Annex 3.

Summary of Scientific Achievements

Wojciech Szajna

Rzeszów, 2018 r.

Contents

1. Personal data

First name and surname: Wojciech Szajna
Academic degree: doctor of physical science

2. Diplomas and academic degrees awarded

1999 | Master of Science in Physics,
Faculty of Mathematics and Natural Sciences,
Pedagogical University in Rzeszów.

2006 | Doctor of Physical Science (with Honours),
Faculty of Mathematics and Natural Sciences,
University of Rzeszów.
The title of the doctoral dissertation: *Analysis of the first–negative* ($B^2\Sigma^+ - X^2\Sigma^+$) *system in the spectrum of the* $^{12}C^{16}O^+$, $^{13}C^{16}O^+$ *and* $^{12}C^{17}O^+$ *molecules.*
Doctoral dissertation supervisor: prof. dr hab. Ryszard Kępa,
The dissertation honored with an individual award of the 1st rank of the Minister of Science and Higher Education in 2006.

3. Information about employment in scientific institutions

1999 – 2001 | assistant lecturer,
Institute of Physics, Faculty of Mathematics and Natural Sciences,
Pedagogical University in Rzeszów.

2001 – 2006 | assistant lecturer,
Institute of Physics, Faculty of Mathematics and Natural Sciences,
University of Rzeszów.

2006 – 2014 | assistant professor,
Institute of Physics, Faculty of Mathematics and Natural Sciences,
University of Rzeszów.

since 2014 | assistant professor,
Department of Experimental Physics, Faculty of Mathematics and Natural Sciences,
University of Rzeszów.

4. Scientific achievements that are the basis for application for the degree of doktor habilitowany

On the basis of the article 16, passage 2 of the Act of 14 March 2003 on Academic Degrees and Scientific Titles and on Degrees and Titles in the Area of Art (Journal of Laws, 2006, passage 882 with amendments in Journal od Laws of 2016, passage 1311), in accordance with the article 179, passage 2 of the Act of 3 July 2018 (Journal of Laws, 2018, passage 1669), as a scientific achievement I present the cycle of **eight articles [H1−H8]**[1] that are thematically connected under a joint title:

High−resolution emission spectroscopy of the AlH and AlD molecules and their positive ions.

4.1. Articles [H1−H8] which constitute scientific achievements

H1. **W. Szajna**, M. Zachwieja.
Emission spectroscopy of the $A^1\Pi - X^1\Sigma^+$ system of AlH.
Eur. Phys. J.D. **55**, 549 – 555 (2009).
DOI: 10.1140/epjd/e2009-00253-y

H2. **W. Szajna**, M. Zachwieja.
The emission spectrum of the $C^1\Sigma^+ - X^1\Sigma^+$ system of AlH.
J. Mol. Spectrosc. **260**, 130 – 134 (2010).
DOI: 10.1016/j.jms.2010.02.004

H3. **W. Szajna**, M. Zachwieja, R. Hakalla, R. Kępa.
The emission spectroscopy of AlH: the $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^+$ states characteristics.
Acta Phys. Pol. A. **120**, 417 – 423 (2011).
DOI: 10.12693/APhysPolA.120.412

H4. **W. Szajna**, M. Zachwieja.
High−resolution emission spectroscopy of the $A^2\Pi - X^2\Sigma^+$ system of AlH^+.
J. Mol. Spectrosc. **269**, 56 – 60 (2011).
DOI: 10.1016/j.jms.2011.05.002

H5. **W. Szajna**, M. Zachwieja, R. Hakalla.
Rotational analysis of the 0 – 0 and 1 – 1 bands of the $A^1\Pi - X^1\Sigma^+$ system of the AlD isotopologue.
J. Mol. Spectrosc. **318**, 78 – 83 (2015).
DOI: 10.1016/j.jms.2015.10.007

---

[1] The numbering of works **[H1−H8]** included in the scientific achievement is in accordance with the List of Publications and Achievements given in Annex 4.

H6. **W. Szajna**, R. Hakalla, P. Kolek, M. Zachwieja.
The new investigation of the $b^3\Sigma^- - a^3\Pi$ system of AlH.
J. Quant. Spectrosc. Radiat. Transf. **187**, 167 – 177 (2017).
DOI: 10.1016/j.jqsrt.2016.09.016

H7. **W. Szajna**, K. Moore, I.C. Lane.
The emission spectroscopy of AlD in the visible region: experimental and theoretical investigations.
J. Quant. Spectrosc. Radiat. Transf. **196**, 103 – 111 (2017).
DOI: 10.1016/j.jqsrt.2017.03.044

H8. **W. Szajna**, R. Hakalla, K. Moore, I.C. Lane.
Fourier transform emission spectroscopy and *ab initio* calculations on the visible spectrum of AlD^+.
J. Quant. Spectrosc. Radiat. Transf. **221**, 118 – 128 (2018).
DOI: 10.1016/j.jqsrt.2018.09.028

4.2. Discussion of the scientific objective of the works [H1–H8], results obtained and prospects of their application

4.2.1. Introduction and research motivation

Molecules containing hydrogen are the subject of a special interest of spectroscopists due to their considerable importance for astrophysical research on interstellar space as well as in an analysis of the atmosphere composition of stars and planets [1]. Among them, an important role is played by aluminum hydride, the occurrence of which is associated with high relative content of aluminum in space [2].

The occurrence of the AlH molecule was confirmed in spectra of M, S and C–type stars [3]. The first identification was made by Herbig [4] in 1956 on the basis of experimental data collected by Merrill [5] from an observation of the emission spectrum of a variable star χ in the constellation of Cygnus. Further research of this author [6] unquestionably confirmed the occurrence of the AlH molecule in the star atmosphere on the basis of identification of spectral lines of the $A^1\Pi - X^1\Sigma^+$. They made it possible to document the phenomenon of inverse predissociation [7, 8] for the first time as a process responsible for the formation of the AlH molecule in the atmosphere of stars.

The latest observations of absorption lines of aluminum–containing molecules (including AlH) in the o (Mira Ceti) star spectrum in the constellation of the Whale [9] gave the basis for investigating the composition and processes responsible for the formation of interstellar dust and their possible relationship with the cycle of star variation. They confirmed the results of previous, extensive interpretations of M–type stars spectra made by Merrill *et al.* [10].

The initial identification of the AlH lines in the sunspot spectrum carried out by Wöhl [11] in 1971 roku was finally proven by Sotirovski [12] and Wallace *et al.* [13]. Data from the spectral atlas of the Sun [13] were used to estimate the effective rotational temperature of the AlH molecule [14].

The diatomic molecules containing hydrogen and deuterium, including aluminum hydride and aluminum deuteride, constitute a large group of molecules studied within the ExoMol project [15]. Based on experimental data, the project aims to develop the broadest possible high temperature line lists [16] of molecules relevant to the exploration of atmospheres of extra solar planets, cool stars and circum−stellar environment [17–19].

Recent years have brought new research prospects for hydrides [20,21] and their ions [22, 23], due to very strong premises for their use in experiments with the laser−cooling of molecules. The AlH^+ molecule with the $A^2\Pi - X^2\Sigma^+$transition is mentioned in the most prospective group due to the fact that this system is very diagonal [22, 23]. Recent experiments [24], with the cooling of the AlH^+ ion in the linear Paul trap, have achived rotational temperatures around 3.8 K with nearly 96% of the population in the ground $v = 0, N = 0$ state.

The physicochemical properties of the AlH molecule also reveal its potential role in research on rocket propellants [25], in experiments with deposition of thin organometallic surfaces [26], in the work on metal hydride photodissociation lasers [27] and van der Waals complex [28–32].

An undoubted impulse to undertake research on emission spectra of the above mentioned molecules was the lack of contemporary experimental material of satisfactory quality, allowing for its full and precise analysis. Most of the available results were based on experiments carried out with conventional emission spectroscopy techniques performed in the 30's and 40's of the last century. The resolving power available then and highly simplified graphical methods of interpretation of experimental data did not give the possibility of a thorough analysis of the spectra. As a result, the description of the energy structure of the molecules being the subject of current research has been incomplete or highly imprecise in many places.

Among modern, high−precision experimental works [33–43] only one [39] related to the spectrum of the electronic−vibrational−rotational transition of the $A^1\Pi - X^1\Sigma^+$ system in the AlH molecule. The rest focused on the analysis of ro−vibrational emission bands of the ground state of AlH [33, 35–38] and AlD [34, 36]. Four works [40–43] were devoted to pure rotational lines, observed in absorption, in the $X^1\Sigma^+$ state in both isotopic species. The situation of experimental works on the spectra resulting from electron transitions in the AlH^+ and AlD^+ ions was even poorer. The "latest" works should be considered from 1980 [44] and 1984 [45], respectively. Both based on classical emission spectroscopy and photographic spectra registration.

In the literature on the subject, at the same time, constant presence of works on theoretical aspects of the energy structure and spectra of AlH [21, 46–50], AlD [51] and AlH^+ [22] was also noted. *Ab initio* calculations were used mainly to estimate the shape of the potential, values of basic molecular constants, the transition dipole moment function and the value of Franck−Condon factors for the observed transitions.

Therefore, it was justified to re−register and analyze the emission spectra of the AlH, AlD, AlH^+ and AlD^+ molecules using modern spectroscopic techniques and modern analytical methods which guarantee adequate resolution of the spectra and high accuracy of the results.

4.2.2. Objective of the research

Spectroscopic techniques provide very precise data allowing for proper planning and conducting experiments in the areas described in the previous chapter. This mainly concerns the frequency of observed rotational transitions and thus the knowledge of energy of ro−vibrational levels in individual electronic states, but also probabilities of transitions between states and presence of intramolecular interactions.

The above conclusions became the main determinant of my research, and thus the scientific objective of the presented article series [**H1**−**H8**], was to: obtain high−resolution electronic−vibrational−rotational spectra of hydrides and deuterides of aluminum and their positive ions, determine precise values of parameters of the ro−vibronic structure of these molecules and identify perturbations in the observed electronic states. Accomplishement of this objective required:

- development of new sources of emission spectra of the molecules studied and methods of their registration which guarantee the best possible intensity of spectra and high accuracy of measurements[2],
- performance of precise spectral analysis and determining accurate values of wavenumbers of the observed spectral lines,
- determination of molecular parameters of the studied electronic states, including experimental data available from measurements in the infrared region,
- identification and an analysis of possible perturbations in the energy structure of the observed electronic states of the molecules studied.

4.2.3. Results

H1. W. Szajna, M. Zachwieja. Emission spectroscopy of the $A^1\Pi - X^1\Sigma^+$ system of AlH. Eur. Phys. J. D. **55**, 549 – 555 (2009).

---

[2] Experimental conditions were described in detail in Chapter 4.2.4

In the work, 6 bands of the $A^1\Pi - X^1\Sigma^+$ system in the region of 18 000 – 25 000 cm^{-1} in the AlH molecule [39,52] were registered and analyzed. A measurement system based on high accuracy dispersive optical spectroscopy (HADOS) was used in the research. The source of the spectra was a water–cooled hollow–cathode (HC) lamp with an aluminum cathode, filled with a mixture of neon (at a pressure of about 3 Tr) and traces of ammonia. The registration was carried out with a reciprocal dispersion of 0.08 – 0.13 nm/mm and theoretical resolving power of approx. 2.28×10^5.

In total, 163 spectral lines belonging to the two strongest $0-0$ and $1-1$ bands and to four definitely weaker non–diagonal bands $0-1$ and $1-0,2,3$ were interpreted and measured. The above mentioned non–diagonal bands have been registered and analyzed for the first time since 1954 [52]. This had a significant impact on the first identification of perturbations occurring in the $A^1\Pi$, $v=1$ level. The registered lines had a spectral width (*full width at half maximum*, FWHM) of about 0.15 cm^{-1} and a very good signal–to–noise ratio (SNR) of 250 : 1, for the strongest lines of the $0-0$ band. As a result, the absolute accuracy of determination of wavenumbers of the lines equalled ± 0.0015 cm^{-1} and was comparable to that achieved in studies on the A – X system of the AlH molecule using a one–meter Fourier transform spectrometer (FTS) [39].

Obtained frequencies of transitions were reduced to molecular parameters describing vibrational levels of both states, with the use of the Hamiltonian of Brown [53] for the $^1\Pi$ and $^1\Sigma^+$ states. The obtained standard deviation of a model–to–measurements fit (1σ) equals 0.0009 cm^{-1} for the $0-0$ band and 0.0014 – 0.0037 cm^{-1} for the remaining bands.

In the work **[H1]**, apart from the individual band analyses, the first merged calculation [54,55] was carried out. The fit included the current registrations in the visible region and Fourier measurements of vibration–rotation transitions of the ground $X^1\Sigma^+$ state in the infrared region [36]. Such a procedure allowed for a significant improvement in accuracy of molecular parameters for the $A^1\Pi$ state thanks to an increase in the set of experimental information about the $X^1\Sigma^+$ state. The values of Λ–doubling constants for the $v=1$ and equilibrium parameters $q_e, \alpha_{q_e}, q_{D_e}, \alpha_{q_{D_e}}$ of the $A^1\Pi$ state were determined for the first time.

The individual analysis of four bands $1-0,1,2,3$ made it possible to discover a very weak perturbation in the $A^1\Pi$, $v=1$, $J=5$ level for both components of the Λ–doubling (Figure 1). These irregularities were not disclosed in the work [39] despite high accuracy of frequency determination of rotational transitions of the A – X, 1 – 1 band declared at around 0.002 – 0.003 cm^{-1}. The shift of the rotational levels $J = 5e$ and $J = 5f$ amounting to $+0.023$ cm^{-1} and -0.005 cm^{-1}, respectively, was observed in all bands of the $1 - v''$ progression.

The attempt to identify the $a^3\Pi$, $v=0$ state as responsible for the observed perturbation of $A^1\Pi$ state requires experimental verification. Previous observations

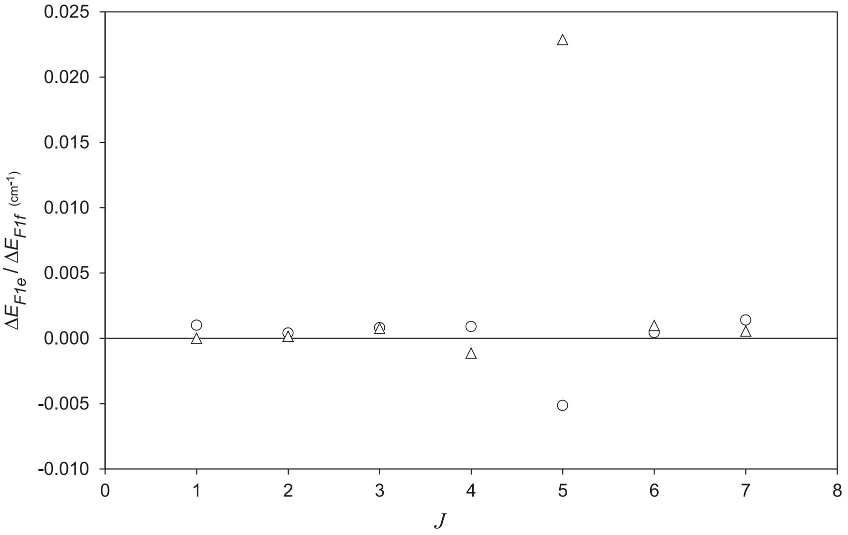

Figure 1: Perturbation in the $A^1\Pi$, $v = 1, J = 5$ level of the AlH molecule (△ $f-$component, ○ $e-$component) presented for the first time by Szajna and Zachwieja [**H1**].

of transitions involving the $a^3\Pi$ state i.e. $b^3\Sigma^- - a^3\Pi$ [56–58] and $c^3\Pi - a^3\Pi$ [59] did not allow for explaining the problem discussed. The reason is the large irregularities observed in the structure of these transitions due to extensive perturbations of the $c^3\Pi$ [59] and $b^3\Sigma^-$ [**H6**] states which magnitude significantly exceeds those observed in the $A^1\Pi$, $v = 1$ state.

My contribution to the work: gathering the existing literature on the subject that is being researched; developing the concept of the work; designing the construction of a discharge lamp and selection the lamp operating conditions (together with M. Zachwieja); the analysis of experimental data and preparation the results for publication (together with M. Zachwieja); editing a complete article manuscript (with the exception of Chapter 2 developed jointly with M. Zachwieja). I estimate my contribution at 50%.

H2. **W. Szajna**, M. Zachwieja. The emission spectrum of the $C^1\Sigma^+ - X^1\Sigma^+$ system of AlH. J. Mol. Spectrosc. **260**, 130 – 134 (2010).

The work presents the results of the spectrum analysis of the $C^1\Sigma^+ - X^1\Sigma^+$ system of the AlH molecule registered in the far ultraviolet region of 42 000 – 45 000 cm^{-1}. The spectrum was excited in a water−cooled discharge lamp with an aluminum cathode open on both sides and two anodes [60] (*composite wall hollow−cathode*, CWHC), which was modified to excite the AlH molecule. The lamp was filled with a mixture of neon and ammonia in a ratio of approx. 15 : 1 at an effective pressure of a mixture of approx. 2.7 Tr. The registration was made using the HADOS technique, with the reciprocal dispersion of 0.05 nm/mm and the theoretical resolving power of 4.56×10^5. The absolute accuracy of the determining wavenumbers of the $0-0$ i $1-1,2$ bands was ± 0.004 cm^{-1} for single lines of average intensity. Verification of previous experimental data revealed erroneous interpretations of some rotational lines [61, 62] and significant differences (ranging from 3 to 5 cm^{-1}) in the values of wavenumbers of the observed rotational transitions [63].

A reduction of the spectrum of the $C^1\Sigma^+ - X^1\Sigma^+$ system to the molecular parameters of the $C^1\Sigma^+$, $v = 0, 1$ levels was performed. The obtained constant values became more accurate in comparison to the data in previous literature [61–63]. The values of the equilibrium parameters of the $C^1\Sigma^+$ state and values of the Franck–Condon factors (FCF) for the $C - X$ transition in the AlH molecule were calculated. The experimental values of rotational terms of the C, $v = 0, 1$ levels were determined by means of the Curl–Dane–Watson procedure [64,65]. This approach allows for separating the statistical information of the regular $X^1\Sigma^+$ state (represented by the effective Hamiltonian) from the perturbed $C^1\Sigma^+$ state (represented by the terms). Molecular constants for the $X^1\Sigma^+$, $v = 0, 1$ levels were fixed to the values obtained in the work [**H1**]. The 1σ value of the model–to–measurements fit was 0.007 cm^{-1} for the $0-0$ band and 0.010 cm^{-1} for the $1-1$ and $1-2$ bands.

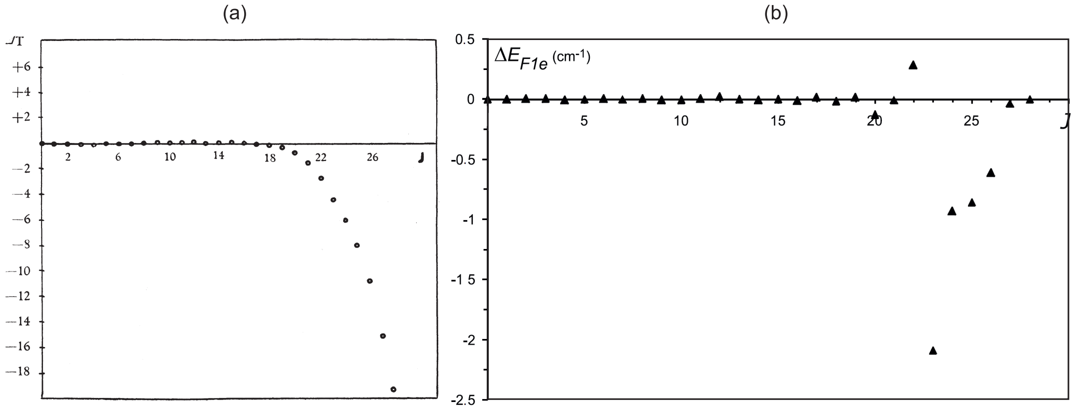

Figure 2: Perturbations observed in the $C^1\Sigma^+$, $v = 0$ level of the AlH molecule: (a) Nilsson [66]; (b) Szajna and Zachwieja [**H2**].

The region of occurrence and the magnitude of perturbations of the $C^1\Sigma^+$, $v = 0$ level were verified, in comparison to the previous observation [66] (Figure 2). The rotational level $J = 23$ was recognized as the one for which the mentioned perturbation reaches the highest value ($\Delta T = -2.09$ cm^{-1}), in contrast to the level $J = 28$ estimated in work [66] ($\Delta T = -19.26$ cm^{-1}). Also, the presence and character of theoretically foreseen perturbations in the $C^1\Sigma^+$, $v = 1, J \geq 5$ levels [67] were confirmed experimentally and the values of these perturbations for the terms $J = 5 - 9$ [66] were verified.

My contribution to the work: developing the concept of the work; designing the construction of a discharge lamp and selection the lamp operating conditions (together with M. Zachwieja); the analysis of experimental data and preparation the results for publication (together with M. Zachwieja); editing a complete article manuscript (with the exception of Chapter 2 developed jointly with M. Zachwieja). I estimate my contribution at 50%.

H3. **W. Szajna**, M. Zachwieja, R. Hakalla, R. Kępa. The emission spectroscopy of AlH: the $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^+$ states characteristics. Acta Phys. Pol. A. **120**, 417 – 423 (2011).

In the work, registration of the AlH molecule spectrum in the region of 20 000 – 21 500 cm^{-1} was carried out, under high−resolution conditions (the reciprocal dispersion 0.09 nm/mm, theoretical resolving power 2.28×10^5) using the HADOS technique. The spectrum studied was produced in a water−cooled discharge lamp with an open aluminum cathode CWHC and two anodes, filled with a mixture of neon and a small admixture of ammonia.

The analysis of the 0−0 and 1−1 bands of the $C^1\Sigma^+ - A^1\Pi$ system and 0−2 band of the $A^1\Pi - X^1\Sigma^+$ system was performed. The former band was originally identified as the 0 – 0 band of the $B^1\Sigma^+ - A^1\Pi$ transition [68]. In total, 121 spectral lines were interpreted and measured, for which the values of wavenumbers were determined with the absolute accuracy ±0.003 cm^{-1}. Reduction of wavenumbers to the molecular parameters of the effective Hamiltonian resulted in a standard deviation of the fit which equals 0.0032 cm^{-1} for the 0 – 2 band of the A – X system and 0.0070 cm^{-1} for the 0 – 0 and 1 – 1 bands of the C – A system.

As a part of the analysis of the experimental data, a merge calculation [54, 55] was performed combining the results of the current observations with those obtained in the works [**H1**, **H2**]. In result, precise molecular constants were obtained for the three lowest−lying singlet states of the AlH molecule. Also, accuracy of the values of vibrational and rotational terms for the $A^1\Pi$, $v = 0, 1$ and $C^1\Sigma^+$ $v = 0, 1$ levels was improved.

My contribution to the work: developing the concept of the work; designing the construction of a discharge lamp and selection the lamp operating conditions (together with M. Zachwieja); the analysis of experimental data and preparation the results for publication (together with M. Zachwieja); editing a complete article manuscript (with the exception of Chapter 2 developed jointly with M. Zachwieja). I estimate my contribution at 40%.

H4. **W. Szajna**, M. Zachwieja. High-resolution emission spectroscopy of the $A^2\Pi - X^2\Sigma^+$ system of AlH$^+$. J. Mol. Spectrosc. **269**, 56 – 60 (2011).

The subject of the work was registration and an analysis of the spectrum of the $A^2\Pi - X^2\Sigma^+$ system of the AlH$^+$ molecule in the 27 000 – 29 000 cm^{-1} spectral region. This was the first observation of the spectrum of this system under high−resolution conditions. The reciprocal dispersion, of 0.06 nm/mm, more than doubled the one achieved in previous works [44, 69, 70]. The spectrum was obtained in a water−cooled lamp with an open aluminum cathode CWHC and two anodes, filled with a mixture of neon and traces of ammonia.

For the first time, the full rotational structure of the $0-0$ and $1-1$ bands was registered: 12 branches up to the $J = 36.5$ in the $0-0$ band, which corresponded to the level of dissociation of the ground $\mathrm{X}^2\Sigma^+$, $v = 0$ state. Thus, the previous suspicions of predissociation in the $\mathrm{A}^2\Pi$, $v = 0, J = 28.5$ state were verified [69]. The first interpretation of lines belonging to six satellite branches allowed us to observe and fully analyze the Λ−doubling in the $\mathrm{A}^2\Pi$ state and and the spin−splitting in the $\mathrm{X}^2\Sigma^+$ state. Over 450 frequencies of rotational transitions were determined with the absolute accuracy of ± 0.003 cm^{-1}.

At the preliminary analysis stage, significant irregularities were found in the splitting of the $e-$ and $f-$components of the rotational terms of the $\mathrm{A}^2\Pi$, $v = 0, 1$ levels. Further interpretations confirmed the occurrence of the anomalous Λ−doubling, which was interpreted as a result of the $\mathrm{A}^2\Pi$ state interacting with the lying above $\mathrm{B}^2\Sigma^+$ state. This interaction also causes extensive rotational perturbations in the $\mathrm{A}^2\Pi$, $v = 1$ level, which region of occurrence and values were determined for the first time as part of the conducted analyses.

The molecular constants of the regular $\mathrm{X}^2\Sigma^+$, $v = 0, 1$ state were calculated by means of the Curl−Dane−Watson method [64,65]. Most of them were determined for the first time. The standard deviation of the model−to−measurements fit was 0.0037 cm^{-1} and 0.0044 cm^{-1}, for the $0-0$ and $1-1$ bands, respectively. The first experimental values of rotational terms of the $\mathrm{A}^2\Pi$, $v = 0, 1$ state were determined.

My contribution to the work: gathering the existing literature on the subject that is being researched; developing the concept of the work; designing the construction of a discharge lamp and selection the lamp operating conditions (together with M. Zachwieja); the analysis of experimental data and preparation the results for publication (together with M. Zachwieja); editing a complete article manuscript (with the exception of Chapter 2 developed jointly with M. Zachwieja). I estimate my contribution at 50%.

H5. **W. Szajna**, M. Zachwieja, R. Hakalla. Rotational analysis of the $0-0$ and $1-1$ bands of the $\mathrm{A}^1\Pi - \mathrm{X}^1\Sigma^+$ system of the AlD isotopologue. J. Mol. Spectrosc. **318**, 78 − 83 (2015).

The work [**H5**] is the first of the presented works concerning the AlD molecule, in which the two strongest $0-0$ and $1-1$ bands of the $\mathrm{A}^1\Pi - \mathrm{X}^1\Sigma^+$ transition were registered and analyzed. The emission spectrum obtained from the CWHC type lamp was registered using the HADOS technique, with the reciprocal dispersion of 0.10 nm/mm and theoretical resolving power of about 2.28×10^5. The discharge lamp was filled with a mixture of neon and deuterated ammonia with a 99% concentration of ND_3 molecules. The 133 spectral lines were measured with the absolute accuracy of ± 0.003 cm^{-1} for the best lines with an SNR value of about 150 : 1. The spectrum of the A − X system of AlD has been registered for the first time since 1948. Nilsson [66] published the results of studies carried out under low−resolution conditions, which was an extension of previous studies on the A − X system [71].

The reduction of the spectrum to the molecular parameters of the effective Hamiltonian [53] was carried out, obtaining a standard deviation of the model−to−measurements fit of 0.0020 cm^{-1} for the 0 − 0 band and 0.0016 cm^{-1} for the 1 − 1 band.

The first merged calculation [54, 55] was performed, combining the current registrations with Fourier measurements of ro−vibrational bands within the ground state of the AlD molecule in the near−infrared region [36]. This approach increased the set of experimental data concerning the ground $X^1\Sigma^+$ state and allowed for a much better determination of molecular parameters of the $A^1\Pi$ state, among which the majority was determined for the first time. A set of Λ−doubling constants was determined for $v = 0, 1$ levels of the $A^1\Pi$ state. The position of the minimum of the potential energy curve of this state was verified and accuracy of the values of the main equilibrium constants was improved.

My contribution to the work: gathering the existing literature on the subject that is being researched; developing the concept of the work; designing the construction of a discharge lamp and selection the lamp operating conditions (together with M. Zachwieja); spectra registration and calibration; the complete analysis of experimental data and preparation the results for publication; editing a complete article manuscript. I estimate my contribution at 70%.

H6. **W. Szajna**, R. Hakalla, P. Kolek, M. Zachwieja. The new investigation of the $b^3\Sigma^- - a^3\Pi$ system of AlH. J. Quant. Spectrosc. Radiat. Transf. **187**, 167 − 177 (2017).

The work presents the results of the analysis of the 0 − 0 i 1 − 1 bands of the first triplet system $b^3\Sigma^- - a^3\Pi$ in the AlH molecule registered under high−resolution conditions using the HADOS technique in the region of 25 900 − 26 500 cm^{-1}. The reciprocal dispersion, 0.08 nm/mm, was almost twice as high as that achieved in previous conventional studies on this system [57, 72].

The source of the emission spectrum was a water−cooled lamp with an aluminum hollow−cathode CWHC and two anodes, filled with a mixture of neon and ammonia, in a quantity ratio of about 10 : 1 with an effective pressure of the mixture of approx. 2.7 Tr. The lamp operated in extreme current conditions. A current of 2×180 mA was applied to both anode−cathode circuits, and the additional current in the anode−anode circuit was 250 mA (standard supply conditions are 2×80 i 150 mA). Those conditions, close to the stable discharge in the lamp, were necessary to register a very weak spectrum of the $\mathrm{b}^3\Sigma^- - \mathrm{a}^3\Pi$ transition. The relative intensity of the $0-0$ band was estimated to be at about 0.01% of the intensity of the strongest $0-0$ band of the $\mathrm{A}^1\Pi - \mathrm{X}^1\Sigma^+$ system. The subsequent, author's attempts to register the $\mathrm{b}^3\Sigma^- - \mathrm{a}^3\Pi$ transition spectrum using a Fourier transform spectometer confirmed the estimated intensity relationships of singlet and triplet transitions in the AlH molecule.

The registration conditions allowed for the first interpretation and measurement of rotational lines of strongly overlapped Q branches in both observed bands. A total of 260 rotational transition frequencies (including 63 for Q branches) were determined with the absolute accuracy of ± 0.005 cm^{-1}. Due to extensive perturbations in the $\mathrm{b}^3\Sigma^-$, $v = 0, 1$ state the analysis of experimental data was carried out in two stages.

In the first stage, the molecular constants of the regular $\mathrm{a}^3\Pi$, $v = 0, 1$ state and rotational terms of the perturbed $\mathrm{b}^3\Sigma^-$ state were determined using the Curl−Dane−Watson method [64,65]. The values of 1σ were obtained as 0.0053 cm^{-1} and 0.0065 cm^{-1}, for the $0-0$ and $1-1$ bands, respectively. Values of the main rotational constants of the $\mathrm{a}^3\Pi$ state, obtained in previous studies [56–58, 72], were verified and their accuracy was improved. The first experimental values of spin−orbit interaction parameters (A_v) and Λ−doubling constants (o_v, p_v, q_v) were obtained for the $\mathrm{a}^3\Pi$, $v = 0, 1$ levels.

In the next step, it was decided to determine the effective molecular parameters for the $v = 0$ level of the $\mathrm{b}^3\Sigma^-$ state, on the basis of regular lines of the $0-0$ band (constants for the state $\mathrm{a}^3\Pi$, $v = 0$ were fixed to the values obtained in the previous step). The fit included lines of the main branches, corresponding to rotational levels up to $N = 16$ in the $\mathrm{b}^3\Sigma^-$ state. As a result, a set of molecular parameters describing the $\mathrm{b}^3\Sigma^-$, $v = 0$ level was obtained, most of which was calculated for the first time, among others, the spin−spin coupling constant (λ) and spin−rotation interaction constants ($\gamma, \gamma_D, \gamma_H$).

The region of occurrence of irregularities in the $\mathrm{b}^3\Sigma^-$, $v = 0$ state in relation to previous reports [56] was verified. Moreover, previously unknown [72] perturbations of rotational terms in the $v = 1$ level were found. An attempt was made to identify the causes of irregularities observed in the $\mathrm{b}^3\Sigma^-$, $v = 0, 1$ state on the basis of theoretically determined intersection points of the ro−vibrational terms of the perturbed state and lying closely $\mathrm{C}^1\Sigma^+$, $\mathrm{d}^3\Sigma^+$ and $\mathrm{c}^3\Pi$ states. It was initially stated that the interaction of the $\mathrm{b}^3\Sigma^-$, $v = 0, 1$ levels, with $\mathrm{c}^3\Pi$, $v = 0, 1$ levels is highly probable. These conclusions are confirmed by the description of extensive perturbations in the $\mathrm{c}^3\Pi$ state given by

Kleman on the basis of observation of the spectrum of the $c^3\Pi - a^3\Pi$ system [59].

My contribution to the work: developing the concept of the work; designing the construction of a discharge lamp and selection the lamp operating conditions (together with M. Zachwieja); spectra registration and calibration; the complete analysis of experimental data (the participation of R. Hakalla in the an attempt to identify levels perturbing the $b^3\Sigma^-$, $v = 0, 1$ state); preparation the results for publication; editing a complete article manuscript. I estimate my contribution at 70%.

H7. **W. Szajna**, K. Moore, I.C. Lane. The emission spectroscopy of AlD in the visible region: experimental and theoretical investigations. J. Quant. Spectrosc. Radiat. Transf. **196**, 103 – 111 (2017).

The main concept of the work was the first combination of experimental and *ab initio* results for the lowest−lying $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^+$ states of the AlD molecule, and electronic−vibrational−rotational transitions observed in emission in the visible region.

The experimental part was carried out in the Materials Spectroscopy Laboratory of the University of Rzeszów (MSL UR), and theoretical calculations in the School of Chemistry and Chemical Engineering of the Queen's University of Belfast in Northern Ireland.

The emission spectrum of the AlD molecule was registered using a Fourier transform spectrometer (BRUKER IFS 125 HR) which is a part of the MSL UR equipment. The AlD molecules were excited in a water−cooled lamp with an aluminum hollow−cathode CWHC and two anodes, filled with a mixture of neon and deuterated ammonia (2.7 Tr Ne + 0.2 Tr ND_3). The instrumental resolution was 0.03 cm^{-1} for the studied spectral region 11 000 – 32 000 cm^{-1}. The registration area was physically limited from the lower frequencies up to 17 700 cm^{-1}, by the use of an appropriate filter (575 nm, EDMUND Optics). Thus, very strong Ne atomic lines were eliminated from the spectrum and the signal−to−noise ratio for the investigated AlD spectrum was improved six times. For the strongest molecular lines, the SNR value was over 1400 : 1. Registrations included the $0 - 0, 1; 1 - 0, 1, 2, 3$ bands of the $A^1\Pi - X^1\Sigma^+$ system and $0 - 0; 1 - 1$ bands of the $C^1\Sigma^+ - A^1\Pi$ system. In the obtained spectrum, a total of 465 spectral lines were identified, for which wavenumbers were determined with the absolute accuracy of ± 0.002 cm^{-1}.

The transition frequencies obtained were reduced to molecular parameters of the $X^1\Sigma^+$, $A^1\Pi$ oraz $C^1\Sigma^+$ states, using the `PGOPHER` program [73]. As an input data set, results of FTS measurements of the vibration−rotation bands of the ground state [36] and frequencies of pure rotational absorption transitions $J = 2 \leftarrow 1$, $J = 3 \leftarrow 2$ oraz $J = 4 \leftarrow 3$, made available by dr. D. Halfen [41], were additionally used. The above sets of experimental data were entered into the calculation taking into account appropriate measurement weights, established on the basis of accuracy of the determined frequencies of the observed rotational transitions, declared in the works [36, 41]. Taking into consideration such an extensive set of experimental data regarding the $X^1\Sigma^+$ state, allowed for much better determination of the parameters of the $A^1\Pi$ i $C^1\Sigma^+$ states. Mainly by eliminating (or significantly reducing) correlation between the determined ground state parameters and both excited state parameters of the AlD molecule.

In total, 930 values of wavenumbers were reduced to 62 parameters describing 12 vibrational levels of the three singlet states: $X^1\Sigma^+$, $v = 0 - 7$, $A^1\Pi$, $v = 0, 1$ and $C^1\Sigma^+$, $v = 0, 1$. The accuracy of most of the values was improved and verified, and some were determined for the first time. The root−mean−square error (rmse) of the unweighed residuals of all line wavenumbers used in the calculation was 0.004 cm^{-1}, which proves that the model was very well fitted to this extensive set of experimental data.

The results of *ab initio* calculations, which supplement the experimental results, were obtained using the `MOLPRO` computing platform [74] with the use SA-CASSCF (*State-Average Complete Active Space Self-Consistent Field*) and MRCI (*Multi-reference Configuration Interaction*) methods. An aug−cc−pV5Z basis set was used on both atoms to describe the atomic orbitals. The active space consisted of all the valence orbitals ($3s3p$ on Al and $1s$ on H) and the $4s$ Rydberg orbital on the aluminum atom (four electrons in eleven orbitals).

As a result, the potential energy curves were obtained as well as a number of molecular parameters for the three lowest−lying singlet states of the AlD molecule. The values of molecular constants for the ground state are highly consistent with the results of the present **[H7]** and previous experimental [36,41,66] **[H5]** and theoretical [49] works. The calculated spin−orbit separation value in the ground (^{2}P) state of Al atom was 116 cm^{-1}, which is very similar to the value obtained experimentally, that is, 112.06495(6) cm^{-1} [75].

The results of the first *ab initio* calculations for the excited $A^1\Pi$ i $C^1\Sigma^+$ states of the AlD molecule are confirmed by the latest results of experimental work **[H5]** and by those carried out as part of the current research. Observed discrepancies in the values of rotational constants do not exceed 0.5% for the $A^1\Pi$ and 2% for the $C^1\Sigma^+$ state, respectively. The theoretically calculated position of the potential curve minimum of the $A^1\Pi$ state is smaller only by 33 cm^{-1} than the value presented in the work **[H5]**. Moreover, it is worth noting that there is a good consistency between the values of the main molecular constants, obtained in *ab initio* calculations, for the $A^1\Pi$, $v = 2$ level which has not been observed in current research (lying above the first dissociation limit) and those determined experimentally in the work [71]

My contribution to the work: developing the concept of the work; establishing the cooperation with a group from the University of Belfast; designing the construction of a discharge lamp and selection the lamp operating conditions; registration and interpretation as well as measurement of the spectra; performing the calculation combining the obtained data and data available from literature from infrared measurements [36, 41]; analyzing the experimental results and preparation for publication; editing a complete article manuscript (except for Chapters 3 and 5 developed by I. Lane and K. Moore); editing the text of the article after co−authors' comments. I estimate my contribution at 70%.

H8. **W. Szajna**, R. Hakalla, K. Moore, I.C. Lane. Fourier transform emission spectroscopy and *ab initio* calculations on the visible spectrum of AlD^+. J. Quant. Spectrosc. Radiat. Transf. **221**, 118 − 128 (2018).

The work [**H8**] is the second one written in collaboration with the School of Chemistry and Chemical Engineering of the Queen's University of Belfast in Northern Ireland. This time, our interest focused on the experimental and theoretical study of the AlD^+ molecule spectrum in the visible region.

The FTS registration of the AlD^+ ion spectrum, carried out in the Materials Spectroscopy Laboratory of the University of Rzeszów, covered the $0-0$ and $1-1$ bands of the $A^2\Pi - X^2\Sigma^+$ system in the 27 000 − 29 000 cm^{-1} region. The registration was made at the instrumental resolution of 0.03 cm^{-1} and 128 scans. For the best molecular lines, an SNR value of approximately 50 : 1 and a spectral width of 0.11 cm^{-1} were obtained. As a source of the emission spectrum, a discharge lamp of the new type, described in Chapter 4.2.4, filled with a mixture of Ne (1.5 Tr) and ND_3 (0.8 Tr) was used for the first time. It was powered by a current of 250 mA. The present author's observations of the visible spectrum of the AlD^+ molecule are the second ones after work of Balfour and Lindgren published in 1984 [45] and the first ones made using the FTS spectrometer.

Nearly 500 molecular spectral lines were interpreted in the spectrum, for which corresponding transition frequencies were determined with absolute accuracy of ± 0.005 cm^{-1}. This value is of a better order compared to the previous study using conventional emission spectroscopy [45]. The measurements of AlD^+ line wavenumbers [45] were verified, which turned out to be lower by a constant value of approximately 0.4 cm^{-1} than those obtained now.

The analysis of experimental data allowed for discovering irregularities in the e and f terms of the $A^2\Pi$, $v = 0, 1$ state. The most probable cause of the observed anomalous Λ−doubling in the $A^2\Pi$ state was its interaction with the $B^2\Sigma^+$ state, which lies approximately 3720 cm^{-1} above [**H8**].

Using the Curl−Dane−Watson method [64, 65], molecular constants of the regular $X^2\Sigma^+$, $v = 0, 1$ state were calculated, whose values were considerably refined relative to the results of the previous work [45]. For the $A^2\Pi$ state, the first values of ro−vibrational terms were determined, and with their help an experimental course of the Λ–doubling for the $v = 0, 1$ levels was plotted (Figure 3(a)).

In the next step, the effective molecular parameters were determined for the $A^2\Pi$ state using the `PGOPHER` program [73]. The results verify the earlier ones to a large degree [45], especially in the area of constants of the fine structure of the $A^2\Pi$, $v = 0, 1$ state. The spin–rotation interaction constants ($\gamma_{0,1}$) as well as a set of the Λ–doubling parameters ($p_{0,1}$ and $q_{0,1}$) were determined for the first time.

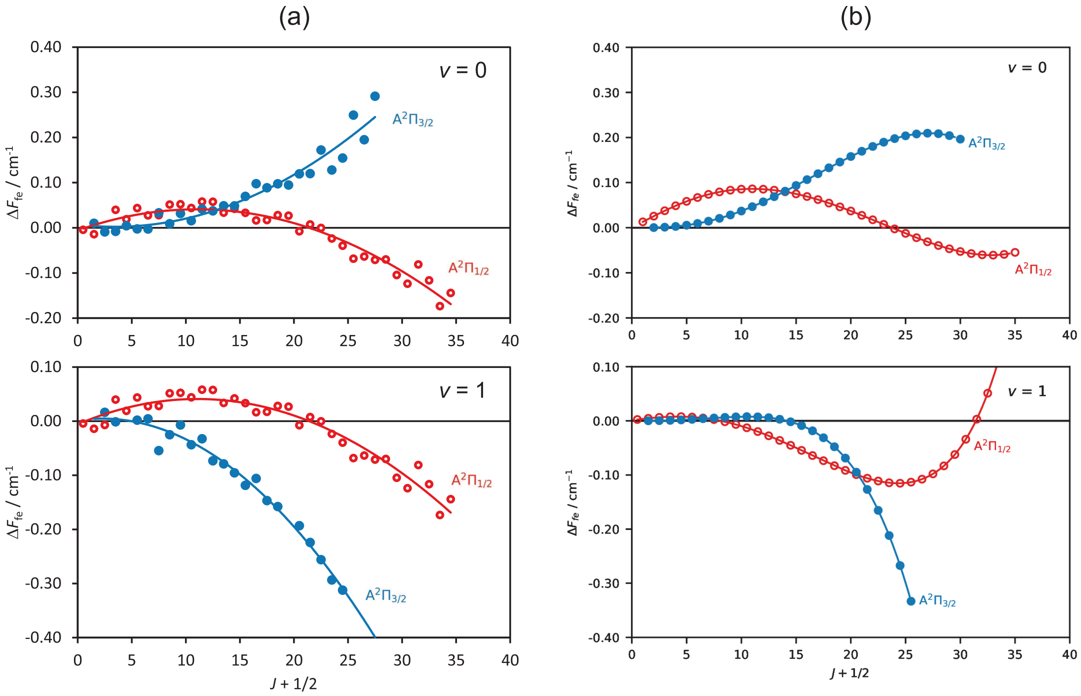

Figure 3: The Λ–doubling of the $A^2\Pi$, $v = 0, 1$ levels of AlD^+ **[H8]**: (a) experimentally observed; (b) theoretically predicted.

The first *ab initio* calculations for the AlD^+ ion included five lowest–lying electronic states. Also, from the point of view of the analysis of the observed spectrum, they included the states $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ but also $1^4\Sigma^+$ and $1^4\Pi$. With the use of the SA–CASSCF and MRCI methods in the augmented aug–cc–pV5Z basis set and the `MOLPRO` suite [74], potential energy curves of the states under consideration and dipole moment functions (DMFs) as well as transition dipole moments (TDMs), among others, were calculated. The active space consisted of all the occupied valence orbitals of the aluminum atom plus the $1s$ orbital from the deuterium atom.

By means of the the `DUO` program [76], the values of ro–vibrational terms for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of AlD^+ were determined. On their basis, theoretically predicted Λ–doubling for the $A^2\Pi$ state was plotted (Figure 3(b)). The results of the *ab initio* calculations present perfect consistency with the experiment for $v = 0$, both in general trends and absolute values of the splitting. Reproduction of the experimental data for $v = 1$ can be considered satisfactory, although their consistency is not so good. The reasons for the discrepancy seem to lie in low accuracy of the theoretical calculation of the position of $B^2\Sigma^+$ state (± 100 cm^{-1}) and in the shape of the potential for this state. Recalculations taking into account the change in the position of state $B^2\Sigma^+$ by a value of ± 200 cm^{-1} did not give a significant improvement in the consistency of the observed and predicted Λ−doubling for $A^2\Pi$, $v = 1$.

The fit of the theoretical values of rotational terms to the Hamiltonian for the $^2\Pi$ and $^2\Sigma^+$ states in the form proposed in the work [45] allowed for determining molecular parameters for levels $v = 0 - 4$ of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states. A very good consistency of *ab initio* constants with the results of present [**H8**] and previous experimental works [45] was obtained. The analysis of the results also indicates the presence of a strong $B^2\Sigma^+$, $v = 0 \sim A^2\Pi$, $v = 3$ interaction.

My contribution to the work: gathering the existing literature on the subject that is being researched; developing the concept of the work; continuing the cooperation with a group from the University of Belfast; designing the new construction of a discharge lamp and selection the lamp operating conditions; registration and interpretation as well as measurement of the spectra; the complete analysis of experimental data; analyzing the experimental results and preparation for publication; editing a complete article manuscript (except for Chapters 3 and 5 developed by I. Lane and K. Moore); editing the text of the article after co−authors' comments. I estimate my contribution at 60%.

4.2.4. Experimental details

Sources of molecular spectra

To excite the emission spectrum of the AlH molecule, studied as part of the work [**H1**], a conventional water−cooled lamp with an aluminum hollow−cathode of Al 99.5 % purity was used. The discharge conditions were optimized in terms of the buffer gas used and its pressure in the lamp, with a view to obtaining the best FWHM and SNR values for the AlH molecular lines. The lamp was filled with a mixture of neon and ammonia (in the ratio of about 15 : 1 at a total pressure of about 3 Tr) instead of the standard molecular hydrogen. The use of NH_3 allowed for the operation of much lower values of current in the anode−cathode circuit. The lamp was supplied with a current of 40 − 60 mA, obtaining the glow discharge stability (and intensity of the spectral lines) for about 4 hours.

In experiments, the results of which were published in the works [**H2**−**H7**] a CWHC type (*composite wall hollow−cathode*) discharge lamp with two anodes designed by Bacis [60] was used. In its original version, the lamp was designed to obtain the spectra of these molecules in the gas phase, the cathode material of which was "built" (e.g. sinter Cu and Se to obtain the CuSe molecule spectra [60]).

For the needs of current research, the lamp was modified and tested to optimize the operating conditions. The tests carried out by the team of M. Zachwieja, W. Szajna, R. Hakalla included selection of materials, lamp geometry and pressure and current operating conditions. As before, the choice of neon as a buffer gas and ammonia (NH_3/ND_3) as a gas "supplying" hydrogen or deuterium atoms into the discharge area proved significant. Finally, the lamp was equipped with a water−cooled aluminum cathode in the shape of a cylinder and two cylindrical anodes placed no more than 5 mm from the surface of the cathode. This arrangement of electrodes enabled the lamp to operate with a simultaneous connection of three power circuits:

- anode I − cathode,
- anode II − cathode,
- anode I − anode II, where one of the anodes becomes a cathode.

Under standard power supply conditions of circuits[3] 80 mA, 80 mA oraz 150 mA, respectively, this lamp gives almost four times higher intensity of molecular spectral lines than a conventional HC lamp used in the work [**H1**]. The lamp was filled with a mixture of Ne (about 2.5 Tr) and NH_3 or ND_3 (about 0.2 Tr). Such conditions guaranteed stability of the discharge for about 6 hours, which was enough time to make satisfactory registrations of the spectra.

Excitation of the visible emission spectrum of the AlD^+ molecule required the development of a new approach. The use of existing sources, lamps of the HC [**H1**] and CWHC type [**H2**−**H7**], did not, however, result in obtaining the desired spectrum of the $A^2\Pi - X^2\Sigma^+$ system with the intensity that allows for its precise analysis. Observations that were made, however, became the basis to draw a conclusion that prolonged discharge causes a decrease in the intensity of the AlH and AlH^+ bands, which were permanently present in the spectrum as "impurity" [**H5**, **H7**]. At the same time, there was a significant increase in the intensity of the AlD molecule spectra and, what was particularly important, of AlD^+. This process proved to be more effective at higher values of the current supplying the anode−cathode circuit ($I > 300$ mA).

On the basis of previous information regarding discharge lamps [77, 78], I planned the construction of a water−cooled HC lamp that ensures isolation of the cathode (discharge area in the cathode) from the glass part of the lamp in which the anode was mounted. Thus, the possibility of arc discharge between the anode and cathode was eliminated [78]. This allowed for a significant increase in the value of acceptable current supplying the lamp (up to 0.5 A).

---

[3] Only for registration of the spectrum of the $b^3\Sigma^- - a^3\Pi$ system in the AlH molecule, as described in point [**H6**] in Chapter 4.2.3, the higher values of the current were used.

During optimization of operating conditions of the new lamp, I performed a series of tests checking the dependence of the position and width of the spectral lines on the current and effective pressure of the buffer gas (Ne) in the lamp.

Current tests carried out in the 50 mA to 500 mA range (every 50 mA) did not show the AlD and AlD$^+$ line shift in the range of declared accuracy of wavenumbers, estimated at ±0.002 cm^{-1} [**H7**] and ±0.005 cm^{-1} [**H8**]. Only the Doppler broadening of the lines was observed from the FWHM value of 0.08 cm^{-1} to nearly 0.10 cm^{-1} for AlD and 0.10 cm^{-1} $\rightarrow$ 0.13 cm^{-1} for AlD$^+$, respectively. The increase in the rotational temperature from 450 K to 900 K, which was the cause of the lines broadening, was determined on the basis of the spectrum simulation [73]. It was performed on the basis of experimental molecular constants AlD and AlD$^+$ and observed intensity of rotational lines.

Tests from 1 Tr do 20 Tr were performed for nine pressure values of Ne in this range, 1.0, 1.5, 2.0, 2.5, 3.0, 5.0, 7.5, 12.5 and 20.0 Tr, at current of 150 mA. The limiting parameters of the test were chosen considering the occurrence and stability of the glow discharge in the lamp. Apart from these values, with a fixed inner diameter of a cylindrical aluminum cathode which was 3.5 mm, the so−called cathode effect was not observed. The effect of pressure increase on the position and spectral width of the AlD and AlD$^+$ lines was not found. Moreover, with the relative accuracy of the FTS measurements declared at 10^{-7}, the remaining effects [79–83] that may influence the shape and position of molecular spectral lines should be considered negligibly small.

The following operating parameters of the new lamp type were finally determined: current of 250 mA, buffer gas pressure of 1.5 Tr and pressure ND_3 of 0.8 Tr. Such conditions were a compromise between the observed intensity of the AlD$^+$ (SNR 50 : 1) and their spectral width (FWHM 0.11 cm^{-1}) [**H8**], dominated by the Doppler broadening.

It should be emphasized here that the stability of the discharge together with the possibility of using higher values of the current, puts this new source of molecular spectra high among those used so far[4]. While registering bands of the $A^2\Pi - X^2\Sigma^+$ system in AlD$^+$, the observed $0 - 0$ band of the $A^1\Pi - X^1\Sigma^+$ system in AlD had a SNR of approx. 3000 : 1. This value is more than twice as good as that obtained in the same apparatus registration conditions in the work [**H7**], where the source of the AlD spectrum was a CWHC type lamp [60].

---

[4] Possibilities of the new type of a discharge lamp have already been used to register the spectrum of the AlD molecule in the ultraviolet region and the visible spectra of the InD and $^{12}C^{17}O^+$. Further information is presented in Chapters 5.2 and 5.3.

The System for Spectrum Registration

The HADOS measurement system based on a 2−m dispersive plane grating spectrograph (PGS) was used to register the spectra that were the subject of analyses, the results of which were presented in the works [**H1**−**H6**]. The new optical high accuracy dispersion spectroscopy system is conversion of a conventional 2−meter spectrograph PGS−2 into a spectrometer equipped with a photomultiplier with a unique possibility of simultaneous registration of the spectrum studied and a calibration spectrum and with precise interferometric measurement of the position of spectral lines.

Structural and adaptive changes, carried out in the team of M. Zachwieja, W. Szajna, R. Hakalla, were described in detail in the work [**H1**] and included:

- the use of a photomultiplier operating in the single photon counting mode as a detector (instead of a traditional photographic plate);
- construction of a system for precise photomultiplier move in the focal plane of the spectrograph and for interferometric measurement of its position (linear stage with the stepper motor and planetary transmission and a laser interferometer);
- development of the method of a simultaneous Th calibration spectrum registration without losing the “quality” of the studied spectrum (temporary redirection of the light beam from the reference source, set perpendicularly, to the photomultiplier aperture through a movable quartz prism with simultaneous cut−off of the studied light beam);
- ensuring rigidity of the entire system by leveling mechanical deformation (placing the spectrometer on a granite plate attached to the supporting wall of the building) and thermal (insulation of the device in combination with temperature stabilization in the range of ±0.1°C).

The structural changes described allowed for compensating the fluctuations of the spectral line positions caused by slight mechanical, thermal (up to about 1°C) and pressure (up to about 1 hPa) disturbances during spectrum scanning.

The use of a movable prism allows for the calibration of the spectrum in real−time scanning. The selected thorium reference lines [84] “appear” in the tested spectrum, each occupying a fragment of a length of approx. 80 μm, which is not then registered. As a result, there is no overlap between both spectra, as is usually the case in instruments where a permanent semi−transparent mirror or a beamsplitter are used.

The precision of the innovative method of registration of the reference spectrum described above and of calibration of the studied molecular spectra was verified by registering the Th atomic spectrum [84] from two, perpendicularly set, identical commercial sources (HC, HAMAMATSU lamps). As a result, the absolute accuracy of the calibration was estimated at ±0.0015 cm^{-1} in the range 11 000 − 22 000 cm^{-1}, ±0.0025 cm^{-1} in the region 22 000−30 000 cm^{-1} and ±0.009 cm^{-1} on the border of vacuum ultraviolet (50 000 cm^{-1}).

The spectra of the AlD and AlD^+ molecules, [**H7**, **H8**], were registered using a Fourier transform spectrometer (BRUKER IFS 125 HR). The spectrometer was adapted to registering spectra from an external source through the use of a quartz planar convex focusing lens, directing the beam of radiation at the input aperture of the FTS. The spectrometer operated in vacuum conditions with effective internal pressure of approx. 2×10^{-3} Tr. Spectra registration in the visible region was made at resolution of 0.03 cm^{-1}. The instrumental half width had no significant effect on the effective FWHM of the molecular lines of 0.08 cm^{-1} for AlD and 0.11 cm^{-1} for the AlD^+ ion. The spectrum was calibrated using the Ne atomic lines [84], which limited the absolute accuracy of determining the wavenumbers of the best molecular lines to ±0.002 cm^{-1}. 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 software attached to the spectrometer [85].

4.3. Summary

One of the main objectives of molecular spectra research is to get to know their energy structure with the highest possible accuracy. On this basis, we can derive information about the motion of the electrons (electronic structure) and the vibration and rotation of the nuclei in the molecule [86]. Further analyses allow us to determine the probability of transitions between individual electronic states and the presence of possible interactions between them.

The aim of the [**H1−H8**] publication cycle, discussed in Chapter 4.2.3 was to register and analyze the emission spectra of the AlH and AlD molecules and their positive ions. Thanks to appropriately selected experimental methods, high−resolution spectra of very good quality were obtained. The interpretations carried out covered in total 2171 spectral lines from 27 bands belonging to 8 systems in all molecules. The obtained lines are characterized by a very good SNR value (approximately 250 : 1 on average, the highest 1400 : 1) and a satisfactory spectral width 0.08 − 0.15 cm^{-1}.

Careful analyses combining current measurements and available experimental literature data in the infrared region [36, 41] produced valuable results, among which the following deserve special attention:

- discovery of a very weak perturbation in the $\mathrm{A}^1\Pi$, $v = 1, J = 5$ level in the AlH molecule [**H1**],
- verification of the character of perturbations in the $\mathrm{C}^1\Sigma^+$, $v = 0$ state and

confirmation of theoretically predicted [67] irregularities in the $C^1\Sigma^+$, $v = 1$ level in the AlH molecule [**H2**],

- determination of absolute values of rotational terms for the $A^1\Pi$, $v = 0, 1$ and $C^1\Sigma^+$, $v = 0, 1$ states of AlH [**H3**],
- discovery of the anomalous Λ−doubling in the $A^2\Pi$, $v = 0, 1$ state and perturbations of rotational terms for these vibrational levels in the AlH^+ molecule [**H4**],
- the first observation of Λ−doubling in the $a^3\Pi$, $v = 0, 1$ state and the verification and analysis of perturbation in the $b^3\Sigma^-$, $v = 0, 1$ state in the AlH molecule [**H6**],
- the first FTS registration of the spectrum of the AlD molecule in the visible region and combination of experimental and theoretical results for the $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^+$ states [**H7**],
- the first observation of the VIS−FT emission spectrum of the $A^2\Pi - X^2\Sigma^+$ system of AlD^+ [**H8**] along with the first *ab initio* calculations for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states and discovery of the irregularities in the Λ−doubling in the $A^2\Pi$ state [**H8**].

As a result of the standard analysis, also, a number of molecular constants and equilibrium parameters were determined which characterize a total of 10 electronic states (24 vibrational levels) in four considered molecules. The accuracy of values of the majority of molecular constants were significantly improved, and many of them were determined for the first time. The main contribution to the above results was efficient sources of emission spectra, high−resolution of registered spectra and high precision of determination of wavenumbers of the observed rotational lines.

Accuracy of the measured frequencies of rotational transitions and obtained values of molecular constants [**H1**, **H2**, **H4**] allowed for their use in work in the field of astrophysics [9, 87], chemistry [88] and in research on laser−cooling of molecules [23, 89].

The original results for the $X^1\Sigma^+$ and $A^1\Pi$ states of the AlH and AlD molecules, published in [**H1**, **H2**, **H3**, **H5**] and cited in [90], co−created the experimental database for the ExoMol project team to develop a list of theoretical spectral lines in the visible range ($0 - 27\ 000$ cm^{-1}) for three isotopologues of aluminium hydride: $^{27}Al^1H$, $^{27}Al^2H$ and $^{26}Al^1H$ [91].

Diatomic, hydrogen and deuterium−containing molecules with their relatively simple electronic structure are also of great interest to theoreticians. In this respect, the results of experimental works can provide support and a kind of "verification tool" for the results obtained by various *ab initio* methods. The results of the author's works have been used several times and cited in the works dealing with this problem in AlH [21,49,50] and AlH^+ [50].

I hope that in the future our current and subsequent results of analyses of emission spectra of hydrides and deuterides of group IIIA metals will provide a rich experimental material useful in many fields of both experimental and theoretical physics.

5. Discussion of other scientific and research achievements

5.1. The course of scientific work before obtaining the doctoral degree

I undertook research work during my studies under the supervision of dr. hab. Ryszard Kępa, conducting the first analysis of the $1-1$ band of the $B^2\Sigma^+ - X^2\Sigma^+$ system in the $^{13}C^{16}O^+$ molecule spectrum in the far ultraviolet region. This achievement became the basis of my master thesis and initiated my interest in the emission spectrum of carbon monoxide ion.

In October 1999 I was employed as an assistant lecturer in the Atomic and Molecular Physics Laboratory at the Faculty of Mathematics and Natural Sciences of the Pedagogical University in Rzeszów, where I continued my research on the spectra of isotopologues of the CO^+ molecule. The subject of my special interest was the $B^2\Sigma^+ - X^2\Sigma^+$system. The result of this research was an extensive description of both electronic states in the $^{12}C^{16}O^+$, $^{13}C^{16}O^+$, $^{12}C^{17}O^+$ and $^{12}C^{18}O^+$ molecules. Registrations of the $B^2\Sigma^+ - X^2\Sigma^+$ system in the $^{12}C^{17}O^+$ molecule were the first observations of the emission spectrum of this isotopologue of CO^+.

In order to obtain the spectrum of the $^{12}C^{17}O^+$ molecule, I proposed a new construction of a hollow−cathode discharge lamp in which a cylinder, made of pure graphite, was fitted, and the lamp was filled with molecular oxygen $^{17}O_2$ without buffer gas. This approach allowed us to overcome problems with the availability of the desired isotopologue of CO or CO_2, from which the spectrum of the CO^+ molecule was usually obtained. The use of a short distance between the electrodes and the lack of buffer gas in the discharge area had a positive effect on reducing the current value supplying the lamp and significantly extended its lifespan. As a result, exposure lasting many hours and obtaining band spectra of very low intensity were possible. For the spectra registration, a PGS−2 plane grating spectrograph with a photographic plate as a spectrum recorder was used.

The results obtained were published in nine papers [**A1**−**A4**, **A6**−**A9**, **A11**] and were presented at several international conferences [**B1**−**B7**][5]. The results concerning the $^{12}C^{16}O^+$, $^{13}C^{16}O^+$ and $^{12}C^{17}O^+$ molecules became the basis of my doctoral dissertation titled *Analysis of the first−negative* ($B^2\Sigma^+ - X^2\Sigma^+$) *system in the spectrum of the* $^{12}C^{16}O^+$, $^{13}C^{16}O^+$ *and* $^{12}C^{17}O^+$ *molecules.* The above−mentioned dissertation was awarded by the Scientific Council of the Faculty of Mathematics and Natural Sciences

---

[5] The numbering of the remaining articles [**A1**−**A21**] and conference presentations [**B1**−**B53**] is consistent with the List of Publications and Achievements given in Annex 4.

of the University of Rzeszów and honored with an individual award of the 1st rank of the Minister of Science and Higher Education in 2006.

5.2. The course of the scientific work after obtaining the doctoral degree

After obtaining the doctoral degree, I took steps to expand the research area with other new diatomic molecules. My choice fell on hydrides and deuterides of selected IIIA group metals, i.e. Al, In and Ga. The next natural step was to include positive ions of these molecules in the research plans. I noticed that despite the nearly 80−year history of spectroscopic research on these molecules, references to experimental data from the 30's and 40's of the last century were still present in contemporary literature on the subject. On the other hand, the astrophysical observations of these molecules and growing interest in the use of metal hydrides and their ions in laser−cooling justified the necessity to update the studies using modern experimental methods, and thus, to expand, improve, and systematize the available results. A series of conducted experiments resulted in eight publications [**H1**−**H8**] constituting the basis of this habilitation application.

I realized that the lack of current research on the emission spectra of the above mentioned molecules may pose a certain obstacle in the search for research centres (scientific partners) to conduct joint experiments in the area being the subject of my interest. I tried to compensate for these deficiencies by establishing national and international cooperation with a team working on *ab initio* calculations for these molecules.

I started the research in 2008 with obtaining the spectrum of a molecule containing aluminum, AlH. The beginning of the research coincided with finalization of the works of the team of M. Zachwieja, W. Szajna, and R. Hakalla on the launch of the high accuracy dispersive optical spectroscopy HADOS laboratory (description in Chapter 4.2.4). Possibilities of the new instrumentation were fully used in the registration, calibration and analysis of the spectrum of the $\mathrm{A}^1\Pi - \mathrm{X}^1\Sigma^+$ singlet transition of the AlH molecule [**H1**].

In 2009 − 2012 I managed the work of the team (cooperation with I. Piotrowska and M. Ostrowska−Kopeć), whose task was to plan research objectives, design, prepare and carry out tender procedures and purchase measuring equipment for the Laboratory for Monitoring and Detection of Radioactive Materials in the emerging Center for Innovation and Transfer of Natural Science and Engineering Knowledge of the University of Rzeszów (CIiTWTP). The main equipment of the laboratory is, among others, two modern measurement stations: a four−track low background alpha spectrometer with the system of sample preparation and a gamma ray analyzer integrated with a gamma spectrometer (CANBER PACKARD) for the analysis of various industrial materials and environmental samples.

At the same time, I participated in the design of equipment for the Molecular Spectroscopy Laboratory (cooperation with M. Zachwieja and R. Hakalla), which was being created in the CIiTWTP structure, as part of the Materials Spectroscopy Laboratory. The main acquisition was the Fourier Spectrometer (BRUKER IFS 125 HR) for the spectral range of 1850 – 50 000 cm^{-1}. As part of the team's work, I completed and carried out a tender procedure for the construction of a vacuum station based on a turbo–molecular pump and a glass vacuum system .

In the years 2006 – 2012, I cooperated in research on the spectra of CH^+ ($A^1\Pi - X^1\Sigma^+$ system) [**A5**, **A10**], CD ($A^2\Delta - X^2\Pi$ system) [**A12**] and CO ($B^1\Sigma^+ - A^1\Pi$ system) [**A13**, **A14**]. In subsequent years, due to health reasons, I did not conduct any active research. I was only able to participate in analyses of the results of research on the CO molecule carried out in our laboratory by R. Kępa [**A16**] and R. Hakalla [**A15**, **A17**, **A18**].

The return to scientific activity, at the end of 2015, allowed me to continue to register spectra of the AlH [**H6**], AlD [**H5**, **H7**] and AlD^+ [**H8**] molecules, and thus, to close the research subject. Papers [**H7**, **H8**] were produced as a result of a cooperation initiated by me in 2016 with a group from the School of Chemistry and Chemical Engineering of the Queen's University of Belfast, headed by Dr. I.C. Lane. They are the first combination of experimental results and the results of *ab initio* calculations for the AlD and AlD^+ molecules.

I also participated in research aimed at obtaining the spectrum and publication of results on the $B^2\Sigma^- - X^2\Pi$ [**A19**] and $C^2\Sigma^+ - X^2\Pi$ [**A21**] systems of the CD molecule and in the work of the international team headed by R. Hakalla on the deperturbation analysis in the $A^1\Pi$, $v = 1 - 5$ state of the $^{12}C^{17}O$ molecule [**A18**].

Seeing a constant interest in the CO^+ [92–99], resulting mainly from its importance in astrophysical research, I undertook the task of exciting and registering the spectrum of the $^{12}C^{17}O^+$ isotopologue in the visible region with the use of the new type of a discharge lamp as a source of the spectrum. Registered by me for the first time with the FT spectrometer, the spectrum of this CO^+ isotopologue included 11 bands belonging to the two systems: $A^2\Pi_i$–$X^2\Sigma^+$ (9 bands) oraz $B^2\Sigma^+$–$A^2\Pi_i$ (2 bands) with a total number of lines of nearly 5 000. The spectrum of the $A^2\Pi_i$–$X^2\Sigma^+$ system became the subject of an analysis carried out jointly with I. Piotrowska and M. Ostrowska–Kopeć, which results were presented in the form of several conference proceedings [**B44**, **B45**, **B47**, **B48**, **B51**].

5.3. Scientific and research plans for the upcoming years

The upcoming research will focus on the registration of the emission spectra of the $E^1\Pi - A^1\Pi$ oraz $G^1\Sigma^+ - A^1\Pi$ systems in the AlD molecule. This will allow us to conduct a deperturbation analysis in the $E^1\Pi$ state and verify initial results obtained by us [**B12**] on the basis of experimental data collected by Lagerqvist et al. [78]. Successful high−resolution registration of the spectrum of the $C^1\Sigma^+ - X^1\Sigma^+$ system of AlD (Figure 4) using the new type of the lamp and HADOS technique allows us to look optimistically at the possibility of exciting emission transitions from the $E^1\Pi$ and $G^1\Sigma^+$ states, lying approximately 10 000 cm^{-1} above the $C^1\Sigma^+$state. These hopes seem to be all the more justified because I successfully registered an analogous spectrum of the $E^1\Pi - A^1\Pi$ system ($0 - 0$ band) in the AlH molecule. Results of the analysis of irregularities that occur in it have already been presented in one of the international conference [**B12**].

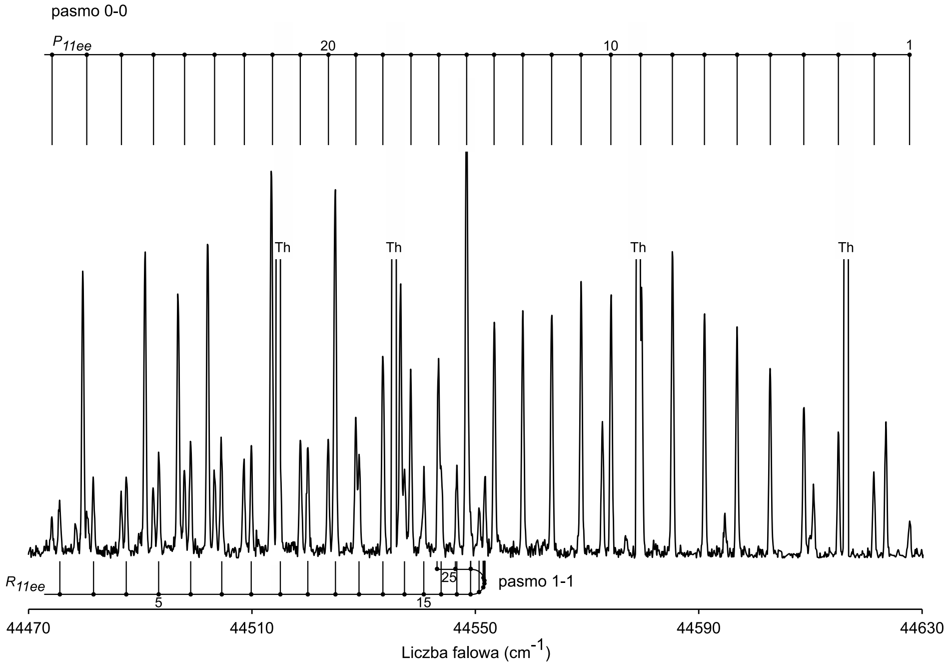

Figure 4: The $0 - 0$ and $1 - 1$ band of the $C^1\Sigma^+ - X^1\Sigma^+$ system of AlD, observed in the region of 44 000 cm^{-1} using the HADOS technique and the new type of a discharge lamp as the emission source. The spectrum was registered with reciprocal dispersion (0.05 nm/mm) three times higher than in the previous registration [62, 100].

The next stage will be obtaining high−resolution FTS spectra of hydrides and deuterides of indium [101, 102], gallium [103, 104] and their positive ions. A particularly considerable challenge will be the excitation of spectra of ionized molecules, which until now have not been observed experimentally.

The first FT emission spectrum of the $A^1\Pi - X^1\Sigma^+$ system (three bands of the $0 - v''$ progression) of the InD molecule in the visible region has already been registered by me (Figure 5) and is currently being analyzed. Work is underway to optimize the discharge conditions. The purpose of these actions is to excite transitions between higher vibrational levels of the $A^1\Pi$, $(v = 1, 2)$ i $X^1\Sigma^+$, $(v = 2, 3)$ states. As in the case of

AlD and AlD$^+$, I plan to continue working with the group from the School of Chemistry and Chemical Engineering of the Queen's University of Belfast in Northern Ireland and combine experimental results with results of *ab initio* calculations.

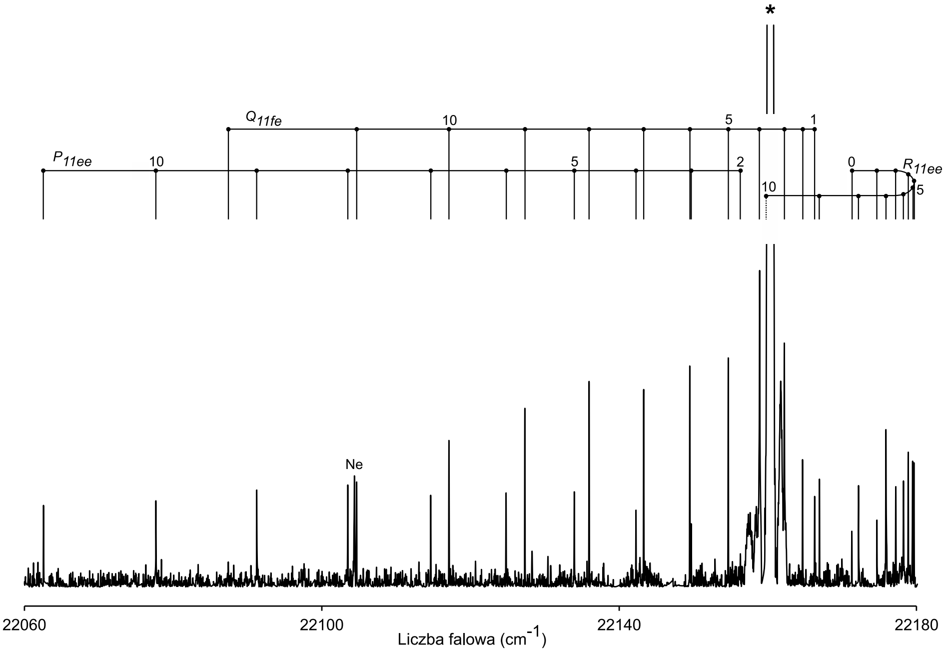

Figure 5: The first FT emission spectrum of the $A^1\Pi - X^1\Sigma^+$ system in the InD molecule. The $0-0$ band was registered at instrumental resolution of 0.03 cm^{-1}, yielding the spectral width of rotational lines of approximately 0.05 cm^{-1} and a signal–to–noise ratio of approximately 50 : 1. A very strong indium atomic line 22 160.35 cm^{-1}, present in the same region, was marked with an asterisk https://www.nist.gov/pml/atomic-spectra-database.

At the same time, in cooperation with M. Ostrowska–Kopeć and I. Piotrowska, registrations and analyses of spectra of the $A^2\Pi_i$–$X^2\Sigma^+$ system will be continued in several isotopologues of the CO$^+$ molecule, i.e. $^{12}C^{17}O^+$, $^{12}C^{18}O^+$, $^{13}C^{17}O^+$ oraz $^{13}C^{18}O^+$. Supplementing the above registrations with FTS spectra of the $B^2\Sigma^+ - X^2\Sigma^+$ system will provide the basis for the first experimental identification of perturbations and deperturbational calculations in the $A^2\Pi_i$ state in these CO$^+$ isotopologues.

It is also justifiable to re–register and re–analyze the $B - X$, $6 - 10$ band of the $^{12}C^{16}O^+$ molecule to complement the interaction characteristics of $X^2\Sigma^+$, $v = 10 \sim A^2\Pi_i$, $v = 0$ for rotational levels $J = 0 - 10$ [105]. The only author's registrations of this band using conventional spectroscopy [**A3**, **A4**] allowed for observation of slight irregularities in its structure and weak effects of interactions of the $X^2\Sigma^+ \sim A^2\Pi_i$ states. Currently, deperturbation analyses are being conducted (the team of R. Kępa, R. Hakalla, W. Szajna) using these measurement data [**A3**, **A4**] and the latest Fourier registrations of the $0-2$ band of the $A^2\Pi_i$–$X^2\Sigma^+$ system in the main isotopologue of CO$^+$.

Recently, I have started cooperation with dr hab. A. Pluta, a voivodship consultant on hematology, from the Department of Hematological Oncology, Oncology Specialist Hospital in Brzozów. Planned joint research will be aimed at obtaining and analyzing ATR−FTIR (*Attenuated Total Reflectance*) spectra of biological samples important in the diagnosis and planning of bone marrow disease treatment [106–108]. The research will be carried out using the FTIR spectrometer (BRUKER VERTEX 70v) being part of the equipment of the Far Infrared Spectroscopy Labratory MSL of the University of Rzeszów.

Going in a similar direction, research on the ATR−FRIT spectrum of urine samples[6] of patients diagnosed with membranous glomerulonephritis has already begun. I am conducing this research together with dr. A. Gala−Błądzińska from the Voivodeship Clinic No. 2 in Rzeszów, an employee of the Medical Faculty of the UR and a voivodeship consultant in the field of clinical transplantation. Confirmation of current, very preliminary results of research [109], and finding potential biomarkers would provide an opportunity to support the process of diagnosing the disease by limiting (or eliminating) the need to perform kidney biopsies.

At the end of 2017, the project *Investigations of high resolution spectra of translucent interstellar clouds and laboratory spectra of transition metal sulfides*, in submission of which I participated, received a positive opinion and funding of the National Science Center as part of the OPUS 13 competition. This project, headed by prof. dr. hab. J. Krełowski from the Center of Astronomy of the Nicolaus Copernicus University in Toruń, is being carried out at the MSL of the University of Rzeszów. The research task of the team in which I work is to obtain laboratory spectra of iron sulfide as a potential carrier of diffuse interstellar bands(DIB's) [110]. These spectra are expected to be obtained by laser induced fluorescence (LIF) method [111] or in parallel experiments with glow discharge in lamps and registration of spectra by means of an FT spectrometer.

To sum up, I express my deep hope that my current work, experience and established cooperation will allow me to successfully continue my research on the spectra of diatomic and polyatomic molecules in the area of the FTS and ATR−FTIR emission and absorption spectroscopy.

References

[1] P.F. Bernath. Int. Rev. Phys. Chem. **4**, 681 (2009).
[2] K. Lodders, H. Palme. Meteor. Planet. Sci. Suppl. **72**, 5154 (2009).
[3] J. Tennyson. Molecules in space. Handbook of Molecular Physics and Quantum Chemistry. John Wiley & Sons Ltd., Chichester, GB (2003).
[4] G.H. Herbig. Pub. Astron. Soc. Pac. **68**, 204 (1956).
[5] P.W. Merrill. Astrophys. J. **118**, 453 (1953).
[6] G.H. Herbig, R.R. Zappala. Z. Astrophys. **68**, 423 (1968).

---

[6] Permission of the Bioethics Committee of the University of Rzeszów 2018/06/14.

[7] E. Hultheén, R. Rydberg. Nature. **131**, 470 (1933).

[8] G. Steinvinkel. Z. Phys. **114**, 602 (1939).

[9] T. Kamński, K.T. Wong, M.R. Schmidt, H.S.P. Müller, C.A. Gottlieb, I. Cherchneff, K.M. Menten, D. Keller, S. Brünken, N.A. Patel. Astron. & Astrophys. **592**, A42 (2016).

[10] P.W. Merrill, A.J. Deutsch, P.C. Keenan. Astrophys. J. **136**, 21 (1962).

[11] H. Wöhl. Solar Phys. **16**, 362 (1971).

[12] P. Sotirovski. Astron. Astrophys. Suppl. **6**, 85 (1972).

[13] L. Wallace, K. Hinkle, W. Livingston. An atlas of sunspot umbral spectra in the visible from 15000 to 25000 cm^{-1} (3920 to 6664 Å), Tech. Rep. 00-001, National Solar Observatory, Tucson, AZ (2000) .

[14] B. Karthikeyan, N. Rajamanickam, S.P. Bagare. Solar Phys. **264**, 279 (2010).

[15] J. Tennyson, S.N. Yurchenko. Mon. Not. R. Astron. Soc. **425**, 21 (2012).

[16] J. Tennyson, S.N. Yurchenko, *i in.* J. Mol. Spectrosc. **327**, 73 (2016).

[17] A.S. Rajpurohit, C. Reylé, F. Allard, D. Homeier, M. Schultheis, M.S. Bessell, A.C. Robin. Astron. & Astrophys. **556**, A15 (2013).

[18] J. Tennyson, S.N. Yurchenko. Mol. Astrophys. **8**, 1 (2017).

[19] J. Tennyson, S.N. Yurchenko. Atoms **6**, 26 (2018).

[20] M.D. Di Rosa. Eur. Phys. J. D. **31**, 395 (2004).

[21] N. Wells, I.C. Lane. Phys. Chem. Chem. Phys. **13**, 19018 (2011).

[22] J.H.V. Nguyen, C.R. Viteri, E.G. Hohenstein, C.D. Sherrill, K.R. Brown, B. Odom. New J. Phys. **13** 063023 (2011).

[23] C.Y. Lien, S.R. Williams, B. Odom. Phys. Chem. Chem. Phys. **13**, 18825 (2011).

[24] C.Y. Lien, C.M. Seck, Y.W. Lin, J.H.V. Nguyen, D.A. Tabor, B. Odom. Nat. Commun. **5**, 4783 (2014).

[25] P.G. Carrick. 31st Joint Propulsion Conference and Exhibit. AIAA-95-2892. (1995).

[26] Y. Zhang, M. Stuke. J. Cryst. Growth. **93**, 143 (1988).

[27] A.C. Erlandson, T.A. Cool. J. Appl. Phys. **56**, 1325 (1984).

[28] M. Yang, M.H. Alexander, S. Gregurick, P.J. Dagdigian. J. Chem. Phys. **102**, 2413 (1995).

[29] E. Hwang, P.J. Dagdigian. J. Chem. Phys. **102**, 2426 (1995).

[30] X. Yang, P.J. Dagdigian. J. Chem. Phys. **109**, 8920 (1998).

[31] B.Nizamow, P.J. Dagdigian. J. Chem. Phys. **113**, 4124 (2000).

[32] M. Pamboundom, J.J. Fifen, C. Nkem, M. Nsangou. Chem. Phys. Lett. **600**, 21 (2014).

[33] J.L. Deutsch, W.S. Neil, D.A. Ramsay. J. Mol. Spectrosc. **127**, 115 (1987).

[34] R-D. Urban, H. Jones. Chem. Phys. Lett. **190**, 609 (1992).

[35] C. Yamada, E. Hirota. Chem. Phys. Lett. **199**, 461 (1992).

[36] J.B. White, M. Dulick, P.F. Bernath. J. Chem. Phys. **99**, 8371 (1993).

[37] F. Ito, T. Nakanaga, H. Takeo, H. Jones. J. Mol. Spectrosc. **164**, 379 (1994).

[38] M. Goto, S. Saito. Astrophys. J. **452**, L147 (1995).

[39] R.S. Ram and P. F. Bernath, Appl. Opt. **35**, 2879 (1996).

[40] D.T. Halfen, L.M. Ziurys. Astrophys. J. **607**, L63 (2010).

[41] D.T. Halfen, L.M. Ziurys. Astrophys. J. **713**, 520 (2010).

[42] D.T. Halfen, L.M. Ziurys. Astrophys. J. **791**, 65 (2014).

[43] D.T. Halfen, L.M. Ziurys. Astrophys. J. **833**, 89 (2016).

[44] M. Rafi, M.A. Baig, M. H. Qureshi. Il. Nuovo Cimento. **56**, 289 (1980).

[45] W.J. Balfour, B. Lindgren. J. Phys. B: At. Mol. Phys. **17**, L861 (1984).

[46] Y. Tsuchiya, T. Ishida, H. Katagriri. Japan J. **12**, 301 (2000).

[47] A. Karton, J.M.L. Martin. J. Chem. Phys. **133**, 144102 (2010).

[48] D-H. Shi, H. Liu, X-N. Zhang, J-F. Sun, Y-F. Liu, Z-L. Zhu. Int. J. Quantum Chem. **111**, 554 (2011).

[49] A. Brown, R.E. Wasylishen. J. Mol. Spectrosc. **292**, 8 (2013).

[50] F. Ferrante, A. Prestianni, N. Armata. Theor. Chem. Acc. **136**, 3 (2017).

[51] F.P. Ureña, M.F. Gómez, J.J. López González, N. Rajamanickam. Astrophys. Space Sci. **272**, 345 (2000).

[52] P.B. Zeeman and G. J. Ritter. Can. J. Phys. **32**, 555 (1954).

[53] J.M. Brown, E.A. Colbourn, J.K.G. Watson, F.D. Wayne. J. Mol. Spectrosc. **74**, 294 (1974).
[54] D.L. Albritton, A.L. Schmeltekopf, R.N. Zare. J. Mol. Spectrosc. **67**, 132 (1977).
[55] J.A. Coxon. J. Mol. Spectrosc. **72**, 252 (1978).
[56] V.W. Holst. Z. Phys. **86**, 338 (1933).
[57] C.N. Challacombe, G.M. Almy. Phys. Rev. **51**, 930 (1937).
[58] C. Tao, X. Tan, P. Dagdigian, M.H. Alexander. J. Chem. Phys. **118**, 10477 (2003).
[59] B. Kleman. Ark. Fys. **6**, 407 (1953).
[60] R. Bacis. Phys. E: Sci. Instrum. **9**, 1081 (1976).
[61] E. Bengtsson. Z. Phys. **51**, 889 (1928).
[62] B. Grabe and E. Hulthén. Z. Phys. **114**, 470 (1939).
[63] Y.Zhu, R. Shehadeh, E. Grant. J. Chem. Phys. **97**, 883 (1992).
[64] R.F. Curl, C.B. Dane. J. Mol. Spectrosc. **128**, 406 (1988).
[65] J.K.G. Watson. J. Mol. Spectrosc. **138**, 302 (1989).
[66] B.E. Nilsson. Ark. Mat. Astro. Fysik. **19**, 35A (1948).
[67] J.M.O. Matos, P-A. Malmqvist, B.O. Roos. J. Chem. Phys. **86**, 5032 (1987).
[68] V.W. Holst. Z. Phys. **90**, 735 (1934).
[69] V.W. Holst. Z. Phys. **89**, 40 (1934).
[70] G.M. Almy, M.C. Watson. Phys. Rev. **45**, 871 (1934).
[71] V.W. Holst, E. Hulthén. Z. Phys. **90**, 712 (1934).
[72] M. Rafi, M. A. Baig, M.A. Khan. Il Nuovo Cimento. **43**, 271 (1978).
[73] C.M. Western. J. Quant. Spectrosc. Radiat. Transf. **186**, 221 (2017).
[74] H.J. Werner, P.J. Knowles, R. Lindh, F.R. Manby, *i in.* MOLPRO 2010, http://www.molpro.net.
[75] J.M. Brown, K.M. Evenson. Phys. Rev. A. **60**, 956 (1999).
[76] S.N. Yurchenko, L. Lodi, J. Tennysona, A.V. Stolyarov. Comput. Phys. Commun. **202**, 262 (2016).
[77] H. Schüler, H. Gollnow. Z. Phys. **93**, 611 (1935).
[78] A. Lagerqvist, L.E. Lundh, H. Neuhaus. Phys. Scri. **1**, 261 (1970).
[79] P.R. Berman. J. Quant. Spectrosc. Radiat. Transf. **12**, 1331 (1972).
[80] L. Galatry. Phys. Rev. **122**, 1218 (1961).
[81] M. Nelkin, A. Ghatak. Phys. Rev. **1935**, A4 (1964).
[82] R. Blackmore. J. Chem. Phys. **87**, 791 (1987).
[83] R. Ciuryło, J. Szudy. R.S. Trawiński. J. Quant. Spectrosc. Radiat. Transf. **57**, 551 (1997).
[84] B. A. Palmer, R. Engleman. Atlas of the Thorium Spectrum. Los Alamos Report LA-9615. Los lamos, USA (1983).
[85] OPUS$^{\mathrm{TM}}$ BRUKER Optik GmBH v.7.5.18 (2014).
[86] Herzberg G. Molecular spectra and molecular structure. I. Spectra of Diatomic Molecules. Van Nostrand-Reinhold. New York, USA (1950).
[87] A.N. Heays, A.D. Bosman, E.F. van Dishoeck. Astron. Astrophys. **602**, 105 (2017).
[88] P. Sriramachandran, B. Viswanathan, R. Shanmugavel. Int. J. Thermodyn. **17**, 27 (2014).
[89] C.M. Seck, E.G. Hohenstein, C.Y. Lien, P.R. Stollenwerk, B.C. Odom. J. Mol. Spectrosc. **300**, 108 (2014).
[90] S.N. Yurchenko, H. Williams, P.C. Leyland, L. Lodi, J. Tennyson. Mon. Not. R. Astron. Soc. **479**, 1401 (2018).
[91] http://exomol.com/data/molecules/AlH/.
[92] X.H. Yang, Y.Q. Chen, P.P. Cai, R.J. Wang, J.J. Lu. Chin. J. Chem. Phys. **13**, 406 (200).
[93] H. Zhuang, X.H. Yang, S.H. Wu, Z.Y. Bi, L.S. Ma, Y.Y. Liu, Y.Q. Chen. Mol. Phys. **99**, 1447 (2001).
[94] W. Li, X.H. Yang, Y.J. Gan, L. Wu, Y.C. Guo, Y.Y. Liu, Y.Q. Chen. Spectrosc. Spect. Anal. **25**, 1250 (2005).
[95] X.H. Yang, Y.D. Wu, Y.Q. Chen. J. Mol. Spectrosc. **245** 84 (2007).
[96] Y.D. Wu, X.H. Yang, Y.C. Guo, Y.Q. Chen. J. Mol. Spectrosc. **248**, 81 (2008).
[97] D. Shi, W. li, J. Sun, Z. Zhu, Y. Liu. Comput. Theor. Chem. **978**, 126 (2011).
[98] X.P. Shao, T.L. Gong, L. Wu, X.H. Yang. J. Quant. Spectrosc. Radiat. Transf. **112**, 1005 (2011).

[99] S.X. Ping, Z. Min, Y.X. Hua. Chin. Phys. B. **22**, 073302 (2013).
[100] M.A. Khan. Proc. Phys. Soc. **79**, 745 (1962).
[101] H. Neuhaus. Z. Phys. **150**, 4 (1958).
[102] H. Neuhaus. Z. Phys. **152**, 402 (1958).
[103] H. Neuhaus. Nature. **180**, 434 (1957).
[104] H. Neuhaus. Ark. Fys. **14**, 551 (1958).
[105] J.A. Coxon, R. Kępa, I. Piotrowska. J. Mol. Spectrosc. **262**, 107 (2010).
[106] G.A. Raouf, W.F. Elkhateeb, H. Toumah, M. Quari, K.A. Jaouni, K. Elkebba. Int. J. Nano. Biomaterials. **2**, 289 (2009).
[107] G.A. Raouf, K. Soad, A. Jaouni. J. Appl. Hem. **4**, 102 (2010).
[108] H. Ghimire, M. Venkataramani, B. Zhen, L. Yuan, A.G. Unil Perera. Nature Sci. Rep. **7**, 16993 (2017).
[109] M.C. Yu, P. Rich, L. Foreman, J. Smith, M.S. Yu, A. Tanna, V. Dibbur, R. Unmin, F.W.K. Tam. Nature Sci. Rep. **7**, 16993 (2017).
[110] H. Van Wincke, M. Cohen, T.R. Gull. Astronom. Astrophys. **390**, 147 (2002).
[111] S. Zhang, J. Zhen, Q. Zhang, Y. Chen. J. Mol. Spectrosc. **255**, 101 (2009).

Rzeszów, 7th November 2018

Wojciech Szajna
....