Appendix 2b

Summary of Professional Accomplishments

Rafał Hakalla

Rzeszów, 2017 r.

Contents

1. First name and surname

Rafał Hakalla

2. Education and degrees

- 1995 r. – MSc degree in physics,
Faculty of Mathematics and Physics, Pedagogical University in Rzeszów.

- 2003 r. – PhD in physics (with honours),
Faculty of Mathematics and Natural Sciences, University of Rzeszów,
Title of thesis: *Analysis of the 3A* ($c^3\Pi – a^3\Pi$) *system in the* $^{12}C^{16}O$, $^{13}C^{16}O$ *and* $^{14}C^{16}O$ *isotopologues,*
The dissertation was awarded the first degree prize by the Minister of National Education and Sport in 2003.

3. Information on employment in scientific institutions

- 1995 – 2001 assistant lecturer in the Atomic and Molecular Physics Laboratory, Faculty of Mathematics and Physics, Pedagogical University in Rzeszów.

- 2001 – 2003 assistant lecturer in the Atomic and Molecular Physics Laboratory, Faculty of Mathematics and Natural Sciences, University of Rzeszów (UR).

- 2003 – 2012 assistant professor w in the Atomic and Molecular Physics Laboratory, Faculty of Mathematics and Natural Sciences, UR.

- 2012 – 2016 assistant professor in Department of Experimental Physics, Materials Spectroscopy Laboratory (LSM) in Centre for Innovation and Transfer of Natural Sciences and Engineering Knowledge (CIiTWTP), Faculty of Mathematics and Natural Sciences, UR.

- 2015 – 2016 post-doctoral internships:
    - University College London (Great Britain), Faculty of Physics and Astronomy. Work in the group of prof. Jonathan Tennyson.
    - Vrije University (Amsterdam, Netherlands), Faculty of Physics and Astronomy. Work in the group of prof. Wim Ubachs.

- since 2016 – senior lecturer in Department of Experimental Physics, LSM, CIiTWTP, Faculty of Mathematics and Natural Sciences, UR.

4. Scientific achievement justifying the application for habilitation

As a scientific achievement, according to Art. 16 passage 2 of the Act of 14 March 2003 r. *on university degrees and university titles and on degrees and titles in the field of arts* (Journal of Laws 2016, item 882 as amended in Journal of Laws of 2016, item 1311), I designate **a cycle of eight publications [H1 – H8]**[*] linked thematically, and entitled:

Spectroscopy of the less – abundant isotopologues of carbon monoxide $^{12}C^{17}O$ *and* $^{13}C^{17}O$ *and deperturbation analyses of the* $A^1\Pi$ *state.*

4.1. The cycle of publications [H1 – H8]

H1. **R. Hakalla**, M. Zachwieja
Rotational analysis of the Ångström system ($B^1\Sigma^+ - A^1\Pi$) *in the rare* $^{13}C^{17}O$ *isotopologue*
Journal of Molecular Spectroscopy, **272**, 11 – 18 (2012)
DOI: 10.1016/j.jms.2011.12.002
I estimate my percentage contribution at 50%

H2. **R. Hakalla**, W. Szajna, M. Zachwieja
Extended analysis of the Ångström band system ($B^1\Sigma^+ - A^1\Pi$) *in the rare* $^{12}C^{17}O$ *isotopologue*
Journal of Physics B: Atomic, Molecular & Optical Physics, **45**, 215102 (2012)
DOI: 10.1088/0953 – 4075/45/21/215102
I estimate my percentage contribution at 80%

H3. **R. Hakalla**, W. Szajna, M. Zachwieja
First analysis of the $1 - \upsilon''$ *progression of the Ångström* ($B^1\Sigma^+ - A^1\Pi$) *band system in the rare* $^{13}C^{17}O$ *isotopologue*
Journal of Physical Chemistry A, **117**, 12299 – 12312 (2013)
DOI: 10.1021/jp4077239
I estimate my percentage contribution at 80%

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[*] The numbering of the **[H1 – H8]** publications designated as the scientific achievement, according to Art. 16 passage 2 of the Act of 14 March 2003 r., is consistent with the List of Publications and Achievements given in Appendix 3.

H4. **R. Hakalla**, W. Szajna, M. Zachwieja
First analysis of the $B^1\Sigma^+$ $(\upsilon = 1)$ *Rydberg state in the lesser – abundant* $^{12}C^{17}O$ *isotopologue on the basis of the* $1 - \upsilon''$ *progression of the Ångström band system*
Journal of Quantitative Spectroscopy & Radiative Transfer, **140**, 7 – 17 (2014)
DOI: 10.1016/j.jqsrt.2014.02.004
I estimate my percentage contribution at 80%

H5. **R. Hakalla**
First analysis of the Herzberg $(C^1\Sigma^+ - A^1\Pi)$ *band system in the less – abundant* $^{13}C^{17}O$ *isotopologue*
Royal Society of Chemistry Advances, **4**, 44394 – 44407 (2014)
DOI: 10.1039/c4ra08222b

H6. **R. Hakalla**
Investigation of the Herzberg $(C^1\Sigma^+ \rightarrow A^1\Pi)$ *band system in* $^{12}C^{17}O$
Journal of Quantitative Spectroscopy & Radiative Transfer, **164**, 231 – 247 (2015)
DOI: 10.1016/j.jqsrt.2015.06.016

H7. **R. Hakalla**, M. L. Niu, R. W. Field, E. J. Salumbides, A. N. Heays, G. Stark, J. R. Lyons, M. Eidelsberg, J. L. Lemaire, S. R. Federman, M. Zachwieja, W. Szajna, P. Kolek, I. Piotrowska, M. Ostrowska – Kopeć, R. Kępa, N. de Oliveira, W. Ubachs
VIS and VUV spectroscopy of $^{12}C^{17}O$ *and deperturbation analysis of the* $A^1\Pi$, $\upsilon = 1 - 5$ *levels*
Royal Society of Chemistry Advances, **6**, 31588 – 31606 (2016)
DOI: 10.1039/c6ra01358a
I estimate my percentage contribution at 60%

H8. **R. Hakalla**, M. L. Niu, R. W. Field, A. N. Heays, E. J. Salumbides, G. Stark, J. R. Lyons, M. Eidelsberg, J. L. Lemaire, S. R. Federman, N. de Oliveira, W. Ubachs
Fourier – transform spectroscopy of $^{13}C^{17}O$ *and deperturbation analysis of the* $A^1\Pi$ $(\upsilon = 0 - 3)$ *levels*
Journal of Quantitative Spectroscopy & Radiative Transfer, **189**, 312 – 328 (2017)
DOI: 10.1016/j.jqsrt.2016.12.012
I estimate my percentage contribution at 60%

Rzeszów, 5.06.2017

Rafał Hakalla

4.2. Discussion of the scientific objective of the [H1 – H8] cycle of publications and obtained results

4.2.1. Motivation and objectives of the research

Carbon monoxide (CO) is in the centre of attention mainly because of its role as a basic astrophysical tracer of molecular gases in interstellar clouds [1], circumstellar matter [2], whole galaxies [3], Doppler red-shifts of a high value [4] and in gamma-ray bursts [5]. In the interstellar medium, CO controls most of chemical reactions that occur in the gas phase [6] and is a precursor of creation of complex molecules [7]. Apart from molecular hydrogen, carbon monoxide is the most abundant molecule that occurs in the interstellar medium. The CO spectrum, studied in the wide spectral range from the sub-millimetre region [8,9] to X-rays [10], was observed, among others, in galaxies [8,11], protoplanetary disks [12,13], comets [14,15], cool dwarfs [16], quasars [17], supernova remnants [18], in interstellar molecular clouds [19], on the Sun [20], as well as in atmospheres of planets [21] and exoplanets [15,22,23]. The CO spectrum, being the result of transitions from excited $B^1\Sigma^+(\upsilon = 0, 1)$ and $C^1\Sigma^+(\upsilon = 0)$ states, was registered, among others, in the atmosphere of Mars and Venus by means of the Hopkins telescope [24], FUSE satellite [25,26] and CASSINI-HUYGENS probe [27]. The abundance of carbon monoxide in the interstellar medium causes a noticeable spectral signal deriving even from less-abundant isotopologues such as $^{12}C^{17}O$ or $^{13}C^{17}O$ [28–30]. Their research is of significant importance for distinct elimination of unfavourable effects of the so-called *depth optical effect* in interstellar absorption [29], estimation of column density of gases in molecular clouds as well as for precise determination of the $^{12}C/^{13}C$ and $^{16}O/^{17}O/^{18}O$ ratios, which is used to: (i) provide important constraints for models of the Galactic chemical evolution, which predict isotopic abundance ratio as a function of stellar nucleosynthesis, (ii) star formation history, and (iii) the degree of mixing of the gas in the inter-stellar medium (ISM) [31,32]. The first observation of the spectrum of the less-abundant $^{12}C^{17}O$ isotopologue in an astrophysical environment was carried out by Encrenaz et al. in 1973 in Orion Nebula [33]. In turn, the spectrum of the $^{13}C^{17}O$ molecule, the least-abundant among stable carbon monoxide isotopologues, was observed for the first time in the ρ-Ophiuchi molecular cloud in 2001 by Bensch et al. [29]. In laboratory conditions, these rare species were studied a few times: $^{12}C^{17}O$ [34–39] and $^{13}C^{17}O$ [34,37,40–45]. However, up to 2012, in the less-abundant $^{12}C^{17}O$ and $^{13}C^{17}O$ molecules, no recording or analysis were made of the Ångström ($B^1\Sigma^+ - A^1\Pi$) and Herzberg ($C^1\Sigma^+ - A^1\Pi$) band systems, which are very important due to their location in the visible range (VIS).

The CO molecule is also very important in research into the atmosphere of the Earth. Its concentration in particular layers of the troposphere, stratosphere, and mesosphere differs significantly. Due to a short lifetime, which is approximately 2 months, changes of the environmental conditions of the Earth are reflected in the atmospheric concentrations of CO much quicker than it is the case of other molecules [46,47]. The CO molecule plays also a significant role in other branches of science such as, among others, technology of new materials (so-called carbonyls), metallurgy, medicine, chemical physics, microbiology, molecular biology, combustion processes and plasma science [48–55].

From the point of view of molecular physics, carbon monoxide plays a substantial role in intra-molecular dynamics modelling, because its spectrum shows the variety of perturbations resulting from spin-orbit interactions and centrifugal perturbation effects, as well as from the mixing of highly-excited Rydberg states [56–58]. The most highly and extensively perturbed electronic state of the CO molecule is the first among excited singlet states: ($2\pi^1$) $A^1\Pi$. It undergoes multistate perturbations of the electronic-vibrational-rotational (*rovibronic*) structure [59–63]. The causes of these irregularities are interactions of closely lying vibrational-rotational (*rovibrational*) levels of the triplet $d^3\Delta_i$, $e^3\Sigma^-$, $a'^3\Sigma^+$ and singlet $I^1\Sigma^-$, $D^1\Delta$ electronic states. The $a^3\Pi$ state, due to its close neighbourhood, could also be a direct reason of the observed perturbations of $A^1\Pi$, but vibrational overlap integrals between the $a^3\Pi$ and $A^1\Pi$ states are too small (of the order of $10^{-4} - 10^{-6}$) for their perturbation to be noticeable. In the main $^{12}C^{16}O$ isotopologue:

- A consistent classification of perturbations was conducted by Krupenie [56] and Simmons et al. [64].
- The first deperturbation calculation of the $A^1\Pi$ state was performed by Field et al. [59,61].
- Extended studies on the perturbations of the lowest vibrational level $A^1\Pi$ (υ = 0) were performed by Le Floch et al. [60].
- Irregularities of the $A^1\Pi$ (υ = 0 – 4) levels were analysed by Le Floch [65,66], who also calculated precise term values of the $A^1\Pi$ (υ = 0 – 8) state.
- A significant contribution to identification and classification of the $A^1\Pi$ perturbations was made by R. Kępa and M. Rytel [67,68].
- Recently Niu et al. [69,70] made reanalysis, more precise than by Field et al. [59,61], of the perturbations in $A^1\Pi$ (υ = 0 – 4).

In other isotopologues of CO, an analysis of perturbations of the $A^1\Pi$ state was performed only by the group of prof. Le Floch:

- Haridass et al. [71] and Gavilan et al. [72] in $^{13}C^{16}O$,
- Haridass et al. [62,73] in $^{12}C^{18}O$ and $^{13}C^{18}O$,
- and Beaty et al. [74] in $^{12}C^{18}O$.

However, up until 2015, the deperturbation analysis of the $A^1\Pi$ state in the less-abundant $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues have never been performed.

The above described state of knowledge and research into the CO molecule made me formulate the following **research objectives**:

A) Main objectives:

● Selection of such radiation sources, methods of sample gas excitation, techniques of spectrum recording and analytical methods, so that accuracy of wavenumber measurements of single lines of average intensity and of a good signal-to-noise ratio (SNR) would be approximately ±0.003 cm^{-1} ($\Delta\lambda/\lambda=\pm2\times10^{-7}$) in the VIS region, in order to investigate all, even very weak perturbations of the studied energy levels in $^{12}C^{17}O$ and $^{13}C^{17}O$.

- Performance of the first recording and analysis of the Ångström ($B^1\Sigma^+ - A^1\Pi$) and Herzberg ($C^1\Sigma^+ - A^1\Pi$) systems in the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues.
- Identification of irregularities of the studied spectra and of all states responsible for observed perturbations of rovibronic structures in $^{12}C^{17}O$ and $^{13}C^{17}O$.
- Performance of global deperturbation analyses of the $A^1\Pi$ state in the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues on the basis of data deriving from the B – A and C – A systems, and also inclusion of the B – X and C – X systems in the analyses in order to decrease correlations between parameters determined in the calculations. As a result of these fits, the following were planned: determination of molecular constants deprived of a mutual influence of the $A^1\Pi$ state and its perturbing states, as well as spin-orbit and rotation-electronic (*L-uncoupling* type) interaction parameters between these states.
- Determination of rovibrational terms of the $A^1\Pi$, $B^1\Sigma^+$, $C^1\Sigma^+$ and $d^3\Delta_i$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $I^1\Sigma^-$, $D^1\Delta$ states in the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues.
- Determination of the isotopologue-independent electronic perturbation parameters: spin-orbit ***a*** for $A^1\Pi \sim d^3\Delta_i$, $A^1\Pi \sim e^3\Sigma^-$, and $A^1\Pi \sim a'^3\Sigma^+$ interactions, as well as rotation-electronic ***b*** for $A^1\Pi \sim I^1\Sigma^-$ and $A^1\Pi \sim D^1\Delta$ interactions. Comparison of the obtained ***a*** and ***b*** values with all, calculated from other isotopologues so far [60–62], in order to finally verify the quality of deperturbation analyses carried out in the $^{12}C^{17}O$ and $^{13}C^{17}O$ molecules.

B) Additional objectives:

- Determination of rotational and vibrational equilibrium constants, band origins and their isotope shifts, parameters of potential curves, relative intensities, parameters of the rovibronic structure in the form of υ_{00}^{CB}, υ_{01}^{CB}, ΔB_{00}^{CB}, ΔB_{01}^{CB} differences, as well as *r*-centroids and Franck-Condon factors (*FCF*) of the states under consideration and transitions in the $^{12}C^{17}O$ and $^{13}C^{17}O$ molecules.
- Performance of an isotopic analysis of highly excited Rydberg $B^1\Sigma^+$ and $C^1\Sigma^+$ states within the Born-Oppenheimer (*BO*) approximation on the basis of data obtained from the highest possible number of the CO species and on such a basis determination of isotopically invariant parameters.
- Identification and analysis of predissociation of the $B^1\Sigma^+$ state, which should occur between its υ = 1 and υ = 2 vibrational levels in the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues. Determination of a more precise dissociation energy value of this state.

4.2.2. Results

[H1] **R. Hakalla**, M. Zachwieja, *Rotational analysis of the Ångström system ($B^1\Sigma^+ - A^1\Pi$) in the rare $^{13}C^{17}O$ isotopologue,* J. Mol. Spectrosc., **272**, 11 – 18 (2012).

The Ångström ($B^1\Sigma^+ - A^1\Pi$) band systems was recorded and analysed for the first time in $^{13}C^{17}O$, the least-abundant isotopologue among stable CO species. The measurement system was based on high-accuracy dispersive optical spectroscopy (HADOS*). Reciprocal dispersion was 0.09 – 0.14 nm/mm, and theoretical resolving power was 1.82 – 2.28 × 10^5. The $^{13}C^{17}O$ molecules were produced and excited in a modified hollow-cathode discharge lamp (*the composite wall hollow cathode: CWHC)*. Its design, modification and preparation for measurements were described in chapter 4.2.4 of this Summary of Professional Accomplishments.

As a result, 192 emission lines belonging to the most intense (0, 1) and (0, 2) bands of the Ångström system in the $^{13}C^{17}O$ isotopologue were obtained in the range 19 300 – 21 200 cm^{-1}. The obtained SNR of the measured lines was 100 : 1 for (0, 1) band and 130 : 1 for (0, 2) band. Absolute accuracy of the wavenumber measurements was approximately 0.002 cm^{-1} for single lines of an average intensity.

In this work, the first observation of multistate and extensive perturbations were observed that occur in a complex $^{13}C^{17}O$ $A^1\Pi$ (υ = 1, 2) levels, for both components of the Λ-doubling. The $a'^3\Sigma^+$ (υ = 10) and $D^1\Delta$ (υ = 1) as well as $e^3\Sigma^-$ (υ = 4) and $d^3\Delta_i$ (υ = 7) rovibronic levels were identified as responsible for perturbations of the $A^1\Pi$ (υ = 1) and $A^1\Pi$ (υ = 2) levels, respectively. The regions of occurrence and magnitudes of the perturbations were determined.

Reduction of the spectrum to molecular parameters of effective Hamiltonian was performed by means of the Curl-Dane-Watson method [75,76], which enabled us to separate statistical information of the regular state (represented by the effective Hamiltonian) from the perturbed one (represented by the terms). A standard deviation (1σ) of the model-to-measurement fit was obtained amounting to 0.0029 cm^{-1} and 0.0013 cm^{-1}, for the $^{13}C^{17}O$ B – A (0, 1) and (0, 2) bands, respectively. It enabled us to determine the first rotational constants B_0 and D_0 of a highly excited $B^1\Sigma^+$ (υ = 0) Rydberg state, which was recognized as regular. The band origins as well as the term value differences between theoretically unperturbed (calculated) and experimental ones for the $A^1\Pi$ (υ = 1, 2) levels in the $^{13}C^{17}O$ molecule were calculated. Also, estimated, effective values of the B_υ and D_υ molecular constants for the $A^1\Pi$ (υ = 1, 2) levels were obtained.

The $^{13}C^{17}O$ spectra were extraordinarily complex due to the fact that they also included analogous bands of three additional, undesirable in this case, $^{13}C^{16}O$, $^{12}C^{17}O$ and $^{12}C^{16}O$ isotopologues. Their occurrence results from the application of oxygen $^{17}O_2$ in the experiment that was of insufficient spectral purity, on which we did not have any influence as the best isotope mixture that we could acquire in the years 2010-2015 and that was affordable, had the content of 70% of $^{17}O_2$ + 30% of $^{16}O_2$. The occurrence of a ^{12}C element in the impurities was the consequence of the process of carbon ^{13}C deposition on the hollow-cathode of the discharge lamp in the process of acetylene $^{13}C_2D_2$ dissociation with 99% ^{13}C spectral purity (see chapter 4.2.4 of the Summary of Professional Accomplishments). Undesirable lines were identified and taken into account when determining positions of the $^{13}C^{17}O$ lines in complex contours of the spectra. However,

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* The *HADOS* abbreviation will be used only for the purposes of the Summary of Professional Accomplishments; it is not accepted in the systematic nomenclature of spectroscopy.

the time needed to interpret and determine wavenumbers of one band of the $^{13}C^{17}O$ molecule, including all perturbations of the $A^1\Pi$ state in four isotopologues simultaneously, was approximately 5 – 6 times longer than in the case of a typical, regular band of the main $^{12}C^{16}O$ isotopologue.

My contribution to the work included gathering current literature related to the subject of this study, designing a modified construction of the discharge CWHC lamp for the $^{13}C^{17}O$ isotopologue in the gas phase (in collaboration with M. Zachwieja), planning and performing the ^{13}C isotope deposition inside the hollow-cathode of the discharge lamp, planning the scope of experimental work, optimization of operating conditions of the lamp and physical conditions of the experiment, performing measurements and calibration of the spectra of the studied bands (in collaboration with M. Zachwieja), selecting physical models and data analysis methods, gathering and analysing the results, identifying perturbations of the $^{13}C^{17}O$ $A^1\Pi$ (υ = 1, 2) levels, preparing and editing the complete manuscript of the publication (except for chapter 2 elaborated together with M. Zachwieja). I estimate my percentage contribution at 50%.

[H2] **R. Hakalla**, W. Szajna, M. Zachwieja, *Extended analysis of the Ångström band system ($B^1\Sigma^+ - A^1\Pi$) in the rare $^{12}C^{17}O$ isotopologue,* J. Phys. B: At. Mol. Opt. Phys., **45**, 215102 (2012).

In the work, the first recording and analysis of the Ångström ($B^1\Sigma^+ - A^1\Pi$) band systems in the $^{12}C^{17}O$ isotopologue were made. The molecules were produced and excited in a modified CWHC discharge lamp. Recording was performed under high resolution with reciprocal dispersion of 0.09 – 0.14 nm/mm and theoretical resolving power 1.82 – 2.28 × 10^5 by means of the HADOS technique. 200 emission lines were obtained which belonged to the most intense (0, 1) and (0, 2) bands of the B – A system, with absolute accuracy of wavenumber measurements amounting to 0.0013 cm^{-1} in the range of 19 250 – 21 300 cm^{-1}. The SNR of the measured lines was 130 : 1 and 150 : 1 for (0, 1) and (0, 2) band, respectively. The influence of undesirable lines of the $^{12}C^{16}O$ B-A (0, 1) and (0, 2) bands, which occurred in the studied spectra, were minimized through their identification and taking them into account while determining positions of the investigated lines in complex contours.

Perturbations of the $^{12}C^{17}O$ $A^1\Pi$ (υ = 1, 2) levels, occurring in both components of the Λ – doubling, were observed for the first time. The $d^3\Delta_i$(υ = 5), $a'^3\Sigma^+$ (υ = 10), $D^1\Delta$ (υ = 1) and $I^1\Sigma^-$ (υ = 3), $e^3\Sigma^-$ (υ = 4), $d^3\Delta_i$ (υ = 7) rovibronic levels were identified as responsible for observed perturbations of υ = 1 and υ = 2 levels of the $A^1\Pi$ state. The regions of occurrence and magnitudes of the perturbations were determined.

Reduction of the spectrum to molecular parameters of effective Hamiltonian was performed by means of the Curl-Dane-Watson method [75,76] obtaining a standard deviation (1σ) of the model-to-measurement fit amounting to 0.0012 cm^{-1} and 0.0011 cm^{-1}, for the (0, 1) and (0, 2) band, respectively. It enabled us to determine the first rotational constants B_0 and D_0 of the $^{12}C^{17}O$ $B^1\Sigma^+$ (υ = 0) Rydberg state. The band origins as well as the value differences between theoretical (unperturbed) and experimental terms for the υ = 1 and 2 levels of the $A^1\Pi$ state were calculated. Also, estimated, effective values of parameters of the $A^1\Pi$ (υ = 1, 2) levels were determined.

My contribution to the work included designing a modified construction of the discharge CWHC lamp for the $^{12}C^{17}O$ isotopologue in the gas phase, planning and performing the ^{12}C atoms deposition inside the hollow-cathode of the discharge lamp, planning the scope of experimental work, optimization of operating conditions of the lamp and physical conditions of the experiment, performing measurements and calibration of the spectra of the studied bands (in collaboration with M. Zachwieja), selecting physical models and data analysis methods, gathering and analysing the results, identifying perturbations of the $^{12}C^{17}O$ $A^1\Pi$ (υ = 1, 2) levels, preparing and editing the complete manuscript of the publication. I estimate my percentage contribution at 80%.

[H3] **R. Hakalla**, W. Szajna, M. Zachwieja, *First analysis of the 1 – υ'' progression of the Ångström ($B^1\Sigma^+ – A^1\Pi$) band system in the rare $^{13}C^{17}O$ isotopologue*, J. Phys. Chem. A, **117**, 12299 – 12312 (2013).

In this work**,** recording and analysis of the 1 – υ'' progression of the $B^1\Sigma^+ – A^1\Pi$ band system and $B^1\Sigma^+ – e^3\Sigma^-$ intercombination system were performed for the first time in $^{13}C^{17}O$. The $^{13}C^{17}O$ molecules were produced and excited in the modified CWHC lamp. Measurement was carried out by means of the HADOS method. The experiment was performed under high resolution with reciprocal dispersion of 0.07 – 0.11 nm/mm and theoretical resolving power amounting to 2.28 – 2.73 × 10^5. In the studied region of 22 700 – 24 500 cm^{-1}, 146 spectral lines were observed, 118 of which were interpreted as belonging to (1, 0) and (1, 1) bands of the B – A system, and the next 28 as belonging to (1, 1) band of a forbidden $B^1\Sigma^+ – e^3\Sigma^-$ transition. SNR of calculated lines was approximately 70 : 1. Absolute accuracy of the best lines was approximately 0.0025 cm^{-1}. The studied spectra were complicated additionally by the overlaps of the B – A (1, 0), (1, 1) bands and (0, 2), (0, 3) band heads of the Herzberg ($C^1\Sigma^+ – A^1\Pi$) system of the $^{13}C^{16}O$, $^{12}C^{17}O$ and $^{12}C^{16}O$ species. By identifying and taking into account these impurities while determining positions of the investigated lines in complex contours, their influence on the studied spectrum was minimized. The other difficulties were much lower intensities and much worse SNR of the lines of the B – A (1 – υ'') progression compared to the 0 – υ'' progression.

An observation of perturbations occurring in the υ = 0 level of the $A^1\Pi$ state was carried out in the $^{13}C^{17}O$ molecule for the first time. The υ = 1 level of the $e^3\Sigma^-$ state was identified as responsible for the discovered irregularities in the region of $A^1\Pi$ (υ = 0, $0 < J < 20$). The regions of occurrence and magnitudes of perturbations were determined in both components of the Λ-doubling of the $A^1\Pi$ state.

Reduction of the spectrum to molecular parameters of effective Hamiltonian was performed by means of the Curl-Dane-Watson [75,76] method obtaining a standard deviation (1σ) of the model-to-measurement fit amounting to 0.0024 cm^{-1} and 0.001 cm^{-1}, for B – A (1, 0) and (1, 1) band, respectively.

In this work, the following were determined in the $^{13}C^{17}O$ molecule for the first time: rotational constants of the $B^1\Sigma^+$ (υ = 1) level, individual effective rotational constants of the $A^1\Pi$ (υ = 0) level, vibrational quantum $\Delta G^B_{1/2}$, vibrational equilibrium constants ω_e and $\omega_e x_e$ of the $B^1\Sigma^+$ state, effective vibrational equilibrium constants ω_e of the $A^1\Pi$ state, equilibrium internuclear distance r_e in the $B^1\Sigma^+$ and $A^1\Pi$ states, B – A (1, 0) and (1, 1) band origins, band system origin $\sigma_e^{B\rightarrow A}$, rotational equilibrium constants of the $B^1\Sigma^+$ and $A^1\Pi$ states, *RKR* parameters of the $B^1\Sigma^+$ and $A^1\Pi$ potential curves, as well as *FCF*, relative intensities and *r*-centroids of the $B^1\Sigma^+ - A^1\Pi$ transition. Thanks to an initial analysis of perturbations of the $A^1\Pi$ (υ = 0) level based on combination differences, rotational constant B_1 of the $e^3\Sigma^-$ (υ = 1) level and band origin $B^1\Sigma^+ - e^3\Sigma^-$ (1, 1) were obtained in the $^{13}C^{17}O$ molecule for the first time.

It was also observed the predissociation of the $B^1\Sigma^+$ state in the $^{13}C^{17}O$ molecule. It was caused by an electronic state, unidentified so far [77]. This phenomenon occurs between υ = 1 and υ = 2 vibrational levels of the $B^1\Sigma^+$ state and appeared through a sudden dramatic weakening of molecular lines both in B – A (1, 0) and (1, 1) band for $J > 20$.

My contribution to the work included performing the ^{13}C isotope deposition inside the hollow-cathode of the discharge lamp, planning the scope of experimental work, optimization of operating conditions of the lamp and physical conditions of the experiment, performing measurements and calibration of the spectra of the studied bands (in collaboration with M. Zachwieja), selecting physical models and data analysis methods, gathering and analysing the results, identifying perturbations of the $^{13}C^{17}O$ $A^1\Pi$ (υ = 0) level, preliminary analysing of the $e^3\Sigma^-$ (υ = 1) level, preparing and editing the complete manuscript of the publication. I estimate my percentage contribution at 80%.

[H4] **R. Hakalla**, W. Szajna, M. Zachwieja, *First analysis of the $B^1\Sigma^+$ (υ = 1) Rydberg state in the lesser – abundant $^{12}C^{17}O$ isotopologue on the basis of the 1 – υ'' progression of the Ångström band system*, J. Quant. Spectrosc. Radiat. Transfer, **140**, 7 – 17 (2014).

In this work, the first recording and analysis of the 1 – υ'' progression of the Ångström ($B^1\Sigma^+ - A^1\Pi$) system in the $^{12}C^{17}O$ isotopologue were performed using a modified discharge lamp CWHC and the HADOS technique. The experiment was carried out under high resolution with reciprocal dispersion of 0.10 – 0.12 nm/mm and theoretical resolving power amounting to $1.82 - 2.28 \times 10^5$. In the studied regions of 22 700 – 23 000 cm^{-1} and 17 200 – 17 500 cm^{-1}, 114 spectral lines were observed that belong to (1, 1) and (1, 5) band of the B – A (J_{max} = 21) system, respectively. SNR of measured lines was 60 : 1 and 40 : 1, for (1, 1) and (1, 5) band, respectively. Absolute accuracy of the wavenumber measurements of the best lines was approximately 0.003 cm^{-1}. While determining positions of the lines occurring in complex contours, the $^{12}C^{16}O$ B – A (1, 1) and (1, 5), $^{12}C^{17}O$ C – A (0, 3), and $^{12}C^{16}O$ C – A (0, 3) overlapping bands were taken into account.

Perturbations of the υ = 5 level of the $A^1\Pi$ state was observed in $^{12}C^{17}O$ for the first time. A υ = 8 vibrational level of the $e^3\Sigma^-$ state was identified as responsible for the discovered irregularities. The regions of occurrence and magnitudes of the perturbations caused by this level in both components of the Λ-doubling of the $A^1\Pi$ state were determined.

Reduction of the spectrum to molecular parameters of effective Hamiltonian was performed by means of the Curl-Dane-Watson [75,76] method obtaining a standard deviation (1σ) of the model-to-measurement fit amounting to 0.0016 cm^{-1} and 0.001 cm^{-1} for $^{12}C^{17}O$ (1, 1) and (1, 5) band, respectively.

In this work, for the first time the following were calculated for $^{12}C^{17}O$: rotational constants of the $B^1\Sigma^+$ (υ = 1) level, individual effective rotational constants of the $A^1\Pi$ (υ = 5) level, vibrational quantum $\Delta G^B_{1/2}$, vibrational equilibrium constants ω_e and $\omega_e x_e$ of the $B^1\Sigma^+$ state, effective vibrational equilibrium constant ω_e of the $A^1\Pi$ state, equilibrium internuclear distance r_e in the $B^1\Sigma^+$ and $A^1\Pi$ states, (1, 1) and (1, 5) band origins of the Ångström system and their isotope shifts, the band system origin $\sigma_e^{B\to A}$, rotational equilibrium constants of the $B^1\Sigma^+$ and $A^1\Pi$ state, parameters of the *RKR* potential curves of the $B^1\Sigma^+$ and $A^1\Pi$ states, as well as *FCF*, relative intensities, *r*-centroids of the $B^1\Sigma^+ - A^1\Pi$ band system.

An analysis of isotopic dependence of the $B^1\Sigma^+$ state within the *BO* approximation was carried out on the basis of the best data from eight species of the CO molecule [67,78,**H3**,**A10**]. Isotopic invariants U_{10} and U_{01} were determined and the parameter U_{10} was improved by almost two orders of magnitude in relation to ref. [78].

In this work, predissociation of the $^{12}C^{17}O$ $B^1\Sigma^+$ Rydberg state was observed, which had already been analysed in the $^{13}C^{17}O$ molecule **[H3]** and also in the remaining six species of the CO molecule **[A11]**. Symptoms of this predissociation were noticed in the B – A (1, 5) band where for $J' > 18$ there appeared a sudden weakening and widening of spectral lines. Thanks to the first observations and analyses of this phenomenon in isotopologues $^{12}C^{17}O$ **[H4]** and $^{13}C^{17}O$ **[H3]** it was possible to determine the value of dissociation energy of the CO molecule as accurate as the value D_e = 90 679.1 (60) cm^{-1}, which was described in detail in our separate work **[A11]**. This enabled us to confirm that the $B^1\Sigma^+$ state predissociates towards the lowest $C(^3P) + O(^1P)$ dissociation limit and also reject assumptions, discussed so far [79,80], that $C(^1D) + O(^3P)$ or $C(^3D) + O(^1P)$ are dissociation products. Very high accuracy of dissociation energy obtained by us also allowed for identification of triplet splitting components of energy states of both carbon and oxygen atoms $C(^3P_0) + O(^3P_2)$ **[A11]**.

My contribution to the work included performing the ^{12}C carbon deposition inside the hollow-cathode of the discharge lamp, planning the scope of experimental work, optimization of operating conditions of the lamp and physical conditions of the experiment, performing measurements and calibration of the spectra of the studied transition (in collaboration with M. Zachwieja), selecting physical models and data analysis methods, gathering and analysing the results, identifying perturbations of the $^{12}C^{17}O$ $A^1\Pi$ (υ = 5) level, preparing and editing the complete manuscript of the publication. I estimate my percentage contribution at 80%.

[H5] **R. Hakalla**, *First analysis of the Herzberg ($C^1\Sigma^+ – A^1\Pi$) band system in the less – abundant $^{13}C^{17}O$ isotopologue*, RSC Adv., **4**, 44394 – 44407 (2014).

The work presents the first measurements and analyses of spectra of the Herzberg ($C^1\Sigma^+ – A^1\Pi$) system in the less-abundant $^{13}C^{17}O$ isotopologue. The measurements were carried out under high resolution (reciprocal dispersion of 0.07 – 0.11 nm/mm, theoretical resolving power 2.28 – 2.74 × 10^5) using HADOS technique. The C – A (0, 1), (0, 2) and (0, 3) emission bands were recorded in the region of 22 950 – 26 050 cm^{-1} with SNR amounting to 60 : 1, 65 : 1 and 55 : 1, respectively. The $^{13}C^{17}O$ molecules were produced and excited in a modified CWHC lamp. Altogether, 224 spectral lines up to J_{max} = 30 were measured and rotationally analysed with absolute accuracy of wavenumber measurements reaching 0.003 cm^{-1}.

In the $^{13}C^{17}O$ $A^1\Pi$ (υ= 3) state, a complex, multistate perturbation was found, as well as states responsible for the observed irregularities. These are $d^3\Delta_i$ (υ = 8) and $a'^3\Sigma^+$ (υ = 13) rovibronic levels. The regions of occurrence and magnitudes of perturbations caused by them in both components of the Λ-doubling of the $A^1\Pi$ state were determined.

A theoretical model was fitted to wavenumbers of $^{13}C^{17}O$ C – A transition by means of the Curl-Dane-Watson [75,76] method obtaining a standard deviation fitting (1σ), which equals 0.0011 cm^{-1} – 0.0016 cm^{-1}. The following parameters were determined for the first time in the $^{13}C^{17}O$ isotopologue: rotational constants of the $C^1\Sigma^+(\upsilon = 0)$ Rydberg state, effective rotational constants of the $A^1\Pi$ (υ = 3) level, vibrational quantum $\Delta G^C_{1/2}$, rotational equilibrium constants of the $C^1\Sigma^+$ state, (0, 1) (0, 2) and (0, 3) band origins of the Herzberg system and their isotopic shifts, vibrational equilibrium constants of the $C^1\Sigma^+$ state determined by means of vibrational quanta $\Delta G^C_{1/2}$ of five species: $^{12}C^{16}O$, $^{12}C^{17}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{13}C^{18}O$. A merged analysis of the bands of the $C^1\Sigma^+ – A^1\Pi$ and $B^1\Sigma^+ – A^1\Pi$ systems **[H1**, **H3]** was performed, which made it possible to draw up a precise relative characteristic of the $C^1\Sigma^+$ (υ = 0) and $B^1\Sigma^+$ (υ = 0, 1) Rydberg states of the $^{13}C^{17}O$ molecule, that is, among others, calculation of υ^{CB}_{00}, υ^{CB}_{01} vibrational quanta. Parameters of the *RKR* potential curves of the $C^1\Sigma^+$ state and first experimental *FCF*, relative intensities, and *r*-centroids of the Herzberg system, as well as isotopic invariants U_{10} and U_{01} in the *BO* approximation in the $^{13}C^{17}O$ molecule were determined. Many vibrational and rotational equilibrium constants of the $C^1\Sigma^+$ state of six species: $^{12}C^{16}O$, $^{12}C^{17}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{13}C^{18}O$, were determined with higher accuracy. Also, it was an opportunity to work out a problem of inconsistency, which had been unresolved since 1969 year, between vibrational equilibrium constants of $^{12}C^{16}O$ $C^1\Sigma^+$ (ω_e = 2175.92 cm^{-1}, $\omega_e x_e$ = 14.76 cm^{-1}) given by Tilford et al. [57,81] and analogous values provided by Kępa et al. [82,83] (ω_e = 2119.23 cm^{-1}, $\omega_e x_e$ = 36.353 cm^{-1}). Both the analyses were based on the data from only one isotopologue. The values published by Tilford et al. [57,81] turned out to be consistent with the values obtained in this **[H5]** work: ω_e = 2173.6 (15) cm^{-1}, $\omega_e x_e$ = 13.45 (76) cm^{-1}.

[H6] **R. Hakalla**, *Investigation of the Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band system in $^{12}C^{17}O$*, J. Quant. Spectrosc. Radiat. Transfer, **164**, 231 – 247 (2015).

In this work, the Herzberg ($C^1\Sigma^+ – A^1\Pi$) band system was obtained and analysed for the first time in the less-abundant $^{12}C^{17}O$ isotopologue. The (0, 1), (0, 2) and (0, 3) emission bands were recorded by means of the HADOS method in the region of 22 800 – 26100 cm^{-1} under high resolution (reciprocal dispersion of 0.07 – 0.11 nm/mm, theoretical resolving power 2.28 – 2.74 × 10^5). SNR of the measured lines was approximately 70 : 1. The $^{12}C^{17}O$ molecules were produced and excited in a modified CWHC discharge lamp. 261 spectral lines of the $^{12}C^{17}O$ C – A system were interpreted. Their wavenumbers were measured with absolute accuracy reaching 0.0025 cm^{-1}.

Extensive, multistate rotational perturbations of the $\upsilon = 3$ level in the $^{12}C^{17}O$ $A^1\Pi$ state were found and interpreted, and also $d^3\Delta_i$ (υ = 8) and $a'^3\Sigma^+$ (υ = 13) perturbing rovibronic levels were identified. The regions of occurrence and magnitudes of perturbations were determined. The discussion was held on the possibility of the $^{12}C^{17}O$ $C^1\Sigma^+$ (υ= 0) level perturbations caused by the close lying $k^3\Pi$ (υ = 1, 2), $c^3\Pi$ (υ = 0), and $D'^1\Sigma^+$ (υ = 7) levels in the region of 92 000 cm^{-1}.

A theoretical model was fitted to wavenumbers of the $C^1\Sigma^+ – A^1\Pi$ (0, 1), (0, 2) and (0, 3) lines by means of the Curl-Dane-Watson [75,76] method, obtaining a standard deviation fitting (1σ) which equals 0.0012 cm^{-1} – 0.0025 cm^{-1}. For the first time the following were obtained in the $^{12}C^{17}O$ molecule: individual and rotational equilibrium constants and the parameters of the *RKR* potential curves of the $C^1\Sigma^+$ Rydberg state, C – A (0, 1), (0, 2) and (0, 3) band origins and their isotopic shifts, $\Delta G^C_{1/2}$ vibrational quantum, as well as *FCF*, relative intensities and *r*-centroids of the Herzberg system.

The first vibrational equilibrium constants of the $^{12}C^{17}O$ $C^1\Sigma^+$ state were determined (by means of vibrational quanta $\Delta G^C_{1/2}$ of six CO species). The vibrational equilibrium constants of $C^1\Sigma^+$ in the $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{17}O$ and $^{13}C^{18}O$ isotopologues were improved. Relative parameters of the rovibronic structure of the $C^1\Sigma^+$ and $B^1\Sigma^+$ Rydberg states were determined in the form of υ^{CB}_{00}, υ^{CB}_{01}, ΔB^{CB}_{00}, ΔB^{CB}_{01} differences in eight isotopologues: $^{12}C^{16}O$, $^{12}C^{17}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{17}O$, $^{13}C^{18}O$, $^{14}C^{16}O$ and $^{14}C^{18}O$. They were compared with the values predicted theoretically. The *RKR* potential curves of the $C^1\Sigma^+$, $k^3\Pi$, $c^3\Pi$, $E^1\Pi$, $B^1\Sigma^+$, and $D'^1\Sigma^+$ states, lying between the first dissociation limit and ionization energy of the $^{12}C^{17}O$ molecule, were plotted. In this work, a comprehensive isotopic analysis of the $C^1\Sigma^+$ Rydberg state was made on the basis of the data from eight CO species. This enabled us to improve isotopic invariants, especially U_{10}, of the $C^1\Sigma^+$ state in the *BO* approximation.

[H7] **R. Hakalla**, M. L. Niu, R. W. Field, E. J. Salumbides, A. N. Heays, G. Stark, J. R. Lyons, M. Eidelsberg, J. L. Lemaire, S. R. Federman, M. Zachwieja, W. Szajna, P. Kolek, I. Piotrowska, M. Ostrowska – Kopeć, R. Kępa, N. de Oliveira, W. Ubachs, *VIS and VUV spectroscopy of* $^{12}C^{17}O$ *and deperturbation analysis of the* $A^1\Pi$, $\upsilon = 1 – 5$ *levels*, RSC Adv., **6**, 31588 – 31606 (2016).

In this work, the first deperturbation analysis of the $A^1\Pi$ state in the $^{12}C^{17}O$ species was made. A complete experimental material, gathered so far and deriving from the experiments conducted by me on this isotopologue **[H2, H4, H6]** was used in the fit. Also, unobserved so far, $^{12}C^{17}O$ (0, 3), (0, 4) and (0, 5) bands of the Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) system **[H7]** as well as $^{12}C^{17}O$ $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) and $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) bands of the Hopfield – Birge systems **[H7]** were added. In order to record the new bands, presented in this work, two different experimental methods were used: (1) HADOS of the emission bands in the VIS range and (2) Fourier – transform spectroscopy (FTS) of the absorption bands in the vacuum ultraviolet (VUV) range.

In the first experiment, VIS – HADOS, the (0, 3), (0, 4) and (0, 5) bands of the $B^1\Sigma^+ \rightarrow A^1\Pi$ transition were observed under high resolution ($1.37 – 1.82 \times 10^5$) in the region of 15 100 – 18 400 cm^{-1}. SNR was approximately 100 : 1. Absolute accuracy of the wavenumber measurements reached 0.003cm^{-1}. The $^{12}C^{17}O$ molecules were produced and excited in a modified CWHC discharge lamp.

In the second experiment, VUV – FTS , spectra of the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) and $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) bands were recorded by means of the Fourier-transform spectrometer (FT spectrometer) installed on the DESIRS beamline of the SOLEIL synchrotron facility [84,85,87]. The measurements were conducted under high resolution (about 3×10^5) in the range of 86 900 – 92 100 cm^{-1}. SNR was 20 : 1. Absolute accuracy of the wavenumber measurements amounted to approximately 0.01 cm^{-1}. Results of analyses of the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ and $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ systems were introduced to the deperturbation calculation in order to:

- achieve an absolute reference of terms of the studied $A^1\Pi$ state,
- verify if the analysis is not influenced by a potential irregularity of the $B^1\Sigma^+$ and/or $C^1\Sigma^+$ Rydberg states being involved in the B – A and C – A transitions,
- include an independent set of molecular constants of the $B^1\Sigma^+$ ($\upsilon = 0$) and $C^1\Sigma^+$ ($\upsilon = 0$) rovibronic levels in the calculation, which should have reduced to a great extent the correlations between the determined model parameters; this, in turn, should have caused an expected convergence of the fit with a greater number of determined, statistically justified parameters.

In total, in the studied regions, 429 spectral lines of the $^{12}C^{17}O$ B – A and B – X, C – X systems were measured and interpreted. The new experimental data were combined with the results obtained in previous works **[H2, H4, H6]**. This comprehensive set of data of 982 spectral lines belonging to 27 bands (12 main bands and 15 bands consisting of so-called *extra lines*) was incorporated into the deperturbation analysis of the $A^1\Pi$ state carried out in the $^{12}C^{17}O$ molecule for the first time. Extra – lines are the spectral transitions involving perturbing states of the studied $A^1\Pi$ state and borrowing intensity from the main lines due to the mixing of the wavefunctions of the states taking part in the perturbations. The analysis took into account interactions of the rovibrational levels of the $A^1\Pi$ state with the $d^3\Delta_i$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $I^1\Sigma^-$, and $D^1\Delta$ states. The calculation was carried out on the basis of the effective Hamiltonian based method used in PGOPHER program written by C. Western [88] (relevant details are provided in chapters 4.2.3 and 5.2 of this Summary). As a result of the deperturbation analysis, the $A^1\Pi$ state and its perturbing states were described by means of a set of 52 independent parameters: deperturbed molecular constants, spin-orbit coupling parameters (in the case of $A^1\Pi \sim d^3\Delta_i$, $A^1\Pi \sim e^3\Sigma^-$ and $A^1\Pi \sim a'^3\Sigma^+$ interactions) and rotational-electronic coupling parameters of the *L-uncoupling* type (in the case of $A^1\Pi \sim I^1\Sigma^-$ and $A^1\Pi \sim D^1\Delta$ interactions). Correlation matrix was verified in detail at every stage of the fit and finally showed a satisfactorily low level of mutual correlations between determined parameters of the model. The root-mean-square error (RMSE) of weighed residuals of all wavenumbers of the lines used in the deperturbation calculation was 0.006 cm^{-1}. Therefore, the fitted model reproduces this extensive set of experimental data very well. In this work, the first deperturbed rotational equilibrium constants of the $^{12}C^{17}O$ $A^1\Pi$ state as well as *FCF* for $^{12}C^{17}O$ $B^1\Sigma^+$ (υ = 0 – 2) → $A^1\Pi$ (υ = 0 – 6), $C^1\Sigma^+$ (υ = 0 – 2) → $A^1\Pi$ (υ = 0 – 6), and $A^1\Pi$ (υ = 0 – 6) → $X^1\Sigma^+$ (υ = 0 – 10) transitions were calculated. 309 terms belonging to the $^{12}C^{17}O$ $A^1\Pi$ (υ = 1 – 5), $B^1\Sigma^+$ (υ = 0), $C^1\Sigma^+$ (υ = 0), $d^3\Delta_i$ (υ = 11), $e^3\Sigma^-$ (υ = 4), $a'^3\Sigma^+$ (υ = 10, 13), $I^1\Sigma^-$ (υ = 3, 6) and $D^1\Delta$ (υ = 1) states were determined.

The precise global deperturbation analysis of the $A^1\Pi$ state also enabled us to determine isotopologue-independent, electronic spin-orbit $\boldsymbol{a}_{A\sim d,e,a'}$ and rotation-electronic $\boldsymbol{b}_{A\sim I,D}$ perturbation parameters, which have so far been determined only three times: in $^{12}C^{16}O$ by Field et al. [61] and Le Floch et al. [60] as well as in $^{12}C^{18}O$ by Haridass et al. [62]. A comparison of these values with our results showed their satisfactory consistency in the three standard deviations (3σ), which proves that the deperturbation calculation performed by us was correct and of high quality.

My contribution to this work included drawing 3 grants **[P1, P2, P4]**[*] to carry out researches and to consult methods of deperturbation analysis; performing the ^{12}C deposition inside the hollow-cathode of the discharge lamp; planning the scope and conditions of experimental work in the HADOS method; performing measurements and calibration of the spectra of the $^{12}C^{17}O$ B – A (0, 3), (0, 4) and (0, 5) bands (in collaboration with M. Zachwieja); gathering and analysing the results for $^{12}C^{17}O$ B – A (0, 3), (0, 4) and (0, 5) bands; identifying perturbations discovered in the $^{12}C^{17}O$ $A^1\Pi$ (υ = 4) level; performing a global deperturbation calculation of the $A^1\Pi$ (υ = 1 – 5) state, consulted at the initial and final stages by M. Niu, R. Field, W. Ubachs and E. Salumbides; determining quantum-mechanical parameters and vibrational overlap integrals as well as isotopologue-independent electronic perturbation parameters ***a*** and ***b;*** preparing and editing the complete manuscript of the publication (except for chapter 1 elaborated together with W. Ubachs as well as chapter 2.2, figures 4, 5

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[*] The numbering of the **[P1 – P6]** projects and research grants is consistent with the List of Publications and Achievements (Appendix 3).

and table 4 worked out by A. Heays); final editing of the manuscript after co-authors' comments. I estimate my percentage contribution at 60%.

[H8] **R. Hakalla**, M. L. Niu, R. W. Field, A. N. Heays, E. J. Salumbides, G. Stark, J. R. Lyons, M. Eidelsberg, J. L. Lemaire, S. R. Federman, N. de Oliveira, W. Ubachs, *Fourier – transform spectroscopy of $^{13}C^{17}O$ and perturbation analysis of the $A^1\Pi$ (υ = 0 – 3) levels*, J. Quant. Spectrosc. Radiat. Transfer, **189**, 312 – 328 (2017).

In this work, the first deperturbation analysis of the $A^1\Pi$ state in the $^{13}C^{17}O$ isotopologue was performed. It took into account results of all studies conducted in the works **[H1, H3, H5]** and also new, unobserved so far, (0, 0) and (0, 3) bands of the Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) system **[H8]** as well as $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0), (1, 0) and $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) bands of the Hopfield – Birge systems **[H8]** were added. To obtain them, two experimental methods were used using Fourier – transform spectroscopy: (1) VIS – FTS and (2) VUV – FTS.

In the first experiment, VIS – FTS, emission spectra of the $^{13}C^{17}O$ $B^1\Sigma^+ \rightarrow A^1\Pi$ (0, 0) and (0, 3) bands were recorded by means of an FT spectrometer calibrated and working in LSM, UR. Instrumental resolution was 0.018 cm^{-1} for the studied region of 17 950 – 22 500 cm^{-1}. The $^{13}C^{17}O$ molecules were produced and excited in a modified CWHC lamp. In the obtained spectrum, 315 spectral lines were identified, of which as much as 122 are extra-lines being the result of transitions from the upper $B^1\Sigma^+$ state to the states perturbing the $A^1\Pi$ state. SNR was approximately 70 : 1 and 100 : 1 for (0, 0) and (0, 3) band, respectively. Absolute accuracy of the wavenumber measurements was 0.003 cm^{-1}.

In the second experiment, VUV – FTS, $^{13}C^{17}O$ $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) and (1, 0) and $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) bands were recorded by means of a FT spectrometer installed on the DESIRS beamline of the SOLEIL synchrotron and working in VUV. In the 86 800 – 92 100 cm^{-1} region, at an instrumental resolution of 0.20 cm^{-1}, 165 spectral lines were measured and identified with absolute accuracy reaching 0.04 cm^{-1}. SNR of the observed lines was approximately 20 : 1.

In the studied regions within the current work, in total 480 lines belonging to the five bands of the $^{13}C^{17}O$ $B^1\Sigma^+ \rightarrow A^1\Pi$, $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ and $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ systems were analysed. These new experimental data were combined with the results obtained from the analyses of the $^{13}C^{17}O$ B → A and C → A band systems **[H1, H3, H5]**. In total, 1003 spectral lines deriving from 30 bands (12 main bands and 18 bands consisting of extra-lines) were used in the first deperturbation analysis of the $A^1\Pi$ state in $^{13}C^{17}O$. In the fit, interaction of this state with rovibrational levels of the $d^3\Delta_i$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $I^1\Sigma^-$ and $D^1\Delta$ states was taken into account as well as weak irregularities of about 0.05 – 0.075 cm^{-1}, which were noticed for the υ = 0 level of the $B^1\Sigma^+$ state. The fit was carried out using PGOPHER program [88]. The model satisfactorily described the $A^1\Pi$ (υ = 0 – 3), $B^1\Sigma^+$ (υ = 0, 1), $C^1\Sigma^+$(υ = 0), $d^3\Delta_i$ (υ = 4, 7, 8), $e^3\Sigma^-$ (υ = 1, 2, 4), $a'^3\Sigma^+$ (υ = 10, 12, 13), $I^1\Sigma^-$ (υ = 2, 3, 5) and $D^1\Delta$ (υ = 1, 4) rovibronic levels, as well as homogeneous spin-orbit $A^1\Pi \sim d^3\Delta_i$, $A^1\Pi \sim e^3\Sigma^-$, $A^1\Pi \sim a'^3\Sigma^+$ interactions, and heterogeneous rotation-electronic $A^1\Pi \sim I^1\Sigma^-$, $A^1\Pi \sim D^1\Delta$ interactions of the *L-uncoupling* type. Correlation matrix showed a satisfactorily low level of mutual correlations between finally determined parameters of the model. As a result of the deperturbation analysis, the $A^1\Pi$ state and its perturbing states were described with the 62 independent parameters: deperturbed molecular constants as well as spin-orbit and rotation-electronic (*L-uncoupling*) perturbation parameters. The RMSE values of weighed residuals of line wavenumbers used in the deperturbation calculation was 0.007 cm^{-1}, which proves that the model was very well fitted to this extensive set of experimental data. 335 terms of $^{13}C^{17}O$ belonging to the $A^1\Pi$ (υ = 0 – 3), $e^3\Sigma^-$ (υ = 1, 4), $d^3\Delta_i$ (υ = 4, 7, 8), $a'^3\Sigma^+$ (υ = 10, 13), $I^1\Sigma^-$ (υ = 2, 3) and $D^1\Delta$ (υ = 1, 4) states were also obtained.

Finally, isotopologue-independent spin-orbit $\boldsymbol{a}_{A\sim d,e,a'}$ and rotation-electronic $\boldsymbol{b}_{A\sim I,D}$ perturbation parameters were determined. The values of determined invariants were compared with results deriving from other deperturbation calculations of the $A^1\Pi$ state of the CO molecule (Field et al. [61] and Le Floch et al. [60] on the basis of $^{12}C^{16}O$, Haridass et al. [62] on the basis of $^{12}C^{18}O$, and Hakalla et al. **[H7]** on the basis of $^{12}C^{17}O$), and they were found in an satisfactory consistency within 3σ. It proves that the deperturbation analysis performed in $^{13}C^{17}O$ was correct and of high accuracy.

My contribution in this work included drawing 2 grants **[P3, P5]**[*] to carry out researches and to consult results of the deperturbation analysis; performing the ^{13}C isotope deposition inside the hollow-cathode of the discharge lamp; planning the scope and conditions of experimental work in the VIS – FTS experiment; performing measurements and calibration of the spectra of the $^{13}C^{17}O$ B – A (0, 0) and (0, 3) bands using FT spectrometer (LSM UR); gathering and analysing the results for $^{13}C^{17}O$ B – A (0, 0) and (0, 3) bands; identifying perturbations discovered in the υ = 3 and υ = 0 (J > 21) levels of the $^{13}C^{17}O$ $A^1\Pi$ state; noticing irregularities of the $^{13}C^{17}O$ $B^1\Sigma^+$ (υ = 0) level (together with A. Heays) and verification of possible perturbing states (together with R. Field); performing a global deperturbation analysis of the $A^1\Pi$ (υ = 1 – 5) level (the final results was consulted with M. Niu, R. Field, W. Ubachs and E. Salumbides); determining quantum-mechanical parameters and vibrational overlap integrals; determining isotopologue-independent electronic perturbation parameters $\boldsymbol{a}$ and $\boldsymbol{b}$; preparing the complete manuscript of the publication (except for chapter 1 elaborated together with W. Ubachs, chapter 2.2 and figures 3-5 worked out by A. Heays and J. Lemaire, as well as chapter 3.1 elaborated together with R. Field); final editing of the manuscript after co-authors' comments. I estimate my percentage contribution at 60%.

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[*] The numbering of the **[P1 – P6]** projects and research grants is consistent with the List of Publications and Achievements (Appendix 3).

4.2.3. Perturbations of the $A^1\Pi$ and $B^1\Sigma^+$ states in CO[*]

The CO molecular orbitals are conventionally labelled in energy and symmetry order: 1σ (σ1s), 2σ (σ*1s), 3σ (σ2s), 4σ (σ*2s), 1π (π2p), 5σ (σ2p), 2π (π*2p), 6σ (3sσ), 7σ (3pσ), where (1 - 2)σ are core orbitals, (3 - 5)σ and (1 - 2)π are valence orbitals, and (6 - 7)σ are Rydberg orbitals. The principal configurations of the electronic states considered in the **[H1 – H8]** publications are:

$X^1\Sigma^+$: $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,1\pi^4\,5\sigma^2$,
$A^1\Pi$ and $a^3\Pi$: $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,1\pi^4\,5\sigma^1\,2\pi^1$,
$a'^3\Sigma^+$, $e^3\Sigma^-$, $d^3\Delta_i$, $I^1\Sigma^-$, and $D^1\Delta$: $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,1\pi^3\,5\sigma^2\,2\pi^1$,
$B^1\Sigma^+$ and $C^1\Sigma^+$: $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,1\pi^4\,5\sigma^1$ ($6\sigma^1$ or $7\sigma^1$),

The spin-orbit interactions between the $A^1\Pi$ state and the $a'^3\Sigma^+$, $e^3\Sigma^-$, $d^3\Delta_i$ states, as well as rotation-electronic interactions of the *L-uncoupling* type between the $A^1\Pi$ state and the $I^1\Sigma^-$, $D^1\Delta$ states, involve a 1π → 5σ orbital promotion. Relationships between perturbation parameters of the interactions and isotopologue-independent electronic perturbation parameters $\boldsymbol{a}_{\mathrm{A\sim d,e,a'}}$ and $\boldsymbol{b}_{\mathrm{A\sim I,D}}$ are as follows [60]:

$$\alpha_{\mathrm{A\sim d}} = \left\langle \mathrm{A}^1\Pi,\ \upsilon_{\mathrm{A}} \left|\mathbf{H}^{\mathbf{SO}}\right| \mathrm{d}^3\Delta, \upsilon_{\mathrm{d}} \right\rangle = -\left(\tfrac{\sqrt{2}}{4}\right)\mathbf{a}_{\mathbf{A\sim d}}\langle \upsilon_{\mathrm{A}}|\upsilon_{\mathrm{d}}\rangle, \tag{1}$$

$$\alpha_{\mathrm{A\sim e}} = \left\langle \mathrm{A}^1\Pi,\ \upsilon_{\mathrm{A}} \left|\mathbf{H}^{\mathbf{SO}}\right| \mathrm{e}^3\Sigma^-, \upsilon_{\mathrm{e}} \right\rangle = -\left(\tfrac{1}{4}\right)\mathbf{a}_{\mathbf{A\sim e}}\langle \upsilon_{\mathrm{A}}|\upsilon_{\mathrm{e}}\rangle, \tag{2}$$

$$\alpha_{\mathrm{A\sim a'}} = \left\langle \mathrm{A}^1\Pi,\ \upsilon_{\mathrm{A}} \left|\mathbf{H}^{\mathbf{SO}}\right| \mathrm{a'}^3\Sigma^+, \upsilon_{\mathrm{a'}} \right\rangle = \left(\tfrac{1}{4}\right)\mathbf{a}_{\mathbf{A\sim a'}}\langle \upsilon_{\mathrm{A}}|\upsilon_{\mathrm{a'}}\rangle, \tag{3}$$

$$2\beta_{\mathrm{A\sim I}}\sqrt{\mathrm{x}} = \langle \mathrm{A}^1\Pi,\ \upsilon_{\mathrm{A}}\,|\mathbf{H}^{\mathbf{RE}}|\ \mathrm{I}^1\Sigma^-, \upsilon_{\mathrm{I}}\rangle = -\sqrt{\mathrm{x}}\,\mathbf{b}_{\mathbf{A\sim I}}\langle\, \upsilon_{\mathrm{A}}|\mathbf{B}(\mathbf{R})|\upsilon_{\mathrm{I}}\rangle, \tag{4}$$

$$\beta_{\mathrm{A\sim D}}\sqrt{\mathrm{x}-2} = \langle \mathrm{A}^1\Pi,\ \upsilon_{\mathrm{A}}\,|\mathbf{H}^{\mathbf{RE}}|\ \mathrm{D}^1\Delta, \upsilon_{\mathrm{D}}\rangle = \sqrt{\mathrm{x}-2}\,\mathbf{b}_{\mathbf{A\sim D}}\langle\, \upsilon_{\mathrm{A}}|\mathbf{B}(\mathbf{R})|\upsilon_{\mathrm{D}}\rangle, \tag{5}$$

where $x = \sqrt{J(J+1)}$, α_i – spin-orbit perturbation parameter, β_i – rotation-electronic perturbation parameter, $\mathbf{H}^{\mathbf{SO}}$ – spin-orbit operator, $\mathbf{H}^{\mathbf{RE}}$ – rotation-electronic operator, $\langle \upsilon_A | \upsilon_{d,e,a'} \rangle$ and $\langle \upsilon_A | B(R) | \upsilon_{I,D} \rangle$ – vibrational overlap integrals. The relationships between the α_i, $\beta_{\mathrm{A\sim I}}$, $\beta_{\mathrm{A\sim D}}$ perturbation parameters used by Field et al. [61], Le Floch et al. [60] and Haridass et al. [62], and η_{i}, $\xi_{\mathrm{A\sim I}}$, $\xi_{\mathrm{A\sim D}}$ used in works **[H7 – H8]**, are as follows **[H7 – H8]**:

$$\eta_i = \alpha_i\sqrt{3}\,, \tag{6}$$

$$\xi_{A\sim I} = \beta_{A\sim I}\sqrt{2}, \tag{7}$$

$$\xi_{A\sim D} = \beta_{A\sim D}, \tag{8}$$

where subscript „*i*" indicates A ~ d, A ~ I or A ~ D spin-orbit interactions. The relationships are the results of the differences in definitions of the interaction parameters, which are the part of the off-diagonal matrix elements in Hamiltonians used in the deperturbation fits in works **[H7 – H8]** and in Ref. [60]. The effective Hamiltonian and matrix elements used in the calculations described in **[H7]** and **[H8]** works are presented in Table 1.

Thanks to precise experimental and analytical methods applied in the work **[H8]**, extremely weak irregularities (0.05 – 0.075 cm^{-1}) were discovered for *J* = 0, 7, 16, 21, 26 and 34 – 36 rotational levels in the lowest *υ* = 0 vibrational level of the $B^1\Sigma^+$ Rydberg state, for the first time in $^{13}C^{17}O$, which is showed in Fig. 1:

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[*] The chapter elaborated on the basis of publication **[H8]**.

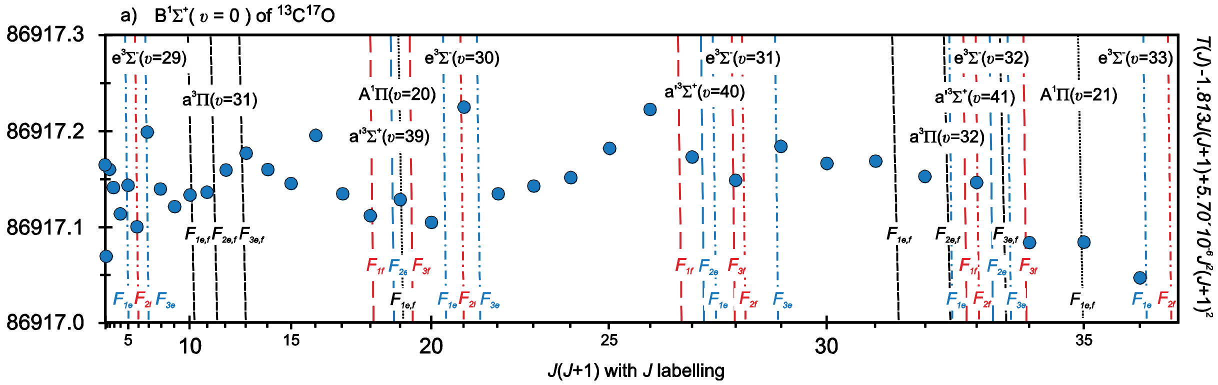

Figure 1. **[H8]** Reduced terms (in cm^{-1}) of the B$^1\Sigma^+$ (υ = 0) level in the less-abundant ^{13}C^{17}O isotopologue together with hypothetically unperturbed rovibrational terms of the states suspected of being the cause of these irregularities.

In the publication **[H8]** we considered in detail all possibilities of perturbations of the B$^1\Sigma^+$(υ = 0) level caused by studied so far in ^{13}C^{17}O **[H1, H3, H5, H8]** rovibrational levels of the electronic states occurring in its vicinity, thus by the A$^1\Pi$, e$^3\Sigma^-$, a'$^3\Sigma^+$, d$^3\Delta_i$, D$^1\Delta$, or/and I$^1\Sigma^-$:

a) The possible rotation-electronic interaction of the *L-uncoupling* type between the B$^1\Sigma^+$ and A$^1\Pi$ states involves a $2\pi \rightarrow 6\sigma$ orbital promotion of an electron. The magnitude of this $2\pi \rightarrow 6\sigma$ perturbation matrix element is likely to be weaker than that for the same type of perturbation, involves a $1\pi \rightarrow 5\sigma$ promotion. This should happen because the 1π and 5σ orbitals are mostly of O-atom localized 2p character while the 2π orbital resembles a dδ Rydberg orbital and the 6σ orbital is an sσ Rydberg orbital. The shape of the 2π molecular antibonding valence orbital resembles that of an atomic Rydberg orbital with orbital angular momentum $2\hbar$ and projection of angular momentum along the molecular axis of $1\hbar$: |2,1>.

b) The spin-orbit (*s-o*) B$^1\Sigma^+ \sim$ e$^3\Sigma^-$ interaction would have to take place with (2π, 5σ) $\rightarrow$ (1π, 6σ) double-promotion of an electron. Since the *s-o* operator is a one-electron operator, which undergoes ΔS = 0, 1 selection rule, so the *s-o* matrix element of the e ~ B interaction is zero in first-order approximation. Only a second-order interaction, mediated by a nearby located vibrational level of the a$^3\Pi$ or A$^1\Pi$ state, could result in a very weak e ~ a/A ~ B indirect perturbation.

Table 1. Effective Hamiltonian and matrix elements used in deperturbation analyses of the $A^1\Pi$ state in $^{12}C^{17}O$ **[H7]** and $^{13}C^{17}O$ **[H8]** [a, b, c, d]

	$A^1\Pi$	$I^1\Sigma^-$	$D^1\Delta$	$e\ ^3\Sigma^-$	$a'\ ^3\Sigma^+$	$d\ ^3\Delta$
$A^1\Pi$	$T_v + \left(B \pm \frac{q}{2}\right)\widehat{\boldsymbol{N}}^2$ $-D\widehat{\boldsymbol{N}}^4 + H\widehat{\boldsymbol{N}}^6$	$\xi_i(I_v) \times$ $\left(\widehat{\boldsymbol{N}}_+\hat{\boldsymbol{L}}_- + \widehat{\boldsymbol{N}}_-\hat{\boldsymbol{L}}_+\right)$	$\xi_i(D_v) \times$ $\left(\widehat{\boldsymbol{N}}_+\hat{\boldsymbol{L}}_- + \widehat{\boldsymbol{N}}_-\hat{\boldsymbol{L}}_+\right)$	$\eta_i(e_v)\hat{\boldsymbol{L}} \cdot \widehat{\boldsymbol{S}}$	$\eta_i(a'_v)\hat{\boldsymbol{L}} \cdot \widehat{\boldsymbol{S}}$	$\eta_i(d_v)\hat{\boldsymbol{L}} \cdot \widehat{\boldsymbol{S}}$
$I^1\Sigma^-$		$T_v + B\widehat{\boldsymbol{N}}^2$ $-D\widehat{\boldsymbol{N}}^4 + H\widehat{\boldsymbol{N}}^6$	0	0	0	0
$D^1\Delta$			$T_v + B\widehat{\boldsymbol{N}}^2$ $-D\widehat{\boldsymbol{N}}^4 + H\widehat{\boldsymbol{N}}^6$	0	0	0
$e\ ^3\Sigma^-$				$T_v + B\widehat{\boldsymbol{N}}^2$ $-D\widehat{\boldsymbol{N}}^4 + H\widehat{\boldsymbol{N}}^6$ $+\frac{2}{3}\lambda\left(3\widehat{\boldsymbol{S}}_z^2 - \widehat{\boldsymbol{S}}^2\right)$	0	0
$a'\ ^3\Sigma^+$					$T_v + B\widehat{\boldsymbol{N}}^2$ $-D\widehat{\boldsymbol{N}}^4 + H\widehat{\boldsymbol{N}}^6$ $+\frac{2}{3}\lambda\left(3\widehat{\boldsymbol{S}}_z^2 - \widehat{\boldsymbol{S}}^2\right)$ $+\gamma\left(\widehat{\boldsymbol{N}} \cdot \widehat{\boldsymbol{S}}\right)$	0
$d\ ^3\Delta$						$T_v + B\widehat{\boldsymbol{N}}^2$ $-D\widehat{\boldsymbol{N}}^4 + H\widehat{\boldsymbol{N}}^6$ $+\frac{2}{3}\lambda\left(3\widehat{\boldsymbol{S}}_z^2 - \widehat{\boldsymbol{S}}^2\right)$ $+\gamma\left(\widehat{\boldsymbol{N}} \cdot \widehat{\boldsymbol{S}}\right) + A\hat{\boldsymbol{L}}_z\widehat{\boldsymbol{S}}_z$ $+\frac{1}{2}A_D\lambda\left(\widehat{\boldsymbol{N}}^2\hat{\boldsymbol{L}}_z\widehat{\boldsymbol{S}}_z + \hat{\boldsymbol{L}}_z\widehat{\boldsymbol{S}}_z\widehat{\boldsymbol{N}}^2\right)$

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[a] According to the work by C. Western [88] and description included in his programme PGOPHER [89].

[b] T_υ means rotation-less energy determined in relation to the υ = 0 level of the $X^1\Sigma^+$ ground state, η_i: spin-orbit interaction parameter, ξ_i: rotation-electronic interaction parameter of the *L-uncoupling* type. Notation of remaining symbols is consistent with the standard introduced by IUPAC (*International Union of Pure and Applied Chemistry*) for parameters of the fine and hyperfine structure of the molecules [90].

[c] The matrix is symmetric, thus the left-sided, non-diagonal elements, not shown in the Hamiltonian, are equivalent to the right-sided, non-diagonal ones. The mutual interactions between the perturbing states are neglected.

[d] Symbols '+' and '–' for the diagonal element of the $A^1\Pi$ state denote levels of symmetry *e* and *f*, respectively.

c) The possibility of a direct *s-o* $B^1\Sigma^+ \sim a'^3\Sigma^+$ perturbation can be ruled out by the $\Delta\Omega = 0$ and ± ↔ ± parity selection rules for this type of interaction. The $a'^3\Sigma^+$ state contains only a 0^- component and the $B^1\Sigma^+$ state consists exclusively of a 0^+ component. Nevertheless, there is possible interaction between the a' and B states, but only via Ω = 1 component of an intermediate $a^3\Pi$ or $A^1\Pi$ state:

$$\left\langle {}^3\Sigma_1^+ \middle| \boldsymbol{H^{SO}} \middle| {}^3\Pi_1 \right\rangle \left\langle {}^3\Pi_1 \middle| \boldsymbol{H^{rot}}(S - uncoupling) \middle| {}^3\Pi_0 \right\rangle \left\langle {}^3\Pi_0 \middle| \boldsymbol{H^{SO}} \middle| {}^1\Sigma_0^+ \right\rangle, \tag{9}$$

or

$$\left\langle {}^3\Sigma_1^+ \middle| \boldsymbol{H^{SO}} \middle| {}^1\Pi_1 \right\rangle \left\langle {}^1\Pi_1 \middle| \boldsymbol{H^{rot}}(L - uncoupling) \middle| {}^1\Sigma_0^+ \right\rangle. \tag{10}$$

It is always possible to evaluate a matrix element using basis functions expressed in any Hund's coupling case. We find *Hund's case (a)* to be most convenient for valence states of almost all diatomic molecules. The *s-o* operator is diagonal in Ω in *Hund's case (a)*. The *s-o* matrix element between pure Ω = 0 and 1 states is rigorously zero. This is true for all S and all Λ basis states. All terms in the field free Hamiltonian are diagonal in parity. The eigenstates of a $^3\Sigma^+$ state for each value of J (J is rigorously conserved at zero electric field; nonzero nuclear spins can weakly break the J quantum number, but this effect is negligible for $^{13}C^{17}O$) are linear combinations of Ω = 0 and 1 for *f*-symmetry and pure Ω = 1 for *e*-symmetry. The $^3\Sigma^+$ (Ω = 0) basis state has *f* symmetry but the $^1\Sigma^+$ state consists exclusively of *e*-symmetry Ω = 0 basis states. Hence, there can be no direct perturbation between $B^1\Sigma^+$ and $a'^3\Sigma^+$ states. Contrary to the opinion of Kovács expressed in his book [91] (Fig. 4.55 p. 267), the F_2 component of $a^3\Sigma^+$ state is a pure Ω = 1 state. It cannot perturb $^1\Sigma^+$ via *s-o* because that is a pure Ω = 0 state. In order for such a perturbation to occur, there needs to be a third electronic state, either $^3\Pi$ or $^1\Pi$, that can perturb via a combination of *L-uncoupling* and *s-o* mechanisms, what it was showed in equations (9) and (10).

However, the above-mentioned possibilities may be insufficient to explain the irregularities occurring in the $^{13}C^{17}O$ $B^1\Sigma^+$ (υ = 0) state, because obtained in the work **[H8]** the vibrational overlap integrals between the $B^1\Sigma^+$ and $A^1\Pi$ and/or $a^3\Pi$ states, $\langle \upsilon_B | \boldsymbol{B(R)} | \upsilon_A \rangle \approx 10^{-3}$ cm^{-1} and $\langle \upsilon_B | \upsilon_a \rangle \approx 10^{-5}$, are too small for such perturbations to be noticeable. For the same reason, the allowed direct interaction between $B^1\Sigma^+$ and $a^3\Pi_{0+}$ states also does not explain the discussed issue. However, it should be noticed that the energy region under consideration is located in a neighbourhood of the first dissociation limit $C(^3P_0) + O(^3P_2)$, which creates the asymptotic convergence limit, among others, for the $A^1\Pi$ and $a^3\Pi$ state. Determination of values of so high located terms by means of equilibrium constants, obtained on the basis of a few first vibrational levels, is based on the very strong extrapolations, which leads to the reasonable uncertainties of the energy level positions.

d) Finally, the interactions between rovibronic levels of the $B^1\Sigma^+$ and $d^3\Delta$, $B^1\Sigma^+$ and $D^1\Delta$ states, as well as $B^1\Sigma^+$ and $I^1\Sigma^-$ states are forbidden by the selection rules for rotational perturbations:

- $\Delta S = 0$ and $\Delta\Omega = 0, \pm1$ (for $B^1\Sigma^+ \sim d^3\Delta$),
- $\Delta\Omega = 0, \pm1$ (for $B^1\Sigma^+ \sim D^1\Delta$),
- ± ↔ ± (for $B^1\Sigma^+ \sim I^1\Sigma^-$).

Because of the above mentioned reasons, so far we have not managed to identify state/states perturbing the $B^1\Sigma^+(\upsilon = 0)$ level of the $^{13}C^{17}O$ molecule. A probable solution is existence of another, unknown so far, Rydberg state of the $^1\Pi$, $^3\Pi$, or $^3\Sigma^-$ type, in the studied region. This hypothesis, however, requires the further investigations, which I intend to carry out in the near future.

4.2.4. Sources of the obtained molecular spectra

In order to obtain emission spectra of the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues, both in the HADOS and in VIS – FTS method, I used a modified, glow discharge, water cooled CWHC lamps [92] with the both-side open and Cr-Ni filler, steel hollow-cathode, as well as two anodes, designed and produced in LSM UR by the team of: M. Zachwieja, W. Szajna and R. Hakalla. The most important modification was such a selection of materials, geometrical dependencies of their component elements and methods of preparation of the workspaces, so that the synthesis of $^{12}C^{17}O$ and $^{13}C^{17}O$ would proceed inside the lamps without participation of any carrier gas. This is how we managed to overcome the greatest limitations of the CWHC lamps, which had produced spectra from a ready composite placed on walls of a hollow-cathode (c*omposite wall*), whose atoms or particles are ejected in the presence of the carrier gas. It is in fact one of the most destructive factors in the process of creating and exciting of the less-abundant $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues, because the carrier gas causes uncontrolled, rapid ejection of the whole, previously deposited (see below), carbon nano-deposit from the hollow-cathode area, which results in a very quick wear of it and goes out of the lamp. At the same time, the unfavourable process of ejecting the cathode material begins (in this case mainly Cr, Ni, Fe and C), whose atomic lines pollute the investigated spectra and cause a significant increase in their backgrounds. The ability to eliminate carrier gas was therefore essential for a suitably long-term process of creating, exciting and relaxation of the isotopologues I have been interested in.

The CWHC lamp can operate in three modes:

(I) anode-cathode,
(II) anode-cathode and cathode-anode,
(III) anode-cathode, cathode-anode, and anode-anode, where one of the anode becomes a cathode.

Thanks to this, it was possible to obtain highly excited rovibronic spectra of the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues.

The working area of the lamp was prepared for the synthesis of the less-abundant $^{12}C^{17}O$ **[H2, H4, H6, H7]** and $^{13}C^{17}O$ **[H1, H3, H5, H8]** molecules and for their excitation, as well as for stable, long-term relaxation of these species in the following way:

a) At first, the CWHC lamps were filled with a mixture of helium and acetylene $^{12}C_2D_2$ (Cambridge Isotopes, spectral purity ^{12}C: 99.99 %) **[H2, H4, H6, H7]** or $^{13}C_2D_2$ (Cambridge Isotopes, spectral purity ^{13}C: 99 – 99.96 %) **[H1, H3, H5, H8, A10, A15]** under the pressure of approximately 6 – 7 Tr.

b) Next, dc electric current was passed through the mixture (U ≈ 350 – 400V, I = 30 – 40 mA) for 80 – 200 hours.

c) After deposition of the suitable amounts of ^{12}C or ^{13}C atoms inside the hallow-cathodes of the lamps, they were evacuated. Next, they were filled with oxygen including isotope $^{17}O_2$ (Sigma-Aldrich, of spectral purity 60% **[H1, H2, H7, A10]** or 70% **[H3, H4, H5, H6, H8, A15]**) under a constant pressure of approximately 2 Tr. Since that moment the lamps were ready to operate.

d) The lamps were used in mode (II). Inclusion of the discharge (III) turned out to be unfavourable, since it caused uncontrolled and too rapid ejections of the whole nano-deposit of carbon from the hallow-cathode to the workspace of the lamps, which results in a very quick wear of them and stopping work of the lamps. At the same time, the adverse processes of ejecting the cathode materials began.

e) Electrodes were working under 2 × 600 – 700 V and 2 × 35 – 50 mA dc conditions. At that time, there was a gradual ejection of carbon deposited inside the cathode, dissociation of molecular oxygen into single atoms, and synthesis of $^{12}C^{17}O$ or $^{13}C^{17}O$.

f) The properly adjusting pressure inside the lamp (about 2 Tr) to a deliberately predefined hollow-cathode filler diameter (5 mm), that is, choosing the length of the free path of electrons with respect to that diameter, resulted in the so-called *cathode effect*, i.e. the focusing of the negative glow of the plasma in the interior of the hallow-cathode and the significant increase of the amperage, and thus the brightness of the source. The estimated temperature of the formed $^{12}C^{17}O$ or $^{13}C^{17}O$ plasma was 600 – 700 K.

These conditions were tested and recognized as optimal to obtain the spectra of the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues, because *plateau* of intensity of molecular lines was constant for approximately 6 hours during the operation of the lamps. This is a sufficient time to carry out satisfactory recording of a single band of the B – A or C – A system using HADOS method (of an average band width of 500 cm^{-1} in the VIS region, with opening time 200 ms of the counter gate), as well as entire VIS spectrum using FTS method (with instrumental resolution 0.018 cm^{-1} and the number of scans 128).

4.3. Summary and importance of the results of the [H1 – H8] cycle of publications as well as discussion of their possible application

The cycle of publications **[H1 – H8]** described above include the first observations and analyses of the Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) and Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band systems, as well as the following systems: $B^1\Sigma^+ \rightarrow d^3\Delta_i$, $B^1\Sigma^+ \rightarrow e^3\Sigma^-$, $B^1\Sigma^+ \rightarrow a'^3\Sigma^+$, $B^1\Sigma^+ \rightarrow I^1\Sigma^-$ and $B^1\Sigma^+ \rightarrow D^1\Delta$ in less-abundant isotopologues of carbon monoxide, $^{12}C^{17}O$ and $^{13}C^{17}O$. Thanks to properly selected experimental methods:

(I) a modified CWHC lamps,
(II) a high-accuracy dispersive optical spectroscopy (HADOS),
(III) and Fourier-transform spectroscopy (VIS – FTS),

high-resolution spectra were obtained of a high quality. For each band, the rotational interpretations of the spectra were made, which were enormously difficult due to specificity of research into multistate perturbed levels and of analyse of the less-abundant isotopologue complex spectra. They ended in recognition of 1722 lines belonging to 52 bands of the B → A, C → A, B → d, B → e, B → a, B → I, and B → D transitions. Obtained lines are characterized by a good SNR reaching up to 150 : 1 and *full width at half maximum* (FWHM) from 0.08 to 0.15 cm^{-1}, with the 0.06 cm^{-1} physical width of the CO lines in the investigated regions. Thanks to this, it was possible to observe even very small irregularities of the rovibronic structures of the bands, and through these, to precisely identify perturbing states.

On the basis of such a prepared extensive experimental material **[H1 – H8]**, the first deperturbation analyses of the $A^1\Pi$ state were carried out in the $^{12}C^{17}O$ **[H7]** and $^{13}C^{17}O$ **[H8]** species. They were very difficult not only because of extensive, multistate perturbations, but also due to scant experimental information on the remaining electronic states in those isotopologues. An independent set of molecular constants of the $B^1\Sigma^+$ and $C^1\Sigma^+$ states from analyses of the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ and $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ systems in the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues were included into the calculations. It resulted in significantly decreasing of the correlations between fitted parameters, causing convergence of the calculations with greater number of statistically justified parameters. In total, in both analyses, 1985 molecular lines were used deriving from 57 bands. The global deperturbation analyses lasted almost two years. A satisfactory set of 114 independent molecular parameters, including 27 parameters of interactions between the $A^1\Pi$ state, and its perturbing states in $^{12}C^{17}O$ and $^{13}C^{17}O$ were obtained. 644 rovibronic terms of the $A^1\Pi$, $B^1\Sigma^+$, $C^1\Sigma^+$, $d^3\Delta_i$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $I^1\Sigma^-$ and $D^1\Delta$ states were determined.

During collection of experimental data for carrying out the deperturbation analyses of the $A^1\Pi$ state in $^{12}C^{17}O$ and $^{13}C^{17}O$, a number of quantum-mechanical parameters were obtained for the first time: rotational and vibrational equilibrium constants, *r*-centroids, parameters of the *RKR* potential curves, relative parameters of the rovibronic structure in the form of υ_{00}^{CB}, υ_{01}^{CB}, ΔB_{00}^{CB}, ΔB_{01}^{CB} differences for the $C^1\Sigma^+$ and $B^1\Sigma^+$ states, band origins and their isotope shifts, relative intensities and *FCF* for B – A and C – A transitions. Identification and analysis of the $B^1\Sigma^+$ state predissociation in $^{12}C^{17}O$ and $^{13}C^{17}O$ was performed. Isotopic analyses of the $C^1\Sigma^+$ and $B^1\Sigma^+$ Rydberg states in the *BO* approximation was conducted and isotopic invariants U_{10} and U_{01} of the states were determined. Thanks to precise experimental and analytical methods, extremely weak irregularities (0.05 – 0.075 cm^{-1}) were revealed in the lowest $\upsilon = 0$ vibrational level of the $B^1\Sigma^+$ Rydberg state, for which the most comprehensive, but still preliminary, analysis was carried out.

Obtained quantum-mechanical parameters of the $^{12}C^{17}O$ and $^{13}C^{17}O$ molecules, and especially rotational and vibrational equilibrium constants can be a significant reason for precise determination of vibrational overlap integrals between rovibronic levels and their supposed perturbing levels in the CO molecule, which can constitute invaluable help for every next deperturbation analysis.

The finalization of the analyses became the determination of isotopologue-independent electronic spin-orbit ***a*** and rotational-electronic ***b*** perturbation parameters for $A^1\Pi \sim d^3\Delta_i$, $A^1\Pi \sim e^3\Sigma^-$, $A^1\Pi \sim a'^3\Sigma^+$ and $A^1\Pi \sim I^1\Sigma^-$, $A^1\Pi \sim D^1\Delta$ interactions in the CO molecule, respectively. These values were compared with all other analogous results obtained so far by Field et al. [61] in $^{12}C^{16}O$, Le Floch et al. [60] in $^{12}C^{16}O$, and Haridass et al. [62] in $^{12}C^{18}O$. Their consistency shows the high quality and accuracy of the deperturbation analyses that I carried out in the works **[H7]** and **[H8]**. Electronic factors of perturbation determined in such a way can be used to predict perturbations occurring in the $A^1\Pi$ state in all other CO species, as well as to interpret spectra, obtained both in laboratory conditions and from inter-stellar medium, which are linked with higher vibrational levels of the $A^1\Pi$ state and its perturbing states.

The results of the global deperturbation analyses of the $A^1\Pi$ state conducted in the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues will become, among – others, part of seeking an explanation of the anomalous electronic isotope shift of CO [93], which can be neither explained within the *BO* approximation, nor can it be so far explained by means of known *non-BO* effects. The project SOLEIL 20160118, which I am currently participating in, aims to explain this extraordinary, maybe completely new, phenomenon. More information on this subject is presented in chapter 5.3 of this Summary.

Rzeszów, 5.06.2017

Rafał Hakalla

5. Discussion of the remaining scientific – research achievements [*]

My research interests are focused on improvements of methods of experimental spectroscopy and on precise analyses of experimental data, giving special attention to the global deperturbation analyses.

5.1. Before the doctoral degree

I already undertook research work in the course of studies, under supervision of dr. Ryszard Kępa, carrying precise re-analyses of the (1, 0) and (0, 0) bands belonging to the $B^1\Sigma^+ – A^1\Pi$ system in the $^{14}C^{16}O$ isotopologue. This accomplishment became the subject of my MSc thesis. Then it was the first time I had taken an interest in the problem of complex perturbations of energy structure of the carbon monoxide molecule.

In October 1995 I was employed as an assistant lecturer in the Atomic and Molecular Physics Laboratory of the Faculty of Mathematics and Physics, Pedagogical University in Rzeszów. In the years 1995 – 2001, I focused my attention on an irregularity of excited electronic states of CO, among others, of the highly lying $c^3\Pi$ triplet state. Its specific location above the first dissociation limit of CO and complex perturbations in it, with almost scant knowledge on its structure (only the lowest vibrational level $c^3\Pi$, $\upsilon = 0$ was known), constituted a great spectroscopic challenge of that time. A conventional method of emission spectroscopy of high resolution, applied by me, which uses a plane-grating spectrograph working in the optical Ebert system enabled me to record many bands of the 3A ($c^3\Pi – a^3\Pi$) system, which as a consequence brought a precise analyses of the $c^3\Pi$ state in three isotopologues: $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{14}C^{16}O$. The results of the research were described in one co-author publication **[A1]** and in two my own works **[A2, A3]**, which were published in a prestigious *Journal of Molecular Spectroscopy*. They were also presented during four international thematic conferences **[K1, K4, K6, K7]**, and finally they became the main topic of my PhD dissertation, entitled: *Analysis of the 3A ($c^3\Pi – a^3\Pi$) system in the $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{14}C^{16}O$ isotopologues,* which was awarded by the Scientific Council of the Faculty of Mathematics and Natural Sciences of University of Rzeszów and it was also awarded the I – st degree prize by the Minister of Education and Sport in 2003.

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[*] The numbering of the remaining publications **[A1 – A16]** and conference presentations **[K1 – K45]** is consistent with the List of Publications and Achievements (Appendix 3).

5.2. After the doctoral degree

After being awarded the doctoral degree in 2003, I decided to extend my research interests to other molecules and new experimental methods in molecular spectroscopy. This direction resulted in an analysis of the CH^+ ion radical **[A4]**, thanks to which I received, among others:

– the most precise, for that time [94], molecular constants, of both the excited $A^1\Pi$ and ground $X^1\Sigma^+$ states,
– *FCF* and *r*- centroids of the A – X band system,
– *RKR* parameters and dissociation energies of the $A^1\Pi$ and $X^1\Sigma^+$ states,
– the first experimental vibrational and rotational equilibrium constants of $A^1\Pi$,
– as well as, the first experimental rovibrational term values of the $A^1\Pi$ (υ = 0, 1, 2 and 3) levels.

I also performed a detailed analysis of the $A^1\Pi$, υ = 0 – 4 levels, and especially $\upsilon \geq 3$, paying special attention to their possible irregularities **[A6]**. Apart from its great astrophysical importance, the CH^+ ion has also attracted much attention (such as AlH or BH molecule) due to its unusual magnetic properties, similar to temperature independent paramagnetism: antishielding, a large spin-rotation constant of the carbon atom, and a large and negative rotational *g*-factor (which are rarely found in the closed shell molecules). Many theoretical and experimental works [95–109], which took up this issues in the subsequent years, mentioned and used my results **[A4, A6]** over the CH^+ radical.

In the years 2004 – 2007, I also collaborated in the analyses of research results of the $B^2\Sigma^+ - X^2\Sigma^+$ band system in the $^{12}C^{17}O^+$ ion molecule **[A5, A7]**. I was still conducting the **[A4 – A7]** studies on the basis of a conventional optical spectroscopy, whose detailed description can be found, among others, in publications **[A1 – A3]**.

At this stage, I had to decide on the subject matter that could constitute the scientific achievement for applying for a habilitation degree. I considered between the CH^+ radical and the CO molecule. The basic isotopologue of the CH^+ has always enjoyed great popularity [95–109]. However, this radical and all its isotopologues are very well known. Its energy structure is rather poor and almost completely regular [95,103,107], and therefore not very interesting from the point of view of the complex intra-molecular interactions. The issue with the CO molecule has been completely different:

(I) It has had numerous isotopologues, of which $^{12}C^{17}O$ and $^{13}C^{17}O$ were almost unexplored.
(II) It has revealed a wealth of diverse energy levels and, above all, perturbations arising from multistate spin-orbital interactions, effects of centrifugal distortion, as well as the mixing of high-excited Rydberg states. [56–58].
(III) Deperturbation analyses of the most interesting $A^1\Pi$ state have never been performed in the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues.

Finally, I decided to investigate the less-abundant $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues of carbon monoxide molecule, because they were a much more challenging scientific issue than the CH^+ radical. My choice, however, was obviously associated with a smaller so-called ‘quotations’ of the publications on this topic, as few spectroscopists decide to take into account the analysis, especially deperturbation one, of the multistate energy structures. In addition, spectra of non-basic isotopologues are cumbersome for analyses due to the relatively low intensities and overlapping spectra of many other species of the given particle. Simultaneously, the experimental information about them is usually quite poor. Due to these difficulties, by no means a lack of interest, few decide to address this issue, especially for the first time. All 8 of my thematic works **[H1 - H8]** constitute the first study of the Ångström and Herzberg bands in the less-abundant $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues as well as works **[H7]** and **[H8]** contain the first deperturbation analyses of $A^1\Pi$ in these isotopologues.

The following briefly describes the preparations to perform a global deperturbation analyses of the $A^1\Pi$ state in $^{12}C^{17}O$ and $^{13}C^{17}O$, including all extensive and multistate perturbations, together with the week ones. To deal with the task, I needed to improve both the experimental and analytical methods. They were supposed to lead to an increase of absolute accuracy of wavenumber measurements from the previous 0.02 – 0.05 cm^{-1} to approximately 0.003 cm^{-1}. For this purpose, in the years 2006 – 2009, I cooperated with M. Zachwieja and W. Szajna with the construction of the laboratory based on high-accuracy dispersive optical spectroscopy (HADOS) as well as in the purchase and starting of the rotational-diffusive vacuum system, in which the vacuum of 10^{-5} Tr was obtained. We designed production and modification of the glow discharge, water cooled CWHC lamps [92] with the both-side open steel hollow-cathode and two anodes, which was described in detail in chapter 4.2.4 of the Summary.

The HADOS system, presented in publications **[H1 – H7]**, is based on a conversion of a conventional 2-meter spectrograph with an Ebert-type optical system and photographic plate recording into the spectrometer equipped with photomultiplier (PMT) operating in the single photon counting mode at the quantum efficiency of approximately 20% and interferometrically controlled by the He-Ne laser. Reflective diffraction grating is immobilized, and the PMT moves with uniform motion along the focal plane of the spectrograph, where a photographic plate was placed so far. Absolute accuracy of determining wavenumbers, of even ± 0.0015 cm^{-1} in the VIS range, was achieved mainly by an innovative way of spectrum calibration. It occurs in a real time of scanning (and not before or after its completion as it usually takes place in spectrographs of this type), through simultaneous recording of the molecular and standard spectrum, which are the atomic lines of thorium (Th). Thanks to this, all fluctuations of line positions caused by small mechanical, thermal (up to about 1^oC), or pressure changing (up to about 1 hPa) during spectrum calibration are compensated. Calibration lines are introduced in the studied spectrum due to controlled by a computer, movable quartz prism, which for a short time ‘switches off’ the source of light and lets in the reference spectrum Th in that place. This ‘cut-out’ is approximately 80 μm of the scan length. Thanks to this, several dozens of selected Th atomic lines appear in the recorded resulting spectrum, not ‘mixed’ with contours of the molecular spectrum as it usually takes place in equipment of this type, where a permanent semi-transparent mirror or a *beamsplitter* is used.

In 2010, after calibration of the HADOS system and numerous tests of modified CWHC lamps, we began first recording of the less-abundant $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues. Obtaining of the carbon monoxide spectrum by means of high-accuracy dispersive optical spectroscopy lasted until the end of 2014 year. As a result, the first recording of the Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) and Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band systems were performed in $^{12}C^{17}O$ and $^{13}C^{17}O$ **[H1 – H7]**. By means of the HADOS system, we also obtained the spectra of the AlH **[A8, A16]**, AlD **[A13]** and CD **[A9, A14]** molecules.

However, the instrumental resolution of the HADOS measurement system (0.15 cm^{-1}) was still not fully satisfactory for the investigation of the CO lines, dominated by the Doppler broadening, with physical FWHM 0.06 cm^{-1} in the VIS region. This problem concerned especially the $^{13}C^{17}O$ molecule, whose each band included analogous bands of three other species of carbon monoxide: $^{13}C^{16}O$, $^{12}C^{17}O$ and $^{12}C^{16}O$. For this reason, a number of studied lines occurred in complex contours. Because of this, I began to seek other, new methods, which would guarantee a much better resolution of recorded spectra. In order to do this, we designed, in collaboration with M. Zachwieja and W. Szajna, a new laboratory (Materials Spectroscopy Laboratory) in CIiTWTP of the University of Rzeszów, put into service in 2012. A Fourier-transform spectrometer (Bruker IFS 125 HR), with the theoretical resolving power of 10^6, was the main purchase. The maximum instrumental resolution of this equipment in the VIS range amounted to 0.0021 cm^{-1} – 0.0045 cm^{-1}. As a result, instrumental half-width (FWHM) had no more any relevant influence on effective FWHM of the studied CO spectral lines.

Because of the low pressure ($p \approx 2$ Tr) of the investigated gases in the CWHC lamps, the pressure broadening and pressure shifting were negligible. In addition, with the relative accuracy of wavenumber measurements of about 10^{-7}, which we achieved using both HADOS and FT spectrometers, other effects that may affect the line shapes (e.g. velocity-changing collisions leading to the Dicke narrowing of lines [110–113], correlations between velocity-changing and state-changing (dephasing) collisions leading to the asymmetry of lines [110,112], or the finite duration of the absorber-perturber collision leading to the collision-time asymmetry and effect of the lines mixing [114]) were negligible. The determination of the spectral line positions obtained by the FTS was made by fitting the Voigt profile to the shape of experimental lines using the non-linear least-squares method in the version of Levenberg-Marquardt [115,116].

Part of the important equipment of the LSM UR was also a turbo-molecular pomp together with a glass vacuum system, designed by us. Thanks to the equipment, the initial vacuum inside the CWHC lamps decreased to 9×10^{-7} Tr. This improved spectral purity of obtained spectra and through this their SNR.

Calibration of the FT spectrometer, in which I took an important part, lasted until 2015 year. I tested, among others, accuracy of spectra calibration by means of a He-Ne laser line (commonly used to control the moveable mirror positions) through:

– producing gas mixtures of carbon monoxide with atoms of Ne or Ar,
– obtaining spectra of such prepared samples and determining wavenumbers of key lines,
– verifications by means of Th and Pb atomic lines.

Apart from that, I performed pressure tests of the FT spectrometer and optimized its operating parameters in various spectral ranges in order to obtain the best possible quality of spectra. By means of such a prepared FT spectrometer, first I recorded emission spectrum of the $^{13}C^{17}O$ isotopologue in the region of 12 000 – 25 000 cm^{-1} with instrumental resolution of 0.018 cm^{-1}. Effective FWHMs of obtained single lines of carbon monoxide were 0.08 cm^{-1} **[H8, A15]**. These values were completely satisfactory from the point of view of an interpretation and spectra analyses, because the number of complex spectral contours in the $^{13}C^{17}O$ spectrum decreased fourfold in comparison to analogous spectra obtained by means of the HADOS method.

In order to perform the global deperturbation calculations of the $A^1\Pi$ state in the $^{12}C^{17}O$ and $^{13}C^{17}O$ species, I needed an appropriate method of a data analysis, which would take into account extensive and multistate perturbations of this state. To consult an appropriate analytical approach, I applied for an individual grant with the LaserLab Europe consortium, and also with my University for the post-doctoral grants for this purpose. The current scientific accomplishments and the objectives of my research plans were positively evaluated. Thanks to this, I received three individual grants: two European ones sponsored by LaserLab Europe (n^o 284464 – *European Community's Seventh Framework Programme* and 654148 – *European Union's Horizon 2020 Research and Innovation Programme*) **[P1, P3]** and one granted by the Dean of the Faculty of Mathematics and Natural Sciences UR **[P2]**.

Within the framework of the grant **[P2]**, in 2015 I went for the post-doctoral internship to University College London (Great Britain), where I worked in the group of prof. Jonathan Tennyson on Department of Physics and Astronomy. During that stay, I made attempts to perform the deperturbation of the $A^1\Pi$ state in the $^{12}C^{17}O$ and $^{13}C^{17}O$ isotopologues, based on *Coupled-Channel deperturbation approach* method [117–120] (so called *CC* method) used by the team of prof. Tennyson in the *DUO* programme, which they created [120]. It turned out that this method allows representing with the same accuracy, within the same model, both local perturbations (usually strong) and those that derive from remote energy states (usually weak and regular). This method needs, however, the input parameters in the form of the complete information on experimental potential energy curves for all electronic states involved in the fit and for distant states as well as dipole moment, coupling and correction curves [120]. This requirement is not feasible at the current stage of the researches of $^{12}C^{17}O$ and $^{13}C^{17}O$, because the majority of electronic states, and especially their highly-excited rovibrational levels, have not been studied yet. An additional, significant numerical problem of the DUO programme was encountered with insufficient initial experimental rovibronic term values, because in this case the DUO were 'mixing' the interpretation of the vibronic states in the regions of strong perturbations.

At 2015 – 2016 years, within the European grants **[P1]** and **[P3]**, I went for the post-doctoral internships to LaserLab Amsterdam (LLAMS), Department of Physics and Astronomy, Vrije University, where I worked with the group of prof. W. Ubachs. During those stays, I was engaged, among others, in a selection of such a deperturbation method that would be appropriate for experimental material gathered for the $^{12}C^{17}O$ and $^{13}C^{17}O$ species. The choice fell on the approach used by prof. C. Western (University of Bristol) in his computer programme *PGOPHER* [88]. This method is based on an effective Hamiltonian. Determined energy levels, frequency of spectral lines and their intensity are the result of diagonalization of the matrix containing only locally interacting states. Non-diagonal matrix elements describe in this case interactions of the perturbed state, in this case $A^1\Pi$, with its perturbing states (e.g. $d^3\Delta_i$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $I^1\Sigma^-$ and $D^1\Delta$), while interactions between perturbing states are neglected. In order to be able to accurately diagonalization, the interactions with distant states are taken into account without actually incorporating them into this diagonal matrix. This is done by Van Veck's transformation [121] in order to improve the matrix elements within the sub-matrices (blocks) [88]. The PGOPHER program also deals with the problem of 'mixing' the interpretation of energy levels in regions of strong local perturbations by creating sub-bases using wavefunction coefficients. This allows each vibronic state to be assigned to another sub-base, and within a given sub-base it has got a clearly defined energy sequence indexed with N and F_n instead of Ω, so that the expected energy order is independent of the molecular constants. Possible mistakes in the interpretation of vibronic states are quite rare and easy to diagnose due to well-designed features in the graphical interface of the wavenumber list (so-called *LineList*) used in the fit. This method proved to be satisfactory at the present stage of the investigation of the $^{12}C^{17}O$ and $^{13}C^{17}O$ species.

In the course of performing the deperturbation analyses, a problem, however, appeared that resulted from lack of connection of molecular information of the $C^1\Sigma^+$, $B^1\Sigma^+$ and $A^1\Pi$ states with the ground $X^1\Sigma^+$ state, both in the $^{12}C^{17}O$ as well as in $^{13}C^{17}O$ isotopologue. All the bands, recorded by me, resulted, however, from transitions between excited states: $B^1\Sigma^+ \rightarrow A^1\Pi$ **[H1 – H4, H7 – H8]** and $C^1\Sigma^+ \rightarrow A^1\Pi$ **[H5, H6]**. As a consequence, I was not able to determine molecular parameters satisfactorily, due to the strong correlations between vibronic term energy values participated in the fit, as well as between these values and spin-orbit and rotation-electronic coupling parameters. To obtain absolute references of the terms, and also to verify the regularity of the $B^1\Sigma^+$ and $C^1\Sigma^+$ states, I began collaborating with an American-French research group (G. Stark, J. L. Lemaire, J. R. Lyons, M. Eidelsberg, S. R. Federman, A. Heays, and N. de Oliveira). They performed measurements using synchrotron radiation generated in SOLEIL (St. Aubin, France), whose absorption spectrum is recorded in one of the end-stations, called DESIRS (*fr. Dichroïsme Et Spectroscopie par Interaction avec le Rayonnement Synchrotron*) [84–87]. There has been installed the FT spectrometer with the Fresnel bimirror interferometer based on wave front division, which has recorded spectra in the VUV range (even up to 250 000 cm^{-1}). Thanks to this collaboration, absorption spectra of the $^{12}C^{17}O$ $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0), $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) **[H7]**, and $^{13}C^{17}O$ $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0), (1, 0), $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ (0, 0) **[H8]** bands, located in the region of 86 000 – 93 000 cm^{-1}, were obtained and analysed. This range has been inaccessible to the HADOS methods. It is also unattainable for classical FT spectroscopy using beamsplitter, because above about 71 500 cm^{-1} of the incident wave frequency this optical element, based on amplitude division, no longer fulfil its role [85]. Thus obtained band I included to the deperturbation analyses. This reduced to a great extent the above mentioned correlations between determined parameters and made them statistically justified. This, in turn, caused an expected convergence of the calculations with a significantly higher number of fitted parameters. I also personally met prof. R. W. Field, with whom I consulted validity of analyses performed by me. They turned out to be fully satisfactory. The results were published in the works **[H7]** and **[H8]**.

During my work in the group of prof. Ubachs, I also participated in precise measurements and analyses of the $A^1\Pi - X^1\Sigma^+$ system in the $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{13}C^{18}O$ isotopologues. Part of the results was already published **[A15]**, and the next are being elaborated. The studies **[A15]** were conducted with the use of three different spectroscopy techniques under high resolution:

(I) Two-photon Doppler-free absorption laser spectroscopy, thanks to which the $^{13}C^{16}O$ $A^1\Pi \leftarrow X^1\Sigma^+$ (0, 0) band were recorded in ultraviolet (UV) region with absolute accuracy of 0.002 cm^{-1}. These measurements I performed together with the group of prof. Ubachs in LLAMS Amsterdam.

(II) Emission Fourier spectroscopy of the $^{13}C^{16}O$ $B^1\Sigma^+ \rightarrow A^1\Pi$ (0, 0) band in the VIS region with absolute accuracy of 0.003 – 0.03 cm^{-1}. These were the first data obtained by means of the FT spectrometer in LSM UR. All the measurements and analyses were performed by myself.

(III) Absorption FTS (SOLEIL) of the $^{13}C^{16}O$ $A^1\Pi \leftarrow X^1\Sigma^+$ (0, 0) band in the VUV region in three temperatures: 90K, 295K, 900K, with absolute accuracy of 0.01 – 0.03 cm^{-1}. The measurements were done by: G. Stark, J. L. Lemaire, J. R. Lyons, M. Eidelsberg, S. R. Federman, A. Heays and N. de Oliveira.

Frequencies of all 397 assigned lines obtained by means of the three above mentioned methods were used to perform the deperturbation analysis of the $^{13}C^{16}O$ $A^1\Pi$ ($\upsilon = 0$) level, which I did together with M. Niu from the LLAMS group.

Publication **[A15]** has been recognized by the prestigious spectroscopic journal *Molecular Physics* [122] as one of the four best works of 2016 year made by young scientists (M. Niu).

In collaboration with the group of prof. Ubachs, so far I performed three global deperturbation analyses of the multistate and extensive perturbed $A^1\Pi$ state: in $^{12}C^{17}O$ **[H7]**, $^{13}C^{17}O$ **[H8]**, and $^{13}C^{16}O$ **[A15]**. In these calculations, altogether 2382 experimental values of wavenumbers were used deriving from 64 bands of the B – A, C – A , C – X, C – X, B – d, B – e, B – a, B – I, B – D, as well as A – X, e – X and d – X systems. As a result, 135 independent molecular parameters were obtained of the states under consideration (especially of the $A^1\Pi$ state), including 31 perturbing parameters of spin-orbit and rotation-electronic (of *L-uncoupling* type) interactions. 796 rovibrational terms of the electronic states under consideration **[H7 – H8, A15],** and 10 isotopologue-independent electronic perturbation parameters **[H7 – H8]** were determined.

The experience that I have gained in various experimental techniques of high-resolution and high-accuracy molecular spectroscopy and in analytical methods taking into account variety of intra-molecular interactions as well as satisfactory results of the global deperturbation analyses that I performed, motivate me to continue further research into diatomic molecules with a complex internal structure, which are also important for astrophysical, physicochemical, and biological processes as well as for research into materials and natural environment of the Earth.

5.3. Scientific – research plans for the coming years

Initial results of the work of the prof. Ubachs team, with whom I collaborate within the area of the recording and analyses of carbon monoxide spectra, revealed a surprising property of this molecule. While carrying out studies on the $a^3\Pi – X^1\Sigma^+$ system in six species of CO by means of laser VUV spectroscopy [93], they observed an unusual isotope shifts, which cannot be explained as a simple dependence of vibrational energy levels on reduced mass of a molecule within the *BO* approximation. Simultaneously, this shift is too big to be explained by known effects of the *non-BO* type. The theory of the *non-BO* effects does not only take into account changes of reduced mass of molecules during isotopic substituting of the nuclei, but also precise distribution of mass between nuclei and electrons. The band origins of the a – X system, measured in the work [93], were corrected taking the *BO* approximation for each isotopologues into account, but in spite of this, they still showed electronic isotope shifts of the 4 GHz value substituting the nucleus of ^{12}C by ^{13}C. Thus, the phenomenon of isotope shift was found, which does not depend on reduced mass of a molecule but on atomic $^{12}C/^{13}C$ constituents. The *non-BO* corrections of this type, dependent on atoms, were obtained for the $X^1\Sigma^+$ ground state of CO by Coxon et al. [123], but their value was much lower than 4 GHz. However, the measurements and analyses conducted so far do not show whether the phenomenon is caused by a shift in the excited $a^3\Pi$ state or in the $X^1\Sigma^+$ ground state. So, this differentiation became a key issue. Numerous perturbations are the additional complications that occur in excited states of the CO molecule. We claim that recordings and analyses of bands involving the ground state and inter alia $A^1\Pi$ state will help us to explain this issue. If this phenomenon, unknown so far, is confirmed in our experiments, it will have considerable importance for the whole molecular physics. Therefore, in 2016, together with prof. Ubachs (as a supervisor) we submitted a project (no. 20160118) to the Scientific Council of the SOLEIL synchrotron, in which we proposed recording of $A^1\Pi – X^1\Sigma^+$ band system in the far ultraviolet (FUV) in the region of 250 nm, as well as the $a'^3\Sigma^+ – X^1\Sigma^+$ band system at the boundary of FUV and VUV in the region of 180 nm in six species: $^{12}C^{16}O$, $^{12}C^{17}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{17}O$, and $^{13}C^{18}O$. The results were to be combined with results obtained in $^{12}C^{16}O$ [69,124,125], $^{12}C^{17}O$ and $^{13}C^{17}O$ **[H1 – H8]**, and $^{13}C^{16}O$ **[A15]** isotopologues. Our project was reviewed and assessed positively.

In February 2017, together with W. Ubachs, A. Heays, and N. de Oliveira, I carried out a series of measurements by means of the VUV – FT spectrometer, installed in the SOLEIL synchrotron. The spectrometer is used for obtaining spectra in the FUV, and above all, in VUV region, down to 40 nm. Additional measurements also included the $a'^3\Sigma^+ \leftarrow X^1\Sigma^+$, $a^3\Pi \leftarrow X^1\Sigma^+$, $e^3\Sigma^- \leftarrow X^1\Sigma^+$, $d^3\Delta_i \leftarrow X^1\Sigma^+$, $I^1\Sigma^- \leftarrow X^1\Sigma^+$, $D^1\Delta \leftarrow X^1\Sigma^+$, and $K^1\Pi \leftarrow X^1\Sigma^+$ systems. We are currently in the process of preparing for the analyses of the recorded bands. They are expected to verify whether we actually deal with a new, unusual phenomenon. We anticipate that these measurements were the beginning of a cycle of working visits in the SOLEIL synchrotron, during which I will be participating in obtaining of spectra of next various systems in different isotopologues of the carbon monoxide molecule.

Together with the project mentioned above, I am going to conduct a much more extensive research into the $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{13}C^{18}O$ isotopologues. I would like to record further bands of the Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) and Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) systems in those species by means of VIS/UV – FTS (LSM UR), the Hopfield – Birge ($B^1\Sigma^+ \leftarrow X^1\Sigma^+$, $C^1\Sigma^+ \leftarrow X^1\Sigma$) systems using VUV – FTS (SOLEIL), and also bands of the Fourth Positive ($A^1\Pi \leftarrow X^1\Sigma^+$) system by means of two-photon Doppler-free laser spectroscopy in LLAMS Amsterdam. The objective is to perform the global deperturbation analyses with the participation of the $A^1\Pi$ state in $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{13}C^{18}O$.

By means of the absorption spectroscopy (LLAMS and SOLEIL) I expect to observe transitions with participation of the $\upsilon > 2$ vibrational levels of the $B^1\Sigma^+$ state in all possible species of the CO molecule. These levels are not accessible to emission spectroscopy due to their position above the first dissociation limit $C(^3P_0) + O(^3P_2)$ of the CO molecule ($90\,679.1 \pm 6$ cm^{-1} **[A11]**).

A challenge that I will face in the near future will be also to find causes of the weak perturbations of rotational structure of the $^{13}C^{17}O$ $B^1\Sigma^+$ ($\upsilon = 0$) level for $J = 0, 7, 16, 21, 26, 34 – 36$, noticed in works **[H8]**. I believe that recordings and analyses of the further systems and bands associated with the highly-excited rovibronic levels of the less-abundant $^{13}C^{17}O$ isotopologue, which I am going to perform in the coming years, will bring a solution to this problem.

The above mentioned, extended recordings of spectra of many various band systems of the CO isotopologues, especially their less-abundant ones, will become the subject of deperturbation analyses performed by means of the *CC* method, as well as the determination of the real molecular potentials for these species using the inverse perturbation analysis (*IPA*) [126–128].

Simultaneously with the extensive research on CO molecule, I continue to participate in the investigating of further systems and bands of the AlH, AlD, CH, CD, CO^+, AlH^+, AlD^+, CD^+ molecules. In order to obtain them in LSM UR we use high-precise UV – VIS spectroscopy (both FT and HADOS).

The tested and calibrated FT spectrometer (LSM UR) is ready now to record high-quality spectra of di- and poly-atomic molecules. It creates the possibility of developing a further collaboration with other research groups in the field of high-resolution and high-accuracy, emission and absorption UV – VIS spectroscopy as well as using by these groups the measurement time accessible in LSM UR.

6. References

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