavity mode and the cavity was locked to the HeNe laser uninterrupted. Using the OFC it was possible to determine absolute stability of the mode of the ring-down cavity locked to the HeNe laser, which is ±1.5 MHz, and to realize the absolute axis for the measured spectra.

Eight transitions were measured directly and the line positions and self-shift coefficients were determined. Experimental profiles were fitted with the speed-dependent Nelkin-Ghatak profile (SDNGP). The accuracy of the determined line position was about 1.1 MHz. Additionally, the position of four lines were determined using relative values from previous experiments [P21]. The discrepancies between ours values and data from HITRAN 2008 database [14] varied from 150 MHz to almost 300 MHz which is two order of magnitude higher than the uncertainties of the reported measurements. As a result, the uncertainty of the available data was reduced by over two orders of magnitude.

[H2] J. Domysławska, S. Wójtewicz, A. Cygan, K. Bielska, D. Lisak, P. Masłowski, R. S. Trawiński, R. Ciuryło, *Low-pressure line-shape study in molecular oxygen with absolute frequency reference.* J. Chem. Phys. **139**, 194312 (2013).

This work is devoted to analysis of the influence of several subtle effects on the spectral line shapes such as: the speed-dependence of collisional broadening and shifting [46], Dicke narrowing [43] and correlation between velocity-changing and dephasing collisions [35] on the shapes of spectral lines in case where the Doppler broadening is dominant. Several line-shape models on the example of an R1 Q2 oxygen B-band transition were tested in order to determine the appropriate method of the oxygen B-band experimental spectra analysis, as well as to verify the potential of the CRDS to analyze a subtle physical effects influencing spectral line shapes. Investigated line is relatively weak so the pressure range was relatively wide and up to 2.93 kPa (22 Torr). Experimental spectra were fitted with: the Voigt profile (VP), the Galatry profile (GP), the Nelkin-Ghatak profile (NGP), the speed-dependent Voigt profile (SDVP), the speed-dependent Nelkin-Ghatak profile (SDNGP) and partially correlated speed-dependent

Nelkin-Ghatak profile (pCSDNGP). For the speed dependence of the collisional broadening and shifting the quadratic [55] and hypergeometric [46] approximations were assumed. To take into consideration the correlation between the velocity-changing and dephasing collisions the frequency of the optical collisions, ν_{opt}/N, in the pCSDNGP was assumed to be a complex number [33, 35] and the multispectrum fitting procedure was performed for the pCSDNGP with quadratic and hypergeometric functions describing the speed dependencies of the collisional broadening and shifting. Data were analyzed using multispectrum fitting technique [51, 53]. To improve the measurements of the frequency axis of the CRD spectrometr described in previous work the measurements procedure was changed and the spectrometer was equipped with the ultra narrow laser (UNL) built at KL FAMO [56] to make possible measurements using OFC at every point of measured spectrum. The beam of the ultra narrow laser was splitted and combined with OFC and probe laser independently. The beat note between the UN laser and the comb was constant at around 30 MHz. The beat note between the tunable probe laser and the UN stabilized laser was detected with a bandwidth over 12 GHz limited by the frequency counter, while the tuning range of the probe laser was not wider than 10 GHz. This setup enables the best performance of the used instruments and the uncertainty of the line position was improved to about 460 kHz with statistical error about 31 kHz, while the OFC was referenced to the Rb frequency standard.

The multispectrum fitting technique advantage for oxygen line shape analysis was confirmed. The results of fitting nine different line shape profiles were presented. Correlations between the imaginary part of the complex narrowing parameter $Im(\nu_{opt})/N$ and the speed dependence parameters for the collisional broadening and shifting with the quadratic and hypergeometric approximations were discussed. Performed analysis confirmed that the Voigt profile is not sufficient to describe the observed line shapes. Best fit is achieved for profiles including both the Dicke narrowing and the speed-dependent effects. The Dicke narrowing accounts for the line narrowing but is rather small and the speed dependence on the absorber velocity is dominant.

[H3] S. Wójtewicz, A. Cygan, P. Masłowski, J. Domysławska, D. Lisak, R. S. Trawiński, R. Ciuryło, *Spectral line shapes of self-broadened P-branch transitions of oxygen B band.* J. Quant. Spectrosc. Radiat. Transfer **144**, 36–48 (2014).

The systematic line-shape study of the twenty self-broadened P-branch transitions using the CRD spectrometer assisted by the OFC is presented in this paper. In the line-shape analysis the line-narrowing effects described by Dicke narrowing or the speed dependence of collisional broadening was considered. The relation between parameters describing the Dicke narrowing with the use of the soft- and hard-collision models was discussed and verified experimentally. Data were analyzed using the multispectrum fitting technique with the VP, GP, NGP and SDVP. The line positions were determined with uncertainties of about 170 kHz. The relative uncertainties for the line intensity, S, and the collisional broadening coefficient, γ_L/N, are around 0.5%. The relative uncertainties for collisional shift coefficient, δ/N, the Dicke narrowing coefficient, ν_{opt}/N, and the speed dependence width parameter, a_W, are in the range from 0.5% to 2%. Comparison with data available in the literature [8–12] shows that obtained uncertainties are one or two order of magnitude lower than the discrepancies with other results. In the previous experiments on the P branch data were analyzed with the Lorentzian ([11]) or Voigt ([9, 12]) profiles or without fitting any line profiles [8, 10]. No experiment resulting in the simultaneous determination of all the line shapes parameters was reported. Uncertainties of the above five reported experiments are from few percent to tens of percent or are not specified. Comparing with the HITRAN 2012 database [17] one can see the few percent differences for line intensity and broadening which is within the declared uncertainties (between 5 and 10 %). Line positions differ by ±50 MHz, while reported accuracy is better than 3 MHz. Improvement of the accuracy of the line shape parameters as compared to other experimental data and the HITRAN database is one order of magnitude or better. The Dicke narrowing parameter (optical collision frequency) and the speed dependence of the line width were determined for the first time.

This results were possible due to improvement of the OFC control program by Menlo Systems which enables remote tuning of the f_{rep} without interruption of the comb stability. The experimental setup has been simplified by dismissing the intermediate UN laser and linked to OFC directly. The probe laser beam was directly beated with the comb beam and the beat frequency was measured at every measurement point. Because the beat detection unit was optimized for 30 MHz the f_{rep} was tuned at every measurement step so that the f_{beat} (the beat note between comb and probe laser) has been as close to 30 MHz as possible. Together with new calibration of the Rb frequency standard it enables to reduce uncertainty of the line position down to 170 kHz.

[H4] J. Domysławska, S. Wójtewicz, P. Masłowski, A. Cygan, K. Bielska, R. S. Trawiński, R.Ciuryło, D. Lisak, *Spectral line shapes and frequencies of molecular oxygen B-band R-branch transitions.* J. Quant. Spectrosc. Radiat. Transfer **155**, 22–31 (2015).

CRD spectrometer assisted by the OFC referenced to the GPS-disciplined Rb frequency standard was used to investigate first eleven self-broadened transitions of the R branch. This is the first systematic study of those transitions. Six different profiles which include soft- and hard-collision approximation and speed dependence, *i.e.* VP, GP, NGP, SDVP, SDNGP and pCSDNGP were fitted to measured spectra using the multispectrum fitting technique. The collisional self-broadening, shifting and narrowing coefficients were determined together with the quadratic speed-dependence as well as phase- and velocity-changing correlations parameters, where applicable. QF defined by equation 8 was specified for all fits. The weakest measured transition, namely R1 Q2, was measured in the pressure range up to 44 Torr (5.87 kPa), while for the stronger transitions the pressure range was limited to the value as low as 6.5 Torr due to higher absorption, hence shorter ring-down time constant. For the stronger lines the limitation for the pressure range makes impossible to use the QF as the criterion to distinguish which profile gives the best fit and the most reliable parameters fitted as it reaches similar values for SDVP, GP and SDNGP.

The absolute frequencies of the transitions were determined with combined standard uncertainties below 150 kHz. Line positions for different profiles are consistent within the uncertainties of the determined values. Comparison with other data [11, 17] shows the discrepancies within the 50 MHz, which is more than two orders of magnitude higher than our uncertainties. Combined standard uncertainties for line intensities, S, are below 0.3% with the systematic errors being dominant. Combined standard uncertainties for collisional broadening coefficient, γ_L/N, are below 0.2%. The comparison of the line intensities, pressure broadening and shifting parameters with other data [9–12, 17] shows high discrepancies, above experimental uncertainties. The speed-dependent parameters, a_W and a_S, as well as the Dicke narrowing coefficients, ν_{opt}/N, were determined for the first time. Their relative uncertainties are of the order of 1% similarly as it was for the P branch. The improvement of the accuracy of the line shape parameters as compared to other experiments and HITRAN database is one order of magnitude or better. The improvement of the accuracy of the basic line shape parameters, that is position, intensity and broadening of the R branch transitions is a result of the better long-term stability of the 10 MHz frequency standard due to the link of the Rb clock (FS725 Rubidium Frequency Standard) to the GPS signal.

[H5] J. Domysławska, S. Wójtewicz, P. Masłowski, A. Cygan, K. Bielska, R. S. Trawiński,

R. Ciuryło, D. Lisak, *A new approach to spectral line shapes of the weak oxygen transitions for atmospheric applications.* J. Quant. Spectrosc. Radiat. Transfer **169**, 111–121 (2016).

The quadratic speed-dependent Voigt profile (qSDVP) is proposed to construct the low pressure $^{16}O_2$ B-band self-broadened transition parameters data base. The qSDVP is consistent with the recent International Union of Pure and Applied Chemistry (IUPAC) recommendation, *Recommended isolated-line profile for representing high-resolution spectroscopic transitions (IUPAC Technical Report)* [49]. Proposed there Hartmann-Tran profile (HTP) well known before as a pCSDNGP [33] assumes the hard collisions for the Dicke narrowing, includes speed dependence of the broadening and shifting in quadratic approximation and phase- and velocity-changing correlations. At the low pressure regime qSDVP and GP can be treated as mathematically equivalent with high accuracy [55]. So that the approach used here can be expanded on the A band lines presented in terms of the GP in Hodges group [57]. From physical point of view GP is not proper to describe the A band, because the Dicke narrowing is small due to correlations and the line shape should be described with the SDVP. All line shapes were measured by the PDH-locked FS-CRDS linked to the optical frequency comb. The signal of the hydrogen maser from the Astrogeodynamic Observatory of Space Research Center in Borowiec was used as the frequency standard for OFC as described in Ref. [58]. Data published before [H3, H4] are complemented with the new measurements fitted with qSDVP using the multispectrum fitting technique. 27 transitions of the R branch and 21 transition of the P branch are presented. The absolute transitions frequencies are determined with accuracy even as good as 150 kHz. Line intensities, pressure width and shift coefficients and the speed-dependent parameters are determined with subpercent accuracy. The review of other results [8–12] reveals lack of reliable data for comparison. For R branch transitions with the total angular momentum quantum number $J'' > 10$ no other results of the experimental pressure broadening coefficients are available. Moreover, for R branch transitions with the total angular momentum quantum number $J'' > 16$ no other results of the experimental shifting coefficients are available. Speed-dependent width and shift parameters for all transitions were determined for the first time. The experimental line positions and intensities show high discrepancies especially for transitions with higher J''. Theoretical data for line intensities in HITRAN are described by 10% uncertainty. One of the reasons is probably the difficulty in data analysis. Due to R-branch turn the transitions with higher J'' are very close or even overlapping with stronger ones. Therefore to obtain reliable results it is necessary to use multifitting method and analyze few transitions at the same time. Also the use of simple VP may cause big errors for determined line shape parameters. For the first time data that allows the oxygen B-band spectrum to be reproduced with the subpercent accuracy are presented.

4.4. Summary

Main achievements of the habilitation work can be summarized as follows:

- first frequency-stabilized cavity ring down spectrometer (FS-CRDS) linked to the optical frequency comb was demonstrated for the absolute frequency axis measurements for the molecular spectra;
- physical effects dominating the oxygen B-band spectral line shapes were verified experimentally, in particular it was shown that speed-dependent effects predominate in the line narrowing;
- the positions of the oxygen B-band lines were determined with respect to the absolute scale, moreover, the accuracy of the absolute line position reached 150 kHz and is three orders of magnitude better than the previous data;

- line shape parameters were determined with subpercent accuracy;
- complete set of spectral line shape parameters for the 46 transitions of the B band was developed enabling the effective reconstruction of the spectrum with the sub percent accuracy – prototype of a spectroscopic data base for atmospheric research that goes beyond the Voigt profile, consistent with the IUPAC recommendation.

Line shape-parameters were determined for tens of B-band transitions. All line-shape parameters were determined in one experiment, in which the frequency axis was measured directly in terms of absolute units. Line-shape analysis was performed with line-shape functions going beyond the Voigt profile. Accuracy of the obtained values is several tenths of a percent. Accuracy of the line positions (transitions frequency) varies from 150 kHz to about 1 MHz. Currently, the oxygen B band is one of the best described molecular spectra, therefore, it is attractive for application in atmospheric physics and as a basis for a new spectroscopic database for the B band, where the uncertainties of parameters are lower than 1%.

Line positions for twelve transitions published in Ref. [H1] were used for an isotopically invariant Dunham fit for the three lowest electronic states of six oxygen isotopologues [59]. Our data together with A-band results from J. Hodges group in NIST were considered the most accurate and significant for the final results. Predicted there line positions are in very good agreement with our subsequent measurements [H2-H5], the discrepancies are 2 MHz or less.

The influence on the development of experimental techniques should also be emphasized. New scheme of the FS-CRDS with PDH-lock of the probing laser linked to the optical frequency comb that is referenced to an atomic frequency standard was adopted in other setups in our laboratories to measure the CO and CO_2 spectra [60, 61] and for CO_2 spectra measurements in the NIST laboratory [62, 63]. The same method of the frequency measurements was also applied in the new cavity enhanced spectroscopic methods that is CMWS (cavity mode-width spectroscopy) and CMDS (cavity mode-dispersion spectroscopy) [64].

Frequency axis uncertainty in CRD spectrometer was limited by a thermal stability of the He-Ne laser used for the cavity length stabilization. In 2016 the spectrometer has been improved – the He-Ne laser was replaced by Nd:YAG laser working at 1064 μm with stability better than 10kHz, which allows for significant reduction of systematic errors on the frequency axis. Using the optical atomic clock from KL FAMO as an absolut frequency reference and averaging a significant amount of measurements should allow for line position determination with accuracy better than 1 kHz.

5. Overview of other research achievements.

My other scientific achievements focus on the development of experimental apparatus and methods and study of atomic and molecular spectra.

5.1. Experimental apparatus and methods

5.1a. Spectrometer for measurements of cadmium lines

As a part of my doctorate the spectrometer for investigation of the of the cadmium spectral absorption line shapes has been developed. The collisional asymmetry of cadmium perturbed by noble gases was measured by means of the absorption in the cell. As a result the collisional asymmetry of the λ=326.1 nm intercombination line of cadmium was determined for the ^{114}Cd-Kr system [P8]. The absorption spectrometer was based on the PGS-2 monochromator equipped with the diffraction grating rotated by stepping motor. The halogen lamp served as an absorption light source while the detection was performed using the photomultiplier working in the photon counting regime. A hollow-cathode Fe lamp was used for calibration of the frequency axis. The measurement procedure and data acquisition was automatically controlled by CAMAC standard system. The quartz cylindrical cells with the side arm containing Cd vapor and Kr perturbing atoms were prepared and filled on the vacuum system by ourselves in our laboratory. The perturbing atoms density was determined at the time of closing and separating the cell from the vacuum system. The Cd atoms density was controlled by the temperature of the side arm, while the main part of the cell was maintained in steady temperature conditions during the whole measurement thanks to the oven with several independent heaters with temperature stabilization.

The collisional broadening and shifting coefficients and dependence of the collisional asymmetry on the Kr density was determined for the first time. For over a dozen years the oven constructed for this study has been used for absorption measurements and for the laser induced fluorescence (LIF) experiment by the group members for over ten years.

After finishing the absorption experiment I took part in the construction of the computer controlled LIF spectrometer activated in 1999. It enables the measurements of the fluorescence in the cell inside the regulated oven. The setup based on the tuned ring laser with the intracavity frequency doubling crystal emitting UV light at the λ=326.1 nm intercombination line of cadmium. Fluorescence has being detected with a photomultiplier working in the photon counting regime which assured high sensitivity with 1 MHz resolution. Frequency axis calibration was performed at the fundamental beam using the I_2 spectrum while the Fabry-Perot interferometer was used to control the linearity. The measurements of the Cd line perturbed by the noble gases and H_2 and D_2 were performed to investigate the influence of the collisional effects on the shape of the emission lines of 114Cd and 113Cd isotopes [P10, P11, P13, P14, P16–P18]. The spectrometer allowed to initiate the laser spectroscopy investigations of the spectral line shapes in Toruń. In addition to the above mentioned publications this spectrometer was used in other research by te team members [65–69].

5.1b. Cs magneto-optical trap.

During the postdoc internship at the Windsor University in Canada with the Prof W.McConkey group I participated in construction of the magneto-optical trap (MOT) for Cs atoms. It was designed to measure the electron impact total cross-section in Cs. The most important issue while building the apparatus was the combination of the electron beam with MOT magnetic field and detection of the weak fluorescence. The MOT consisted of a stainless-steel, ultrahigh vacuum chamber evacuated with an ion pump that provided a typical operating pressure of 6×10^{-8} Torr and an ultimate background pressure of roughly 10^{-9} Torr. Operating the trap in the range of pressures up to 2×10^{-7} Torr at or below the Doppler limit temperature for cesium of 124 mK it was possible to maintain a steady state trap population of 10^7 atoms with typical trap size of the order of 1 mm. The trapping and repumping lasers, operating at 852 nm, were independently stabilized to Doppler-free saturated Cs absorption spectrum. The use of an AOMs on the output of each laser provided a precise control of laser's frequency and also provided a convenient means of gating the laser beam. The anti-Helmholtz coils pair provided the magnetic trapping field gradient of approximately 10 G/cm for an operating current of 6 A. A pulsing circuit switched by a TTL signal was designed to rapidly dissipate the coil current, so to minimize the magnetic field decay time. It was necessary to avoid the interaction of the magnetic field on the electron beam and keep the trapped atoms as long as possible in the trapping region. During the experiment the repumping beam and the magnetic field were periodically turned off to allow for the free expansion of the trapped atoms cloud and for the observation with the aid of the photomultiplier. The comparison of the time variation of the freely expanding cloud fluorescence with and without the electron beam allows for the determination of electron impact total cross-sections in Cs [P12]. Similar investigations were performed before only for trapped Rb atoms. In this MOT the electron impact total cross-sections for the electron beam energy from 100eV to 400 eV was measured and compared with new *ab initio* calculations because previous data showed large discrepancies. Study using this experimental setup was continued for the electron beam energy below 100 eV [70, 71]. Results are in agreement with previous calculations [P12].

5.1c. Cavity ring-down spectrometer

First oxygen B-band spectrum registered by means of the FS-CRDS in Toruń was published in 2009 [72]. The spectrometer was essentially identical to those developed at the National Institute of Standards and Technology (NIST) in Gaithersburg [32]. The ring-down cell was constructed at NIST. The resonator is made of two concave mirrors, having 1 m radius of curvature, distant by 73 cm. The resulting free spectral range (FSR) is about 203 MHz. The mirrors reflectivity is 0.99975 for $\lambda = 689$ nm (diode laser probe beam) and 0.95 for $\lambda = 633$ nm (HeNe laser used for cavity length stabilization). One of the mirrors is mounted on the piezoelectric actuator which enables to control the optical pathlength in the cavity up to 12 μm. FS stands for the frequency stabilization of the cavity length with respect to the frequency reference. It is realized by locking one of the cavity modes to the frequency of the thermally stabilized HeNe laser. CRD spectroscopy relies on the determination of the absorption coefficient on the basis of the ring-down constant. To do the measurements the cavity is optically pumped (the single cavity resonance is excited) and after the light intensity leaking out of the cavity reaches the certain level the light is switched off and the exponential light decay is registered. Due to the very high reflectivity of the cavity mirrors, the light travels back and forth many times before leaving the cavity so the optical path in the empty cavity can be thousands of meters. The the ring-down constant depends on the presence of the gas in the cavity. The determined decay constant for different frequencies allows to record the absorption line profile. Typical distance between the measurements points on the spectrum equals FSR, which is achieved by tuning the probe laser over the comb of the cavity modes. In order to make smaller steps an acousto-optic modulator (AOM) is used to shift the HeNe frequency by a fraction of FSR. The comb of cavity modes locked to the HeNe laser follows the frequency change of the AOM. Common frequency step with our CRDS is 50 MHz.

In 2010 the spectrometer has been improved by implementation of the Pound-Drever-Hall (PDH) method to lock the probe laser to the cavity [P19]. Before that, the probe laser frequency was slowly modulated around the actual cavity resonance in order to create the error signal for the slow feedback loop which enabled for the compensation of the slow probing frequency drift. Ring-down events exhibited random fluctuations in timing and intensity, however, it did not affected the ring-down time constant. The PDH method takes advantage of the strong frequency dependence near resonance in the phase of the reflected field from a high-finesse resonant cavity. As a consequence the substantial reduction in the laser line width occurred from typical 200 kHz to less than 1 kHz, well below cavity mode width which is over a dozen kHz, as well as almost four-fold increase in the maximum probe laser beam intensity transmitted through the ring-down cavity. Much higher repeatability enabled to achieve ring-down signal acquisition rates up to 14.3 kHz compared to 25 Hz achievable with a low-bandwidth lock, which represents a 500-fold increase in acquisition rate, thus a significantly higher number of decays can be measured and averaged per one point of the spectrum with higher signal-to-noise ratio (SNR). The implementation of the PDH method and improved efficiency was described in Ref. [P19]. Further substantial improvement was the development of the electronic setup and procedure for correction of the effect of amplitude modulation of the error signal and other sources of offsets that are inherent in the PDH feedback loop [P20]. The potential of the new PDH-locked FS-CRDS for the precise analysis of the high quality spectra was extended significantly by identifying and eliminating the nonlinearities in the experimental setup [P21]. Recording the ring-down decays in the wide range of measurements conditions, followed by a fitting of a single and averaged ring-down decays in the wide range of parameters allowed to select the proper analog-to-digital converter and to establish the reference condition for best SNR. As a result it was possible to determine line intensities with relative uncertainties below 0.4% [P21]. All the improvements allowed for the continuous measurements for over 24 hours in order to average multiple spectra. In Ref. [P22] the potential of the improved spectrometer to measure optical spectra with extremely high SNR was demonstrated on the example of the R7 Q8 oxygen B-band line. The obtained SNR was of 220000:1 after 33 hours of measurement and averaging of over a 1000 spectra.

5.2. Line shape measurements of the atomic and molecular transitions

5.2a. Intercombination line of the ^{114}Cd *and* ^{113}Cd *isotopes.*

The $\lambda = 326.1$ nm intercombination Cd line is the effect of the 5^1S_0 - 5^3P_1 transition. The even-even ^{114}Cd isotope has no hyperfine structure, therefore it was a perfect subject for the first investigation of the Cd line shape perturbed by He and Ne [P4, P6] and Kr [P5] in the low pressure range with the aid of the spectrometer with the pressure scanned Fabry-Perot interferometer. In this experiments the collisional broadening and shifting parameters were determined. They were the first experimental results for this Cd transition perturbed by Ne and Kr. In the higher pressure range the collisional asymmetry parameter was determined for the Cd-Kr system using the absorption spectrometer with PGS-2 monochromator [P8]. The above results were used for verification the interaction potentials obtained from the *an initio* calculations [73, 74] as well as from other experiments, namely, Morse potential from atomic beam experiments [75], van der Waals and Lennard-Jones potentials from the absorption on the far wings [76]. The conclusion from our investigations is as that the essential contribution to the pressure broadening and line asymmetry comes from the region of small values of the interatomic distances, while the shift coefficient depends mainly on the values of interaction potentials at very large distances. Regarding our results Czuchaj improved the interaction potentials for Cd–noble gas systems including some correction, like spin-orbit interaction [77–79]. Collisional effects on the intercombination line of the ^{114}Cd perturbed by other noble gases as well as H_2 and D_2 were measured by means of LIF [P10, P11]. Experimental techniques and data analysis methods developed during the experiment described above were exploited for the study of the ^{114}Cd perturbed by N_2 and CH_4 [68].

It is worth to emphasize the most important results and conclusions from all the above research. It was shown that the speed-dependent effects can be observed not only when the perturber mass is greater than the emiter mass but also for the system with perturber/emiter mass ratio as low as 0.35. The dependence of the Doppler width on the pressure is a sensitive indicator of the accuracy of the interaction potential where used for the calculation of the speed-dependent effects.

The intercombination line of the even-odd isotope of cadmium, ^{113}Cd, has two hyperfine-structure components. The main goal of the investigation of this isotope was observation of the line-mixing asymmetry in the atomic system. The observed asymmetry in the Cd-Ar system was not explicable by the only collisional asymmetry [P16, P17]. In Ref. [P16] first observation of the line-mixing asymmetry in the atomic system was reported. Total observed asymmetry was influenced by three different effects which were very difficult to distinguish by observation. Those are: the collisional asymmetry resulting from the finite duration of collision, speed-dependent asymmetry caused by the dependence of the line width and shift on the emiter or absorber velocity and line mixing asymmetry. This issue was discussed in details in Ref. [P17].

The hyperfine and isotope structure of the intercombination line was determined from the measurements by means of LIF technique. Two samples of different abundance were measured, ^{113}Cd (95.8% enrichment) and ^{114}Cd (98.8% enrichment). Relative position of all eight isotopes as well as the hyperfine splitting for odd isotopes were determined.

The simultaneous measurement of diffusion and reflection coefficients for cadmium vapor in an electrodeless discharge was stimulated by the Dicke narrowing studies in the Cd-Xe system [P15].

5.2b. Oxygen line shape measurements

Six lines of the B-band R branch of the were investigated using PDH locked FS-CRDS [P21]. The results confirmed that the VP is insufficient to describe observed spectra. Line shapes were analyzed with GP and SDVP which includes the line narrowing. It was shown that using VP may cause the 25% error in the obtained self broadening parameter. Very precise line shape investigation were performed on the R7 Q8 transition. The averaging over 1000 single line profiles yielded the record signal-to-noise ratio of 220000 and quality of the fit factor (QF) above 75000 [P22,P23].

5.2c. Other line shape measurements

The neon lines shapes emitted from the glow discharge indicated departure from the Voigt profile. The observed deviation of the measured line profile in a very low pressures was caused by the excitation mechanism – the dissociative recombination [P3]. The speed dependence of the pressure shifting and broadening was observed in the selfperturbed Ne lines emitted from the glow discharge where the mass ratio equals 1 [P9]. The broadening and shifting parameters of the doppler-free thallium transition perturbed by the noble gases observed by two-photon excitation were reported in Ref. [P7]. The cross-section measurements were performed for cold Cs atoms trapped in MOT. The electron impact total cross-sections in Cs over the energy range 100–400 eV was determined experimentally together with the Convergent Close Coupling calculations over the energy range 0.3–400 eV [P12].

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Jolanta Domysławska