Jacek Szczepkowski

Scientific Achievements Report

Warszawa 2023

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I. Name

Full Name: Jacek Szczepkowski

- II. Diplomas, degrees conferred in specific areas of science or arts, including the name of the institution which conferred the degree, year of degree conferment, title of the PhD dissertation.
 - 1999 bachelor's degree in physics and computer science, Institute of Physics, Wyższa Szkoła Pedagogiczna* in Słupsk
 - 2001 master of science in physics, Institute of Physics, Pomorska Akademia Pedagogiczna* w Słupsk
 - 2009 Ph.D. in physics (cum laude), Faculty of Physics and Astronomy, Nicolaus Copernicus University in Toruń, Title: *The cold collisions of lithium isotopes and sodium atoms in the magneto-optical trap.* Supervisors: dr univ-prof. Laurentius Windholz (TU Graz), dr hab. prof-AP Ewa Paul-Kwiek (AP Słupsk)

III. Information on employment in research institutes or faculties/departments or school of arts.

- 2001-2003 Assistant, Institute of Mathematics, Pomorska Akademia Pedagogiczna* in Słupsk
- 2003-2006 Assistant, Institute of Physics, Pomorska Akademia Pedagogiczna* in Słupsk
- 2006-2009 Assistant, Institute of Physics, Akademia Pomorska* w Słupsku
- od 2009 Assistant Professor, Institute of Physics, Polish Academy of Sciences in Warszawa

^{*} current name of the University: Uniwersytet Pomorski w Słupsku (Pomeranian University in Słupsk)

IV. Description of the achievements set out in Article 219(1) para. 2 of the Act of 20 July 2018. Law on Higher Education and Science (Journal of Laws of 2021, pos. 478 with later amendments).

Title of the scientific achievement being a series of publications set out in Article 219(1) para. 2b of the Act of 20 July 2018. Law on Higher Education and Science (Journal of Laws of 2021, pos. 478 with later amendments):

Electronic structure of the KCs molecule.

IV.1. Publication series forming the scientific achievement

 A1. J. Szczepkowski*, A. Grochola, W. Jastrzębski, P. Kowalczyk, On the 4 ¹Σ⁺ state of KCs molecule, J. Mol. Spectrosc. 276, 19-21 (2012)

IF(2012): 1,529 Number of citations: 16

A2. J. Szczepkowski*, A. Grochola, W. Jastrzębski, P. Kowalczyk, R. Vexiau, Nadia Bouloufa-Maafa, O. Dulieu, P. Kowalczyk, Study of excited electronic states of the ³⁹KCs molecule correlated with the K(4²S)+Cs(5²D) asymptote: experiment and theory,

J. Quant. Spectrosc. and Radiat. Transfer 291, 108330, (2022)

IF(2022): 2,300 Number of citations: 1

 A3. J. Szczepkowski*, A. Grochola, W. Jastrzębski, P. Kowalczyk Study of 4 ¹Π state in KCs molecule by polarisation labelling spectroscopy, Chem. Phys Lett. 576, 10–14, (2013)

IF(2013): 1,991 Number of citations: 12

 A4. J. Szczepkowski*, A. Grochola*, W. Jastrzębski, P. Kowalczyk Experimental investigation of the 6¹Σ⁺ 'shelf' state of KCs, Chem. Phys Lett. 614, 36–40, (2014)

IF(2013): 1,897 Number of citations: 7

A5. J. Szczepkowski*, A. Grochola, P. Kowalczyk, W. Jastrzębski, E. Pazyuk, A.V. Stolyarov*, A. Pashov*, *The spin-orbit coupling of the 6¹Σ*⁺ and 4³Π states in KCs: observation and deperturbation, J. Quant. Spectrosc. and Radiat. Transfer 239, 106650, (2019)

IF(2019): 3,047 Number of citations: 4

A6. J. Szczepkowski*, Polarisation labelling spectroscopy of the 5 ¹Π state in KCs molecule, Chem. Phys Lett. 638, 78–81, (2015)

IF(2015): 1,860 Number of citations: 6

A7. J. Szczepkowski*, A. Grochola, P. Kowalczyk, W. Jastrzębski, Spectroscopic study of the C(3) ${}^{1}\Sigma^{+} \leftarrow X {}^{1}\Sigma^{+}$ and c(2) ${}^{3}\Sigma^{+} \leftarrow X {}^{1}\Sigma^{+}$ transitions in KCs molecule, J. Quant. Spectrosc. and Radiat. Transfer **204**, 131-137 (**2018**)

IF(2018): 2,955 Number of citations: 12

A8. J. Szczepkowski*, A. Grochola, P. Kowalczyk, W. Jastrzębski, Determination of the C(3)¹Σ⁺ state potential energy curve in KCs molecule based on polarisation labelling spectroscopy data, Spectrochim. Acta A 224, 117331 (2020)

IF(2020): 4,098 Number of citations: 5

A9. J. Szczepkowski*, A. Grochola, P. Kowalczyk, W. Jastrzębski, Observation of D(2)¹Π~(2)³Π~(2)³Σ⁺ states in KCs by polarisation labelling spectroscopy technique, Modelling of the D(2)¹Π~(2)³Π₁ system.
 J. Quant. Spectrosc. and Radiat. Transfer 248, 106984 (2020)

IF(2020): 2,468 Number of citations: 2

Title of the second scientific achievement

Energetic structure of bipolar dimers build of a strontium and alkali metal atom

IV.2. List of publications in which the second scientific achievement has been presented

B1. J. Szczepkowski*, A. Grochola, P. Kowalczyk, O. Dulieu*, R. Guérout,
P. S. Żuchowski*, W. Jastrzębski, *Experimental and theoretical study of the* B(2)²Σ⁺ →X(1)²Σ⁺ system in the KSr molecule,
J. Quant. Spectrosc. and Radiat. Transfer 210, 217-224 (2018)

IF(2018): 2,955 Number of citations: 5

B2. A. Ciamei*, J. Szczepkowski*, A. Bayerle*, V. Barbé, L. Reichsöllner, S.M. Tzanova, C.-C. Chen, B. Pasquiou, A. Grochola, P. Kowalczyk, W. Jastrzębski, F. Schreck, *The RbSr*²Σ⁺ ground state investigated via spectroscopy of hot & ultracold molecules, Phys. Chem. Chem. Phys. 20, 26221-26240 (2018).

IF(2018): 3,567 Number of citations: 22

Bibliometric data of publications representing scientific achievements updated on 20.09.2023. Impact Factor (IF) index of journals determined using Journal Citation Reports (https://jcr.clarivate.com). Number of citations determined using Web of Science Core Collection (https://www.webofscience.com).

^{* -} corresponding author

IV.3. Statement of individual contribution to publications

Statement of individual contribution to the individual publications comprising the achievements I declare that my contribution to the preparation of publications listed in the presented achievements was as follows::

- Paper [A1] formulation of the research problem, development of the concept of carrying out the research, formulation of conclusions, modification of the experimental system (reconstruction of the laser system for pumping with a new excimer laser, writing software controlling the experiment and calibration of data based on readings from the WS7 wavemeter), construction and optimization of the operation of the heat-pipe type spectroscopic cell for the production of KCs molecules, participation in the measurements (preparation of the measurement system, management of all measurement sessions, calibration of spectra), development of the concept of data analysis, participation in data analysis (identification of spectral lines, determination of the obtained results), participation in the preparation of the correctness of the obtained results), participation in the preparation of the draft and final version of the article. Coordinating the work of the team during the research work
- Paper [A2] formulation of the research problem, development of the research concept, performance of measurements (preparation of the experimental system, management of all measurement sessions, calibration of spectra), formulation of conclusions, development of the concept of data analysis, participation in data analysis (writing software supporting identification of spectral lines in the case of the occurrence of interactions between multiple states, preliminary identification of spectral lines), verification of the correctness of the obtained results, modification of the experimental system, coordination of the work of the Polish team and cooperation with Prof. O. Dulieu's group. Participation in the preparation of the draft and final version of the article.
- Paper [A3] formulation of the research problem, development of the research concept, formulation of conclusions and verification of the correctness of the obtained results, participation in the measurements (modifications of the experimental system, preparation of the experimental system, management of all measurement sessions, calibration of spectra), development of the concept of data analysis (development and implementation of a technique for the analysis of complementary spectra and writing a software to support this analysis), participation in data analysis (preliminary identification of spectral lines, determination of the potential energy curve and spectroscopic constants). Participation in the preparation of the draft and final version of the article. Coordination of the work of the team.
- Paper [A4] formulation of the research problem, development of the research concept, formulation of conclusions and verification of the correctness of the obtained results, Execution of measurements (preparation of the experimental system, management of all measurement sessions, calibration of spectra),

development of the concept of data analysis, participation in data analysis (preliminary identification of spectral lines, determination of the potential energy curve and spectroscopic constants), modification of the experimental setup (construction of a sample beam generation station based on a single mode laser including reconstruction/renovation and commissioning of the Coherent ring 899 laser), participation in preparation of the draft and final version of the article. Coordination of the team's work.

- Paper [A5] formulation of the research problem, formulation of the research concept, formulation of conclusions verification of the correctness of the obtained results, performance of measurements (preparation of the experimental setup, management of all measurement sessions, calibration of the spectra), formulation of the concept of data analysis, preliminary analysis of the measurement data (preliminary identification of the spectral lines in the Warsaw coordination of the team and cooperation spectra), with Prof. A. Stolyarov and Prof. A. Pashov's groups. Participation in the preparation of the draft and final version of the article.
- Praca [A6] single-author publication.
- Paper [A7] formulation of the research problem, development of the research concept, formulation of conclusions and verification of the correctness of the results obtained, participation in the performance of measurements (preparation of the experimental setup, management of all measurement sessions, calibration of spectra), development of the concept of data analysis, participation in data analysis (preliminary identification of spectral lines in the spectra, determination of the potential energy curve and spectroscopic constants). Participation in the preparation of the draft and final version of the article. Coordination of the work of the team.
- Paper [A8] formulation of the research problem, development of the research concept, formulation of conclusions and verification of the correctness of the results obtained, participation in the measurements (preparation of the experimental setup, management of all measurement sessions, calibration of spectra), development of the data analysis concept, participation in data analysis (preliminary identification of spectral lines in the spectra, determination of the potential energy curve and spectroscopic constants), participation in the preparation of the draft and final version of the article. Coordination of the team's work.
- Paper [A9] formulation of the research problem, development of the research concept, formulation of conclusions, performance of measurements (preparation of the experimental setup, management of all measurement sessions, calibration of spectra), development of the concept of data analysis, performance of deperturbation analysis (writing the software for two-channel deperturbation, construction of the model and, together with

Prof. P. Kowalczyk and Dr. Hab. Anna Grochola, performance of iterative data analysis - spectral line assignments). Participation in preparation of the draft and final version of the paper. Coordination of teamwork.

In the study of the energy structure of KSr [B1] and RbSr [B2] molecules, a system for measuring thermoluminescence and Laser Induced Fluorescence, built by me from scratch, was used, as well as an ECDL laser with an active frequency stabilization system (partly funded by the Miniatura grant).

- Paper [B1] formulation of the research problem, development of the research concept, formulation of conclusions, construction of a high-temperature heatpipe cell, performance of measurements, development of data analysis strategy including: writing software for simulation of thermally excited fluorescence spectra, writing software for determination of spectroscopic constants based on position of band heads. Participation in preparation of the draft and final version of the article, coordination of team work and cooperation with groups of prof. O. Dulieu and Prof. P. Żuchowski. Receiving the funds from NCN (Miniatura) and MNiSW (Polonium) for the research.
- Paper [B2] formulation of the research problem, development of the research concept, formulation of conclusions, construction of a high temperature heat-pipe cell, performance of thermally and Laser Induced Fluorescence measurements, performance of simulations of thermally induced fluorescence, development of the concept and participation in data analysis including: analysis of measurement data from the Warsaw laboratory using software from work [B1]. Management of global fitting of measurement data from both experiments and *ab initio* calculations, and work of Prof. F. Schreck's PhD student Dr. A. Ciamei during the global fitting process, preparation together with Dr. A. Ciamei software for determination of the potential energy curve on the basis of the results of *ab initio* calculations and the results of spectroscopic measurements performed under ultralow and high temperature conditions. Participation in preparation of the Warsaw team and cooperation with Prof. F. Schreck's group.

The statements of the Co-authors on their contribution to the respective publications are included in Appendix No.7 "Co-authors' statements".

IV.4. Introduction

Over the past decade, there has been a significant increase in interest in polar molecules with a permanent electric or magnetic dipole moment from researchers working in the physics of ultracold matter. The long-range nature of dipole interactions, together with the possibility of controlling them using external electric or magnetic fields [1] can be used to control chemical reactions in ultracold gas [2, 3], process quantum information [4, 5], study fundamental properties of matter [6-9] and strongly correlated few- or many-body quantum systems [10-14]. To perform the above experiments, it is necessary to obtain a trapped ultracold (~ μ K/nK) or quantum degenerated gas of polar molecules in the absolute rovibrational ground state. Obtaining a molecular gas with such parameters under laboratory conditions is possible by associating molecules from a trapped ultracold atomic gas [15, 16] or by direct laser cooling of the molecules [17]. To date, such gas has only been obtained for a few polar molecules: KRb [9] and RbCs [10,11] using stimulated Raman adiabatic passage (STIRAP), LiCs using a photoassociation process [12] and SrF [18-20] and CaF [21] using a direct laser cooling method.

The methods employed in the experiments for obtaining ultracold molecules and their transfer to the desired energy state require very precise knowledge of the energy structure of these molecules. This includes information about energies of specific rovibrational levels of individual states and probabilities of transitions between these levels, proportional to Franck-Condon factors, transitions dipole moments, as well as information about interactions between specific electronic states. The high requirements for the accuracy and extent of information needed for ultracold experiments mean that data from experiments performed with high resolution spectroscopic methods must be combined with the results of quantum chemistry calculations.

In the articles listed in the previous section, the results of studies of the energy structure of representatives of two groups of polar molecules are presented. These results are particularly interesting to researchers working on obtaining them under ultralow temperature conditions. The first group of molecules consists of heteronuclear alkali metal dimers, the second of dimers is built of alkali metal and strontium atoms. Molecules in the first group have a permanent electric dipole moment in their electronic ground state, while molecules in the second group, in addition to their electric dipole moment, also have a magnetic dipole moment in their electronic ground state due to an unpaired electron and are therefore called bipolar. This feature makes it possible to control interactions between such molecules in ultralow temperature conditions using both magnetic and electric fields.

Studies of the energetic structure of heteronuclear alkali metal dimers have been carried out for many years, but there are still *terra incognita* in this research area. Until recently, such lack of knowledge has been associated with KCs molecules. The research work performed by me in the Warsaw laboratory has contributed significantly to filling the information gap on the energetic structure of the excited electron states of this molecule and this information is important e.g. for groups of Prof. S. Cornish (Durham) and Prof. H-C. Nägerl (Innsbruck), which are currently working on obtaining these molecules under ultracold conditions.

In the case of molecules built from alkali metal and strontium atoms, until 2014 their energetic structure was known only from a few *ab intio* calculations [22-25]. By the time of writing this guide, only six experimental papers on this group of molecules had been published, including two resulting from my research [26-29,B1,B2]. The work I have undertaken on this topic is a direct response to the needs of

Prof. F. Schreck's group (Amsterdam), working on the preparation of ultracold RbSr molecules.

The presented guide to scientific achievements consists of two parts. The first is dedicated to the results of a comprehensive study of the energetic structure of the KCs molecule, carried out using the polarisation labelling spectroscopy method. In this study, potential energy curves of ten excited electronic states of this molecule of both singlet and triplet multiplicity [A1-A9] have been derived from the measured positions of the energy levels, most of them for the first time. A full rovibrational resolution of the obtained spectra has been achieved. In two cases, described in publications [A5,A9], an analysis of interactions between neighbouring electronic states of singlet and triplet multiplicity has been carried out.

The second part of the guide describes the results of research on the properties of bipolar molecules: KSr and RbSr. The publication [B1] describes studies of the ground state and the first excited state of ${}^{2}\Sigma^{+}$ symmetry in the KSr molecule, based on the analysis of the thermally induced fluorescence spectrum between these states and results of *ab initio* calculations carried out by three different methods by independent groups of theoreticians. This is the first publication in which the molecular constants of the electronic states of KSr are derived based on the results of spectroscopic measurements. The publication [B2] reports spectroscopic studies of the RbSr molecule carried out at high and ultralow temperatures. In the Warsaw laboratory, measurements have been carried out under high temperature conditions using the techniques of thermally and laser induced fluorescence occurring between the B(2)² Σ^+ i X(1)² Σ^+ states. Independently, measurements of the positions of the weakly bound energy levels in the ground state conducted using two-photon spectroscopy and magnetoassociation spectroscopy under ultracold conditions have been performed for this molecule by Prof. Florian Schreck's group (Amsterdam). Global analysis of the results of both experiments together with the results of ab initio calculations allowed for the determination of the semiempirical ground state potential energy curve and the determination of dispersion coefficients. Measurements performed at high temperatures also allow for the determination of the spectroscopic constants of the B(2) $^{2}\Sigma^{+}$ state of the RbSr molecule.

IV.5. Electronic structure of the KCs molecule

IV.5.1. Motivation and state of the art

Until recently, the energetic structure of the KCs molecule was among the least known of the alkali metal dimers. Walter and co-workers, in their systematic study of the absorption spectra of alkali metals [30], assigned only one weak band located in the visible range to this molecule. This information seemed to discourage spectroscopists for many years. Until 2008, the only semiempirical characterisation of the energetic structure of the KCs molecule was based on the fact that some spectroscopic constants of its ground state were estimated by interpolating the corresponding experimental values for K₂ and Cs₂ molecules [31]. There was also very limited interest in this molecule among theoreticians. Until 2000, only the ground electronic state had been characterised on the basis of quantum mechanical calculations performed by Igel-Mann et. al. [32]. The rapid development of 'cold physics', mentioned in the introduction, brought wider interest in the KCs molecule because of a relatively high value of its permanent electric dipole moment [33, 34]. In 2002, DeMille [4] proposed a scheme to realise quantum computations using ultracold KCs molecules in the absolute rovibrational electronic ground state. New trends at first inspired quantum chemistry calculations [35-37], and then experiments employing modern spectroscopic methods. The first experimental paper on the electronic structure of KCs had been published in 2008 [38]. This publication, prepared in the groups of Prof. R. Ferber (Riga) and Prof. E. Tiemann (Hanover), describes the rovibrational energy structure and provides the potential energy curve of the KCs ground electronic state. Subsequent studies conducted by the Riga group provided information on the long-range part of the ground electronic state potential energy curve, and in the following years on the electronic states $a(1)^{3}\Sigma^{+}$ [39, 40, 41], $E(4)^{1}\Sigma^{+}$ [42, 43], $A(2)^{1}\Sigma^{+}$ and $b(1)^{3}\Pi$ [44, 45], $B(1)^{1}\Pi$ [46, 47], $D(2)^{1}\Pi$ [48] and $(1)^{3}\Delta$ [49].

In 2011, I started a systematic study of the electronic structure of the KCs molecule at the Institute of Physics of the Polish Academy of Sciences in Warsaw. Apart from the motivation arising from the needs of cold physics, one of the reasons that drew my attention to this molecule was the complex energetic structure predicted from *ab initio* calculations and the presence of strong interactions between electronic states, causing both local and global perturbations in the positions of rovibrational levels. On the one hand, the presence of such perturbations greatly complicates the analysis of spectroscopic data, on the other hand, in the case of perturbations caused by interactions between states of different multiplicity, it allows, among other things, an observation of nominally forbidden transitions from the ground (singlet) state to energy levels of excited states of triplet character. It is possible due to the mixing of the wavefunctions of the interacting exited electronic states. Such transitions are used to transfer weakly bound molecules formed by magneto- or photoassociation to the absolute rovibrational ground state using the stimulated Raman adiabatic passage (STIRAP) [50].

In a study performed using polarisation labelling spectroscopy technique (PLS), I obtained information on the rovibrational energy structure of several excited electronic states of KCs (Fig. 1). Based on these data, I determined, mostly for the first time, potential energy curves for electronic states: $E(4)^{1}\Sigma^{+}$ [A1], $3^{1}\Pi$, $3^{3}\Pi$, $4^{3}\Sigma^{+}$ [A2], $(4)^{1}\Pi$ [A3], $(6)^{1}\Sigma^{+}$ [A4,A5], $(4)^{3}\Pi$ [A5], $(5)^{1}\Pi$ [A6], $c(2)^{3}\Sigma^{+}$ [A6], $C(3)^{1}\Sigma^{+}$ [A6,A8], $D(2)^{1}\Pi$, $(2)^{3}\Pi$, $(2)^{3}\Sigma^{+}$ [A9]. Furthermore, papers [A5, A9] present the deperturbation analysis performed in order to describe the observed interactions between neighbouring singlet and triplet states.



Fig. 1 Electronic structure of the KCs molecule [35]. The spectral range covered by my study is indicated in yellow. The lines in black indicate the states of symmetry ${}^{1}\Sigma^{+}$, red - ${}^{1}\Pi$, green - ${}^{3}\Sigma^{+}$, blue - ${}^{3}\Pi$.

IV.5.2. Experimental techniques and data analysis methods

Preparation of KCs molecules - heat-pipe oven spectroscopic cell

KCs molecules were produced in a linear heat-pipe oven. In the middle part of the oven, approximately 5 g of metallic potassium and caesium with a natural isotopic composition was placed. In addition, the inside of the oven was filled with approximately 5 Torr of argon as a buffer gas. Its role was to ensure optimum circulation of the atomic vapours in the oven and to prevent them from contacting the surface of the windows. The central part of the oven was heated to approximately 400 °C. The temperature gradient created along the oven initially resulted in a partial separation of the two metals, due to their different melting points. However, after some time, liquid metal droplets formed at the boundary of the heating zone, consisting of an eutectic alloy of K and Cs formed by the mixing of their vapours. The formation of the alloy caused the oven to operate stably for many months without the need for regeneration, which involved replacing the metallic deposit of potassium and caesium.

• Polarisation Labelling Spectroscopy (PLS) method

In studies of the energetic structure of KCs molecules, the Polarisation Labelling Spectroscopy (PLS) technique was used. This is an experimental pump-probe technique [51, 52] in which appropriately selected polarisation of two laser beams allows observation of rovibrational spectra only from selected ("labelled") levels of the ground state. The two laser beams, pump and probe, intersect at a small angle in the molecular sample. During the measurement, the wavelength of the probe beam is tuned to the selected rovibrational transition between the ground state and the excited state, whose energetic structure is known. At the same time, the wavelength



Fig. 2 Scheme of excitation of a molecule in polarisation labelling spectroscopy technique. The 'labelled' energy level in the ground state, common for transitions excited by pump and probe beams, is shown in red.

of the pump beam is tuned in the energy region corresponding to the optical transitions between the ground state and the investigated state. This is shown schematically in Fig. 2. A pump beam of relatively high intensity and properly chosen polarisation produces an optical anisotropy in the sample as a result of optical pumping. As a result, when transitions for the weak probe beam start from the same rovibrational level in the ground state, the polarisation of the probe beam changes after passing through the sample, what is recorded by the detection system. The signal registration only takes place when the polarisation of the probe beam changes, what causes the reduction of the number of observed spectral lines. Due to this limitation, the rotational structure in the recorded spectrum is fully resolved, as the spectral lines simultaneously excited by the pump laser beam do not overlap. Typically, only one or a few ground-state levels are 'labelled' by the probe beam and their oscillation and rotation quantum numbers are known. Another advantage of using the PLS technique is that the symmetry of the sampled states can be determined. This follows directly from the selection rules for pump-probe transitions.

This has been discussed in detail in the paper [52]. For example, when the probe beam is tuned to transitions between ${}^{1}\Sigma \leftarrow {}^{1}\Sigma$, states and the pump beam is circularly polarised, only transitions with $\Delta J=\pm 1$ (P and R lines) will be observed regardless of the symmetry of the excited state under investigation, whereas when the polarisation of the pump beam is changed to linear, for the ${}^{1}\Sigma \leftarrow {}^{1}\Sigma$ transitions much weaker P and R lines ($\Delta J=\pm 1$) than in the case of circular polarisation will be observed, whereas for the ${}^{1}\Pi \leftarrow {}^{1}\Sigma$ transitions Q lines ($\Delta J=0$) will dominate over much weaker P and R lines ($\Delta J=\pm 1$).

• Inverted Perturbation Approach (IPA) method

The construction of the potential energy curves is based on the Inverted Perturbation Approach (IPA), a fully quantum technique whose numerical implementation developed in our group is widely used to describe potentials of even very exotic shapes [53, 54]. In this method, the main goal is to find such a correction $\delta U(R)$ to the approximate initial potential $U_0(R)$ that the set of eigen energies obtained by the numerical solution of the Schrödinger equation with such a corrected potential reproduces the experimentally measured values of the energies of the rovibrational levels. This is an iterative procedure that treats the resulting corrected potential $U_0(R) + \delta U(R)$ as a subsequent, more accurate approximation of the true potential. Typically, iterations are continued until the discrepancies between calculated and experimental energy values are comparable to the measurement uncertainty of the experimental ones.

Using the perturbation theory, we can calculate the effect of the correction to the potential $\delta U(R)$ on the energy. In the standard approach, the correction to the potential is known and corrections to energy δE are sought. In this case it is the opposite - we know the values of the corrections to the energy, which are the difference between the measured and calculated values, and we are looking for the corresponding correction to the potential - this is the so called inverse spectroscopic problem.

The shape of the potential $U_0(R)$ itself can be described by either model potentials e.g. Morse, Lennard-Jones, Extended Morse Oscillator etc. [53] or functions that can reproduce a more complicated potential shape, e.g. Chebyshev polynomials. In the approach used in this work, the potential as well as the correction to it are described in terms of a set of points interpolated by a cubic spline function. Using such a representation allows even very exotic shapes of the potential energy curve, e.g. with multiple local minima [54], to be represented.

IV.5.3. Overview of the results of the spectroscopic study of the KCs molecule

The publication [A1] presents the structure of the highly excited rovbirational energy levels of the $4^{1}\Sigma^{+}$ in the KCs molecule. Furthermore, the construction of the experimental setup and the spectroscopic technique are also discussed.

The $4^{1}\Sigma^{+}$ state in KCs is an example of an electronic shelf-type excited state. The broadened shape of the potential energy curve of this state is a result of the anticrossings between neighbouring ${}^{1}\Sigma^{+}$ valence states with the lowest ionic state having the same symmetry. The broad potential well makes this state an attractive candidate for the realisation of various spectroscopic schemes, allowing for excitation or emission near the inner classical turning point of the oscillator, usually located at small internuclear distances, as well as the outer turning point, located at large internuclear distances. Therefore, the rovibrational levels of the $4^{1}\Sigma^{+}$ state can be used to excite fluorescence to lower electronic states, allowing for the determination of potential energy curves of these states over a wide range of internuclear distances [38, 39, 44, 45, 46]. This state can also be used to transfer ultracold KCs molecules from energy levels located close to the dissociation limit (populated in photo- or magnetoassociation process) to the absolute rovibrational electronic ground state [43, 41].

This state was at first partially characterised by Busevica *et. al.* [42]. In an experiment conducted in Riga, laser induced fluorescence from the $4^{1}\Sigma^{+}$ state to the electronic states located below was recorded with a Fourier transform spectrometer. Analysis of the recorded spectra provided information on vibrational levels from v'=2 to v'=74 in the $4^{1}\Sigma^{+}$ state. The highest vibrational level observed in this experiment was located about 226 cm⁻¹ below the atomic asymptote $K(4^{2}S_{1/2})+Cs(5^{2}D_{1/2})$. It was also found that there was no local perturbation of the positions of the energy levels in the $4^{1}\Sigma^{+}$ state in the observed energy range. Thus, the potential energy curve created by the IPA method on the basis of the measured energies of the rovibrational levels allows for an interpolation of the positions of unobserved energy levels with the same accuracy as in the case of experimentally derived energy levels.

In the experiment of Busevica et. al. [42], fluorescence from excited levels of the $4^{1}\Sigma^{+}$ state to the $a^{3}\Sigma^{+}$ state was also observed, even though such transitions are forbidden in the dipole approximation. The authors explain this phenomenon by the presence of spin-orbit interactions between the $4^{1}\Sigma^{+}$ state and the neighbouring $(2,3)^3\Pi$ states, resulting in a mixing of the wavefunctions of the energy levels of these states. However, it is surprising that in the $4^{1}\Sigma^{+}$ state local perturbations observed as changes of positions of individual rotational levels within a given vibrational transition, resulting from direct interaction with the nearest vibrational level of the $2^{3}\Pi$ or $3^{3}\Pi$ state, are not observed. This type of local perturbation has been observed for interaction between the A(2)¹ Σ^+ and b(1)³ Π states in KCs. In this experiment, however, the energy region for vibrational levels v'>70, where, according to the results of ab initio calculations Korek et. al. [35, 36], the effect of the presence of energy levels of the $3^{3}\Pi$ state, which may cause this type of local perturbations in the positions of energy levels in the $4^{1}\Sigma^{+}$ state, was not investigated. In this spectra region the mixing of the wavefunctions of the energy levels of the $4^{1}\Sigma^{+}$ and $3^{3}\Pi$ states should make it possible to observe transitions between the ground state and the $3^{3}\Pi$ state, as it was in the case of the A(2)¹ Σ^{+} and b(1)³ Π states in the KCs molecule.

The analysis of the distribution of Franck-Condon factors, calculated on the basis of theoretical potential energy curves, allowed us to assume that it would be possible to observe energy levels close to the dissociation limit in the $4^{1}\Sigma^{+}$ state with transitions involving low excited vibrational energy levels (v"≥4) of the ground state. Information on such transitions is especially valuable if one is trying to obtain a deeply bound KCs molecule directly by photoassociation, while information on levels close to the dissociation limit should make it possible to determine dispersion coefficients describing the long-range part of the interaction between the potassium and caesium atoms. The above arguments were the main motivation for continuing the study of the structure of the energy levels of this state.

In my experiment, positions of energy levels in the $4^{1}\Sigma^{+}$ state were determined by analyses of the excitation spectrum $4^{1}\Sigma^{+} \leftarrow X^{1}\Sigma^{+}$ recorded using the polarisation labelling spectroscopy (PLS) technique. The low intensity probe beam was generated by a self-made pulsed dye laser pumped by an excimer laser (Light Machinery IPEX-848). The wavelength of the probe laser was tuned to the transitions between the vibrational levels of the ground state and the low excited vibrational levels of the $4^{1}\Sigma^{+}$ state, the wavelength of which was known from previous measurements [42]. The wavelength of the pump beam, generated by a Lumonix HD500 pulsed laser, was tuned from 569.8nm to 564.4nm (17550÷18300 cm-1). This range corresponded to transitions from the ground state to highly excited vibrational levels in the $4^{1}\Sigma^{+}$ state. Calibration of the absolute wavelength of the pump beam was based on the periodic reading of the HighFinesse WS7 wavemeter during the scan, while the linearity of the scanning was controlled by recording transmission fringes from a 0.5 cm Fabry-Pérot etalon. The uncertainty in the determination of the pump beam wavenumber by this method was less than 0.05 cm⁻¹. The wavelength of the probe laser was controlled by the same wavemeter.

In the PLS measurements, signals were recorded for transitions from v"=4-6 levels in the ground state to subsequent vibrational levels in the $4^{1}\Sigma^{+}$ state. In a multistep analysis of the recorded signals, all observed spectroscopic lines were assigned to transitions between these two states $(4^{1}\Sigma^{+} \leftarrow X^{1}\Sigma^{+})$. Basing on the experimental data, an information was obtained on the positions of 570 energy levels in the $4^{1}\Sigma^{+}$ state. Most of these levels were not observed in the Busevica *et. al.* [42] experiment. The highest observed vibrational level v'=91 was located about 27 cm⁻¹ below the atomic asymptote, and its classical external turning point was located at a distance of about 12.6 Å and did not cross the value of the LeRoy radius (about 15.1 Å). Therefore the values of the dispersion coefficients from ab initio calculations [55] were used to describe the long-range part of the interaction between K and Cs atoms.

Finally, based on the collected information on the energies of more than 2200 rovibrational levels obtained in both experiments and the values of the dispersion coefficients C_6 and C_8 derived from *ab initio* calculations, an empirical potential energy curve of the $4^1\Sigma^+$ state was constructed using the IPA method. The energy of the rovibrational levels calculated using the empirical potential energy curve agreed with the experimentally measured values within the range of experimental uncertainty for all observed energy levels in the $4^1\Sigma^+$ state. This indicates the absence of measurable local perturbations in the observed range of transitions, what does not support the theoretical predictions about occurrence of this type of perturbations. We can assume therefore that the interactions between the $4^1\Sigma^+$ state and neighbouring triplet states cause rather global 'regular' shifts of all vibrational energy levels in the $4^1\Sigma^+$ state by an effective potential energy

curve. This curve allows to reproduce, after solving the radial Schrödinger equation, the energies of the rovibrational levels in the $4^{1}\Sigma^{+}$ state with experimental precision.

The situation is different in case of $3^{1}\Pi$ state witch is correlated with the same atomic asymptote K(4²S)+Cs(5²D) as the 4¹Σ⁺ state (Fig. 3). The presence of strong interactions, both global and local, between the $3^{1}\Pi$ state and neighbouring states with triplet multiplicity has been confirmed by our research, **the results of which are presented in the article [A2] from 2022.** Undertaking this research required modifications to both the measurement techniques and analysis methods used, as



Fig. 3 *Ab initio* potential energy curves for the Hund's coupling case (a) converging to the $K(4^2S)+Cs(5^2D)$ asymptote (solid line) and Hund's coupling case (c) $\Omega=1$ dissociating to $K(4^2S)+Cs(5^2D_{1/2,3/2})$ (dashed line). The calculations have been made by Prof. O. Dulieu's group.

well as collaboration with the group performing *ab initio* calculations. A single mode laser served for labelling energy levels in the PLS spectroscopic measurements, and the method of recording of complementary spectra was used. To analyse the experimental data, a coupled channel approach, based on the results of recent *ab initio* calculations, was used. Details of the measurements and data analysis techniques were presented in papers [A3-A9], which historically preceded the presented work [A2].

Measurements were performed with the PLS technique, using the transitions $4^{1}\Sigma^{+} \leftarrow X^{1}\Sigma^{+}$ and $1^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ to label the rovibrational energy levels in the ground state. The choice of these transitions allowed energy levels with *e* and *f* parity to be observed efficiently [52]. The spectral range in which the pump laser was tuned (17500 cm⁻¹ - 18600 cm⁻¹) included transitions between the ground state and the $3^{1}\Pi$ state. In the recorded spectra, a pattern of P, Q and R lines was observed, indicating transitions to the $^{1}\Pi$ state for the Hund's case (a) of the angular momenta coupling in the molecule. However, for the region above 18200 cm⁻¹, a greater number of spectral lines were observed than would be implied by the presence of transitions to a single electronic state. The pattern of P Q, R spectral lines can be found also for $\Omega=1\leftarrow\Omega=0^{+}$ transitions [36], which take into account the strong spin-orbit interaction, in this region we should observe transitions to the $\Omega=0^{+}$ state (component of the $4^{1}\Sigma^{+}$ state) and states 8,9,10,11 $\Omega=1$, which are components of the states: $1^{3}\Delta$, $3^{1}\Pi$, $3^{3}\Pi$ and $4^{3}\Sigma^{+}$ (Fig. 3). Transitions to the $^{1}\Sigma^{+}$ state ($\Omega=0^{+}$) were easily identified

from the results presented in [A1]. The pattern of the remaining spectral lines indicated the presence of transitions to one Ω =1 state in the region below 18200 cm⁻¹ and four $\Omega=1$ states above this energy, i.e. the observation of some states only becomes possible in the region of the $3^{1}\Pi$ state. This indicates a situation in which transitions to Ω =1 components of triplet states can only be observed due to mixing of their rovibrational energy levels wavefunctions with the wavefunctions of rovibrational energy levels of the $3^{1}\Pi$ state, from which they can only 'borrow' the transition dipole moment. This hypothesis would explain why transitions to the 8Ω =1 state (which is a component of the $1^{3}\Delta$ state) were not observed below 18200 cm⁻¹. Verification of this hypothesis was possible by carrying out a coupled channel analysis, which takes into account mutual interactions between states. The idea of such analysis was discussed in detail in the paper [A5]. However, the results of *ab initio* calculations available in the literature [36] were insufficient for this purpose, due to the lack of information about the diagonal and non-diagonal matrix elements describing the spin-orbit interactions, which in this case play a dominant role in the interactions between states. Prof O. Dulieu's group performed new calculations, providing the necessary information for further analysis. The high accuracy of the ab initio result was confirmed by the consistency of the shape of the calculated and empirically determined potential energy curves of the $4^{1}\Sigma^{+}(\Omega=0^{+})$ state. Using the results of Prof. O. Dulieu's group, simulations of the positions of energy levels for all states were performed, taking into account their mutual interactions. The percentage contribution of the wave function of the $3^{1}\Pi$ state energy levels to the wavefunctions of the individual energy levels of triplet states was also calculated. In the calculations we took into account the spin-orbit interactions between the states $1^{3}\Delta$, $3^{1}\Pi$, $3^{3}\Pi$ and $4^{3}\Sigma^{+}$ (Fig. 4).

The results of the simulations confirmed the hypothesis that due to a small mixing of the wavefunctions of the $3^{1}\Pi$ and $1^{3}\Delta$ states in the region below 18200 cm⁻¹ we can neglect in this spectral region the spin-orbit interaction in the description of energy levels (Hund's coupling case (a)). This explains the absence of spectral lines in the recorded spectra, corresponding to transitions to energy levels belonging to the Ω =1 component of the $1^{3}\Delta$ state in this region. A strong spin-orbit interaction has been confirmed by the calculations for the region above 18200 cm⁻¹. It causes that the wavefunctions of the observed rovibrational energy levels of $3^{3}\Pi$, $4^{3}\Sigma^{+}$, $1^{3}\Delta$ states have a significant admixture of the wavefunctions of the $3^{1}\Pi$ state's energy levels. Therefore Hund's coupling case (c) is more suitable for describing the situation in this spectral region, and as a consequence it was possible to observe transitions to the four Ω =1 states in the experiment.



Fig. 4 Degree of mixing of wavefunctions of $3^{1}\Pi$ state energy levels with wavefunctions of neighbouring states energy levels, expressed by the contribution of the $3^{1}\Pi$ state wavefunctions Ψ , calculated in a simplified coupled channel model. Open circles denote energies of the experimentally observed rovibrational levels.

All spectral lines were recorded for transitions from the vibrational level v''=0in the ground state, and the range of observed energy levels in the excited states, starting from the deeply bound vibrational level v'=7 in the $3^{1}\Pi$ state (9 Ω =1) up to the dissociation limit of 8,9 Ω =1states. This type of interaction, resulting in a mixing of the wavefunctions of the singlet and triplet states, could be used in the optical transfer of ultracold KCs molecules to the absolute rovibrational ground state. A possible scheme for obtaining molecules in this state could involve the initial generation of KCs molecules in a weakly bound triplet-like state $(a^{3}\Sigma^{+})$ e.g. by magnetoassociation, from which they could then be excited to the $\Omega=1$ component of the $3^{3}\Pi$ or $4^{3}\Sigma^{+}$ states, for which there are strong interactions with the $3^{1}\Pi$ state. The admixture of the wavefunctions of the $3^{1}\Pi$ state, which internal turning point lies at the same internuclear distance as the turning point of the v"=0 level in the $X^{1}\Sigma^{+}$ state, would allow for transfer from the excited state to the absolute rovibrational electronic ground state. The experimental results allow us to conclude that all observed levels theoretically allow this type of transfer. However, in order to determine the efficiency for individual transitions, it is necessary to perform a full deperturbation analysis comprising all five states: $4^{1}\Sigma^{+}$, $1^{3}\Delta$, $3^{1}\Pi$, $3^{3}\Pi$, $4^{3}\Sigma^{+}$, and their mutual interactions.

In the paper [A3], results of studies of the energetic structure of the KCs molecule in the spectral range from 21000 cm⁻¹ to 23000 cm⁻¹ were presented. In this spectral region, according to theoretical predictions, transitions between the ground state and the $7^{1}\Sigma^{+}$ and $4^{1}\Pi$ states should be observed. Further analysis of the results of *ab initio* calculations suggests a high probability for both global and local perturbations due to interactions with the neighbouring triplet states $(6,7)^{3}\Sigma^{+}$, $(4,5)^{3}\Pi$ and $2^{3}\Delta$.

The experiment performed in the Warsaw laboratory used the same experimental setup and measurement method (PLS) as in the work [A1]. To calibrate

the wavelength of the pump laser, spectral lines from the optogalvanic spectrum of neon and argon, recorded simultaneously during laser scans, and a periodic wavelength readout from a WS7 wavemeter were used. The wavelength of the probe laser was tuned to transitions between the $4^{1}\Sigma^{+}$ and $X^{1}\Sigma^{+}$ states. The self-made pulsed dye laser used to produce the probe beam had a spectral width of the generated light of about 0.5 cm⁻¹, which, combined with the relatively small value of the rotational and vibrational constant of the $4^{1}\Sigma^{+}$ state, caused that up to a dozen rovibrational energy levels in the ground state were labelled simultaneously for a given wavelength. This resulted in a rather complex pattern in the recorded spectroscopic signal. To analyse the measurements, I developed a method to increase the selectivity of the labelled levels without modifying the experimental setup. This method involved recording two spectra, in which the same rovibrational level was labelled in the ground state using different wavelengths of the probe laser, what corresponds to transitions from a given rovibrational level in the ground state to different rovibrational levels in the $4^{1}\Sigma^{+}$ state. As a result the additionally labelled rovibrational levels in the ground state in the two measurements were different. By multiplying the obtained spectra by each other, only spectral lines corresponding to transitions from a single rovibrational level in the ground state, common for both recorded spectra, were present in the resulting spectrum. On a similar principle, it is possible to exploit the situation where transitions from rovibrational levels in the ground state having the same rotational number but different vibrational numbers are observed in two spectra. Before multiplication, it is then sufficient to shift the recorded energy values by the difference in energy between the vibrational levels labelled in the two spectra. A potential drawback of this method is the doubling of the time required for the measurements (two complementary scans). However, this is not lost time, as each measurement, in addition to repeating information on the energies of transitions starting from the same energy level in the ground state, also contains information from the presence of transitions from additionally labelled levels. With the knowledge of the ground state potential energy curve and the knowledge of the $4^{1}\Sigma^{+}$ state potential energy curve, it is possible in the next step of data analysis to identify these transitions and assign the correct quantum numbers to the remaining recorded lines.

In the investigated spectral region, with linear polarisation of the pumping beam, dominant Q lines were observed in the recorded signals, which, according to the selection rules for the PLS method [52], unambiguously identified the symmetry of the investigated excited state as ${}^{1}\Pi$ (Ω =1 in the Hund's coupling case(c)). As expected, the observed spectral lines corresponded to transitions between the ground state and the $4{}^{1}\Pi$ state. A total of 3267 spectral lines were identified in the experimental data, from which positions of 1992 rovibrational levels in the $4{}^{1}\Pi$ state were determined. While determining the vibrational numbering of the energy levels in the excited state, the lowest experimentally observed vibrational level was assigned the value v'=0 and the highest was assigned the value v'=19. The assumed assignment of the vibrational numbering was confirmed later, during the analysis of the intensities of the lines as a function of the vibrational numbering in the recorded signals in respect to the values predicted from the distribution of Franck-Condon factors. The Franck-Condon factors were calculated based on the potential energy curve of the $4{}^{1}\Pi$ state, constructed with the assumed vibrational numbering.

Attempts to describe the values of energy of the rovibrational levels using Dunham coefficients revealed a number of differences between the energy values calculated from the obtained coefficients from those measured in the experiment. The differences were up to several wavenumber for individual rovibrational levels and their distribution pattern was characteristic for a presence of local perturbations.

Shifts of the entire vibrational levels (v'=0, 1, 11 and 12) were also observed, up to a dozen wavenumbers with respect to the values calculated from the obtained Dunham coefficients. The reason for such large discrepancies may be strong perturbations, causing a shift of the whole system of vibrational levels due to interaction with neighbouring electronic states, or inadequacy of the model used. The Dunham coefficients correctly describe a case when a shape of a potential energy curve is 'regular', i.e. close to the shape of the Morse potential. On the basis of the results of ab initio calculations this condition is fulfilled in the case of calculations performed using Hund's coupling case (a). However, when spin-orbit interactions are included in the calculations and we are dealing with Hund's case coupling (c), the potential energy curve of the 15 Ω =1 state (component of the 4¹ Π state) has an irregular shape, so that the use of Dunham coefficients is inadequate. In this situation, the IPA method was used to construct the potential energy curve, and the potential was represented in the form of a set of points. Due to the presence of a large number of locally perturbed levels we applied a weighted curve fitting strategy to all the data when constructing the potential, instead of discarding the perturbed levels. In short, instead of excluding some arbitrarily selected levels from the input data as perturbed, we reduced the influence of these levels on the fit by defining the weight of each level in such a way, that the influence of the perturbed levels on the fit decreases as the residuum values of their energies increase [56]. As a result of the described procedure, the values of eigen energies obtained during guantum-mechanical calculations using the experimental potential energy curve reproduced the experimental energies of the vibrational levels v'=2-10 and v'=13-19 with a standard deviation of 0.6 cm⁻¹. In the case of the remaining vibrational levels, i.e. v'=0, 1, 11, 12, deviations of the energies calculated using the obtained potential were similar to those calculated from the Dunham coefficients. This indicates that shifts of the mentioned vibrational levels are a result of interactions with energy levels of the neighbouring states, rather than due to an irregular shape of a potential energy curve of this state. This hypothesis is also confirmed by comparing the shape of the obtained potential with the results of ab initio calculations for the Hund's coupling case (a) and (c) (Fig. 5).

This comparison shows that the experimentally obtained potential energy curve does not follow the complex pattern of anti-crossings predicted by the calculations related to the Hund's coupling case (c), and its shape is similar to the potential energy curve of the $4^1\Pi$ state obtained by the calculations for the Hund's



Fig. 5 Comparison of the shape of the experimental potential energy curve of the 4¹Π state (red dots) with the results of *ab initio* calculations performed assuming Hund's coupling case (a) [35] (top panel) and Hund's coupling case (c) [36] (bottom panel).

coupling case (a). The observed vibrational levels v'=0,1 are located in the region of the crossing of the potential energy curves of the $6^{3}\Sigma^{+}$ and $4^{1}\Pi$ states (respectively, the anti-crossing of states 14 and 15 Ω =1 in the case of Hund's coupling case (c)), what may result in such significant shifts of these levels as a result of the spin-orbit interaction. Because of the presence of so many perturbations, a more accurate description of the energies of the observed levels was obtained by determining the spectroscopic constants G_{ν} , B_{ν} , D_{ν} for each vibrational level separately. It reduced the maximum values of deviations of the line position predictions in respect to the experimentally measured values from 13 cm⁻¹ to 2 cm⁻¹. For applications requiring higher accuracies than the presented models offer, a list of the energies of the observed rovibrational levels has been attached to the paper.

In summary, mainly spectroscopic lines corresponding to transitions between the ground state and the $4^{1}\Pi$ state were identified in the investigated spectral region.

Based on these observations, the potential energy curve of this state was determined experimentally for the first time. The presence of additional spectral lines was also noted, mostly corresponding to transitions between the ground state and triplet states that interact with the $4^{1}\Pi$ state. However, no spectral lines corresponding to $7^{1}\Sigma^{+}\leftarrow X^{1}\Sigma^{+}$ transitions were found in the recorded spectra. One of the most likely reasons for the absence of such lines in the spectra could be the small value of the transition dipole moment between these states, since the predicted value of the Franck-Condon factors is comparable to those for the $4^{1}\Pi\leftarrow X^{1}\Sigma^{+}$ transitions. In order to comprehensively describe the energies of the observed rovibrational levels in the $4^{1}\Pi$ state, a multi-channel model is required, which takes into account couplings between neighbouring states. The construction of such a model is planned in collaboration with Prof. A. Pashov's group.

The paper [A4] presents the first experimental observation of the energetic structure of the $6^{1}\Sigma^{+}$ state. From *ab initio* calculations, the irregular shape of the potential energy curve of this state is predicted due to anticrossings between the states of the same symmetry. The comparison of the results of *ab initio* calculations with experimental data in case of a state with such a complicated shape of the potential energy curve provides a unique opportunity to verify the quality of the computational methods.

Measurements were performed using the PLS method and the experimental setup was slightly modified from that used in earlier studies. The main change was the use of a single mode ring dye laser (Coherent 899-21) for probe beam generation. In addition we used pulsed dye laser with light frequency tuned to $B(1)^1\Pi \leftarrow X^1\Sigma^+$ transitions. The wavelength of the ring dye laser light was actively stabilised using a WS7 wavemeter. The use of spectrally narrow light from the ring laser, with a frequency tuned to the $4^1\Sigma^+ \leftarrow X^1\Sigma^+$ transitions, results in a labelling only a single rovibrational level in the ground state. This made the analysis of the recorded signals much simpler compared to situation when the pulsed laser labels several levels simultaneously. The presence of transitions from only one rovibrational level in the ground state appeared to be crucial for the interpretation of the complex pattern of recorded spectral lines.

Due to the irregular shape of the potential energy curve, the distance between vibrational levels in this state is highly variable. Near the minimum of the potential well, where it is relatively narrow, theoretical calculations [35] predict that spacing between successive vibrational levels should be about 40 cm⁻¹. In the region of the first shelf in the outer wall of the potential, the calculated distance between levels decreases to ca. 20 cm⁻¹, while above the inner barrier, in the widest part of the potential well, the spacing decreases to c.a. 10 cm⁻¹. In the recorded PLS signals, we observed more irregularity in the distances between spectral lines than could be inferred from the shape of the $6^{1}\Sigma^{+}$ state potential energy curve derived from *ab initio* calculations. Moreover, the number of observed spectral lines for transitions from a single rovibrational level in the ground state could only be explained by the observation of transitions to more than one excited state. Ab initio calculations [35] show that, in addition to the $6^{1}\Sigma^{+}$ state, in the investigated spectral region there are $4^{3}\Pi$ and $(5,6)^{3}\Sigma^{+}$ excited states to which transitions from the ground state are nominally forbidden in the Hund's case (a) of the angular momentum coupling. However, calculations performed for the Hund's coupling case (c) [36] predict that transitions from the ground state $1\Omega = 0^+$ to states $(9,10)\Omega = 0^+$ (components of the $6^1\Sigma^+$

and $4^{3}\Pi$ states) and $(12,13,14)\Omega=1$ (components of the $4^{3}\Pi$, $5^{3}\Sigma^{+}$ and $6^{3}\Sigma^{+}$ states) can be observed. In the case of transitions between $\Omega=1$ and $\Omega=0^+$ states, according to the selection rules, the spectral lines of the P,Q and R branches should be present in the recorded PLS signals, whereas in the case of transitions between two $\Omega=0^+$ states, only the P and R lines should be present. As shown in the work [52], the use of ${}^{1}\Sigma^{+}\leftarrow {}^{1}\Sigma^{+}$ ($\Omega=0^{+}\leftarrow \Omega=0^{+}$) transitions for level labelling is not the optimal PLS configuration for observing Q lines, as the intensity of these lines is then very low. In order to confirm the presence or absence of Q lines due to selection rules rather than experimental conditions, measurements were performed with wavelength of the probing beam tuned to $B(1)^1\Pi \leftarrow X^1\Sigma^+$ transitions and linear polarisation of the pump beam. In this configuration of the PLS, if only Q lines are present, their intensity is approximately four times higher than the intensity of P and R lines [52]. Despite such favourable conditions no Q lines were found in the recorded spectra. This indicates that the observed complex pattern of spectral lines is due to the presence of interactions between the $6^{1}\Sigma^{+}$ state and $\Omega=0^{+}$ components of neighbouring triplet states.

In the recorded spectra, 1611 lines corresponding to transitions from the ground state to the $6^{1}\Sigma^{+}$ state were identified, what resulted in the determination of the energies of 1028 rovibrational levels for 41 vibrational levels of this state, with a rotational guantum number in the range $J' = 28 \div 141$ in the main isotopologue ³⁹K¹³³Cs. Due to the unfavourable distribution of Franck-Condon factors and the presence of strong perturbations, it was impossible to record transitions to the lowest vibrational levels of the $6^{1}\Sigma^{+}$ state, what made the direct determination of the absolute vibrational numbering of the energy levels in this state impossible. Therefore, the chosen numbering is based solely on a comparison of the observed positions of the intensity minima of the spectral lines in several vibrational progressions with those predicted from the values of the Franck-Condon factors. The Franck-Condon factors were calculated on the basis of the known ground state potential and a series of hypothetical potentials, constructed for the different vibrational numberings of the levels in the $6^{1}\Sigma^{+}$ state using the IPA method. Due to the presence of perturbations for many of the rovibrational levels of the investigated state, the previously discussed method of fitting with weights [56] was used in the construction of the potential energy curve. A series of potential energy curves were then derived using different vibrational numberings, so that the position of the observed levels could be reproduced with the same accuracy. In the process of comparison, the best agreement of the distribution of line intensity minima was obtained with the vibrational numbering v'=6-46 of the observed levels in the $6^{1}\Sigma^{+}$ state, nevertheless a shift of this numbering by $\Delta y' = +/-1$ cannot be fully excluded.

The shape of the obtained potential energy curve is consistent with the results of calculations performed under the assumption of Hund's coupling case (a). For this reason the investigated state was determined as $6^{1}\Sigma^{+}$. The high similarity of the shape of the theoretical and experimental potentials should be emphasised here, as the observed differences were of the order of 100 cm^{-1} , in comparison to the differences of several hundred wavenumbers that usually occur. This shows the high quality of the *ab initio* calculations by Korek *et.al.* [35] for such an exotic shape of the potential energy curve.

The experimental data allow for rough determination of the properties of the electronic state responsible for most of the perturbations in the $6^{1}\Sigma^{+}$ state. The typical perturbation pattern that emerges allows us to determine the energies of two consecutive vibrational levels and to estimate the value of the rotational constant $B_{0} \approx 0.020 \text{ cm}^{-1}$ and the spacing between vibrational levels $G_{\nu} \approx 40 \text{ cm}^{-1}$ in the

perturbing state. Both values are in good agreement with theoretical predictions [35] for levels with v' > 20 in the $4^3\Pi$ state ($G_v \approx 40.5 \text{ cm}^{-1}$, $B_0 \approx 0.022 \text{ cm}^{-1}$).

The first experimental characterisation of the $6^{1}\Sigma^{+}$ state allowed for the identification of 1028 rovibrational levels belonging to this state. They are located in the spectral range in which the interactions with neighbouring triplet states were weak enough to allow their unambiguous assignment. The experimental data were described by a single-channel (adiabatic) model, in which the deviations between the measured and model-calculated energy values came to several wavenumbers in individual cases. Such value is well beyond the measurement uncertainty (0.1 cm⁻¹) with which these levels were determined. Further analysis of the experimental data requires the development and use of a multi-channel model, which takes into account information about the shapes of the potential energy curves of all interacting states in this spectral region and the type and strength of the mutual interactions between them.

The publication [A5] presents the results of the deperturbation analysis of the $6^{1}\Sigma^{+}$ and $4^{3}\Pi$ coupled states system carried out for the first time. The analysis takes into account the results of the studies presented in [A4], supplemented with the results of new measurements that provide information on transitions to unobserved energy levels in both states. For the first time, besides the potential energy curves, also the value of the spin-orbit interaction between the $6^{1}\Sigma^{+}$ and $4^{3}\Pi$ states was also determined.

The present measurements, performed with the PLS technique, focused on the spectral region from 20000 cm⁻¹ to 20700 cm⁻¹. In this region, transitions to a number of previously unobserved energy levels located below the lowest (v'=6) vibrational level identified so far [A4] in the $6^{1}\Sigma^{+}$ state were recorded. In the course of the analysis, around 2550 spectral lines were identified in the spectra recorded in both experiments [A4,A5], the position of which was determined with an accuracy better than 0.1cm⁻¹. The experimental data provided information on the energies of 1655 rovibrational levels in the system of interacting states $6^{1}\Sigma^{+} \sim 4^{3}\Pi$.

The identification of the spectral lines was carried out basing on a multichannel model, taking into account the interactions of the $6^{1}\Sigma^{+}$ state with neighbouring states of triplet multiplicity. Both the process of analysis of the experimental data and the construction of the model were carried out in an iterative way. At each subsequent deperturbation step, the developed model was used to predict the positions of the spectral lines, and the spectra were then re-analysed to identify new lines or, if necessary, reassign them in case the previous assignment was incorrect. The model parameters were then modified basing on the supplemented experimental data set. The procedure was repeated until all lines were correctly assigned and a final model, reproducing with the experimental accuracy the energies of all observed rovibrational levels, was built.

Based on observations made in previous work [A4], i.e.

- only transitions to energy levels of *e* parity were present in the spectra, what means that the studied states are of ${}^{1}\Sigma^{+}$ or $\Omega=0^{+}$ symmetry;
- the distances between vibrational levels of the perturbing state were in agreement with the values predicted from *ab initio* calculations for the $4^3\Pi$ state (taking into account the spin-orbit interaction, this state splits into four components: $\Omega=0^-$, $\Omega=0^+$, $\Omega=1$, $\Omega=2$);

the energy levels in the system $6^{1}\Sigma^{+} \sim 4^{3}\Pi$ of interacting states were described by a Hamiltonian matrix in which diagonal elements corresponded to the values of energies of rovibrational levels of the $\Omega = 0^+$ components of the $6^1\Sigma^+$ and $4^3\Pi$ states, and off-diagonal matrix elements to the values of spin-orbit interaction between these states. The model also takes into account the spin-orbit interactions of the $\Omega=0^+$ components of the $6^{1}\Sigma^{+}$ and $4^{3}\Pi$ states with all other electronic states in the form of effective second-order corrections to the diagonal elements of the Hamiltonian. The values of the model parameters were determined by fitting the eigen energies of the Hamiltonian to the experimental energies of rovibrational levels using the IPA method. The eigen energies of the Hamiltonian were calculated using the Fourier Grid Hamiltonian method [57]. In order to verify the unambiguity of the results obtained, a process of modelling was carried out basing on two sets of initial parameters. In the first set, the empirical potential energy curve of the $6^{1}\Sigma^{+}$ state [A4] and the potential energy curve of the $4^3\Pi$ state obtained from *ab initio* calculations provided in the discussed work [A5] were used as initial values of the model parameters. The values of the off-diagonal spin-orbit interaction were described by a function with a constant initial value. In the second set, the results of ab initio calculations [A5] were used as initial values for all parameters.

After the procedure of optimisation of the parameters with the IPA method, the model reproduced the energies of 1635 rovibrational levels with a root mean square deviation of 0.089 cm⁻¹ for the first set of initial parameters and 0.087 cm⁻¹ for the second set. In both cases, the shapes of the obtained potential energy curves were very similar to the shapes of the potential energy curves obtained from *ab initio* calculations [A5]. The main differences occurred in the obtained shapes of the functions which describe the spin-orbit interaction. In the second set the shape of the obtained spin-orbit function was closer to the theoretical predictions [A5], while for the first set it was completely different. The reason for the observed discrepancy may be the effective character of the model parameters, in which interactions not directly included in the model have an effect on the shape of the potential energy curves, as well as spin-orbit interaction functions simultaneously.

The paper [A6] presents the results of the first experimental study of the $5^{1}\Pi$ state in KCs. This is the highest ${}^{1}\Pi$ excited state for which *ab initio* calculations were performed [35]. Therefore, one could expect significant discrepancies between the experimental and theoretical values of the molecular constants. The energetic structure of this state was determined on the bases of measurements conducted using polarisation labelling spectroscopy. The same configuration of the experimental setup was used in this study as in the measurements reported in the [A4, A5] papers. The probe laser was tuned to the $4^{1}\Sigma^{+} \leftarrow X^{1}\Sigma^{+}$ transitions, while the pump laser was tuned within the range in which $5^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ transitions are predicted theoretically [35]. i.e. from about 22200 cm⁻¹ to 24000 cm⁻¹. In the recorded signals, the pattern of P, Q and R lines, characteristic for ${}^{1}\Pi \leftarrow {}^{1}\Sigma^{+}$ transitions, were present. According to theoretical predictions [35], these lines may correspond to either $4^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ or $5^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ transitions. In a preliminary analysis, using the results from [A3], all lines corresponding to transitions to the $4^{1}\Pi$ state were identified. In the subsequent analysis, 1442 spectral lines corresponding to transitions from the ground state to 24 vibrational levels of the $5^{1}\Pi$ state were identified, what allowed finally for determination of the energies of 1146 rovibrational levels in the $5^1\Pi$ state, with uncertainty of less than 0.1 cm⁻¹. In the process of the determination of the absolute vibrational numbering of the energy levels, it was assumed that the vibrational number v'=0 could be assigned to the lowest observed vibrational level in the investigated state. This assumption was confirmed at the last stage of data processing by comparing, for several recorded vibrational progressions, the distribution of the minima of the intensities of the spectral lines with the values of the Franck-Condon factors calculated basing on the experimental potential energy curves.

In the first approach, Dunham coefficients were used to describe the rovibrational energy levels in the 5¹ Π state. This is justified by the fact that, according to ab initio calculations [35], the potential energy curve of this state should have a regular shape, close to the Morse curve. The number of coefficients was chosen in such a way that their uncertainty should not exceed 4%. It turned out that energies of rovibrational levels calculated basing on the Dunham coefficients deviated from the experimental values with a standard deviation of 0.56 cm⁻¹, five times larger than the measurement uncertainty. Furthermore, for 16% of the energy levels, the absolute values of these deviations were in the range from 0.5 cm⁻¹ to 4 cm⁻¹. Nevertheless, for the first five vibrational levels, the fitted Dunham coefficients reproduced the experimental values with a standard deviation of less than 0.1 cm⁻¹. For vibrational levels v'>4, a characteristic pattern of anti-crossings was observed in the distribution of deviations of the energies of the experimental levels from the calculated values for both, e and f parity levels. The simultaneous occurrence of deviations for both parities may be caused by interactions between the 5¹ Π state and neighbouring triplet states (Ω =1 components in the Hund's coupling case (c)).

A direct fit of the potential energy curve to the determined energy levels was then performed with the IPA method. In order to minimise the influence of the perturbed levels on the shape of the potential energy curve, a fitting strategy with weights [56] was applied, similar to the work of [A3,A4]. The accuracy of the reconstruction of all experimental rovibrational energy levels as a result of solving the Schrödinger equation with the obtained potential energy curve was $\sigma = 0.53$ cm⁻¹ and was comparable to the result obtained when Dunham coefficients were used for the description.

The shape of the obtained experimental potential energy curve is very regular (close to a Morse one) and corresponds to the Hund's coupling case (a). It does not agree with the complex curve shape predicted by *ab initio* calculations performed taking in to account spin-orbit interactions [36] (Hund's coupling case (c)). The global and local perturbations predicted by these calculations for vibrational levels with v'<5, resulting from the anti-crossings between the states $18\Omega=1$ and $19\Omega=1$, were also not observed. Therefore, the investigated state was labelled as $5^{1}\Pi$ and the obtained spectroscopic constants were compared with values derived from calculations that did not take into account spin-orbit interactions [35]. This comparison confirmed the expected discrepancy between the experimental and calculated results - about 1.6 cm^{-1} for the rotation constant, about 49 cm⁻¹ for the depth of the potential well and 0.11 Å for the equilibrium inter-nuclear distance. It should also be noted that there is a large discrepancy in the shape of the outer wall of the experimental and theoretical [35] potential energy curve of the $5^{1}\Pi$ state.

In next experiments aiming to investigate the energetic structure of the KCs molecule **[A7-A9]**, I turned my attention to the electronic states correlated with the first two excited atomic asymptotes: K(4s)+Cs(6p) and K(4p)+Cs(6s) (Fig. 6). These states are most often used in photoassociation process or a transfer of ultracold molecules to a desired energy state, including the absolute rovibrational electronic ground state. The spectral region related to these states has been previously the

subject of the research performed in Prof. R. Ferber's group (Riga).



Fig. 6 Potential energy curves of electronic states correlated with K(4s)+Cs(6p) and K(4p)+Cs(6s) atomic asymptotes obtained from *ab initio* calculations [35]. The energy value is given relative to the ground state minimum $(X^{1}\Sigma^{+}T_{e}=0cm^{-1})$.

Using high-resolution Fourier spectroscopy of laser induced fluorescence, Prof. Ferber's group obtained information on the position of energy levels in the states $A(2)^{1}\Sigma^{+}$, $b(1)^{3}\Pi$ [44, 45], $B(1)^{1}\Pi$ [46, 47] correlated with the asymptote $K(4^{2}S)+Cs(6^{2}P)$ and in the state $D(2)^{1}\Pi$ [48] correlated with the asymptote $Cs(6^{2}S)+K(4^{2}P)$. During the research carried out in Riga, both global and local perturbations were found in the studied spectral range. The experimental data provided the determination of a shape of the spin-orbit interaction function only between the $A(2)^{1}\Sigma^{+}$ and $b(1)^{3}\Pi$ states by deperturbation analysis, what was presented in Tamanis *et al* [45]. In the case of the $B(1)^{1}\Pi$ and $D(2)^{1}\Pi$ states, it has not been possible to perform such an analysis due to the lack of sufficient experimental data on the electronic states interacting with them. These are triplet states as well as the $C(3)^{1}\Sigma^{+}$ state, which was responsible for a part of local perturbations of the positions of the energy levels in the $B(1)^{1}\Pi$ state reported in Birzniece *et al.* [46]

The paper [A7] reports the results of an experimental study of the energetic structure of the $C(3)^{1}\Sigma^{+}$ and $c(2)^{3}\Sigma^{+}$ electronic states using polarisation labelling spectroscopy. For both states, a potential energy curve based on spectroscopic data has been determined for the first time. In the experimental setup, dye laser light with a fixed wavelength tuned to the $E(4)^{1}\Sigma^{+} \leftarrow X^{1}\Sigma^{+}$ transitions was used for the labelling of energy levels in the ground state. A pump beam tuned from 11800 cm⁻¹ to 14000 cm⁻¹ was generated by an optical parametric oscillator with an optical parametric amplifier (OPO/OPA, Sunlite EX, Continuum) pumped with the third harmonic of a Nd:YAG laser (Powerlite 8000). Wavelength calibration of the tunable OPA/OPA laser system was performed on the

base of the recorded optogalvanic spectrum of the argon lamp and the transmission signal from a Fabry-Pérot interferometer with FSR = 1 cm⁻¹. The calibration method allowed for determination of the positions of spectral lines with an uncertainty below 0.1 cm⁻¹. The recorded PLS signal revealed the presence of spectral lines associated with transitions to five excited electronic states in the KCs molecule, what resulted in the high complexity of the recorded spectra. In the first stage of the analysis, lines corresponding to transitions to the A(2)¹ Σ^+ , b(1)³ Π [45] and B(1)¹ Π [46] states were identified basing on research work performed in Prof. R. Ferber's group. In the next stage, due to earlier information on the positions of several vibrational levels in the $C(3)^{1}\Sigma^{+}$ state [46], lines corresponding to $C(3)^{1}\Sigma^{+}\leftarrow X^{1}\Sigma^{+}$ transitions were identified relatively easily. However, at this stage of the analysis, unassigned vibrational progressions of the P and R line patterns, corresponding to the $c(2)^{3}\Sigma^{+} \leftarrow X^{1}\Sigma^{+}$ transitions as it was later shown, still remained in the recorded spectra. In the case of the KCs molecule, direct optical excitation from the ground singlet state to the triplet state is possible due to strong spin-orbit coupling causing mixing of the energy levels of the neighbouring singlet and triplet states. Such transitions have been observed previously in the KCs molecule [45], [A5,A6].

During the analysis, a total of 766 spectral lines were identified, which correspond to transitions to 25 vibrational levels in the $c(2)^{3}\Sigma^{+}$ state. Irregular spacing between successive vibrational levels was found in this state, what can result from irregular shape of the potential energy curve. This type of shape is only predicted by ab initio relativistic calculations [36, 37], in which the $c(2)^{3}\Sigma^{+}$ state is represented as a pair of states: $3\Omega = 1$ and $3\Omega = 0^{-1}$. Under this assumption, the observed spectral lines would correspond to transitions from the ground state to the 3Ω =1 state if the patterns of P, Q and R lines in the vibrational progressions were evident in the recorded signals. However, since we did not observe the Q lines in the $3\Omega=1 \leftarrow 1\Omega=0^+$ transitions in the studied region, we can assume that the observation of the Ω =1 component of the $c(2)^{3}\Sigma^{+}$ state is mainly possible as a result of indirect mixing of the wavefunctions of the e parity levels of this state with the e parity levels of the A(2)¹ Σ^{+} or C(3)¹ Σ^+ state via the b(1)³ Π state. Such a hypothesis is partially supported by the predicted large values of the matrix elements of the spin-orbit interaction between the $b(1)^{3}\Pi$ and $c(2)^{3}\Sigma^{+}$ states [37], and observed strong interactions between the A(2) $^{1}\Sigma^{+}$ and $b(1)^3\Pi$ states [45]. In addition, the large distances between the f parity levels of the $c(2)^{3}\Sigma^{+}$ and $B(1)^{1}\Pi$ states in the studied area results in relatively small mixing of their wavefunctions due to spin-orbit interactions. As a consequence, f parity levels of the $c(2)^{3}\Sigma^{+}$ state have mainly a triplet charter and are not observed due to direct excitation from the ground state, which implies the absence of Q lines in the molecular spectrum.

Based on the spectroscopic data, the potential energy curve of this state was constructed using the IPA method. The shape of the outer wall of the obtained potential was in agreement with the theoretically predicted shape of the potential of the Ω =1 component of the c(2)³ Σ ⁺ state, taking into account the spin-orbit interaction in calculations [36, 37]. Particularly high agreement was observed in the area of the anti-crossing of the Ω =1 components of the c(2)³ Σ ⁺ and b(1)³ Π states. However, we cannot assume here that we are dealing with a pure Hund's coupling case (c), since in spectra associated with an Ω =1 state we should observe the P, Q and R branches, whereas we observed only the P and R branches. It is therefore reasonable to refer to this state as c(2)³ Σ ⁺.

In this spectral region, approximately 440 spectral lines were associated to transitions from the ground state to the $C(3)^{1}\Sigma^{+}$ state. This allows the determination of energies of 390 rovibrational levels in the $C(3)^{1}\Sigma^{+}$ state. In the work of Birzniece *et al.* [46] the vibrational numbering of the energy levels in the C(3)¹ Σ^+ state was established on the basis of an analysis of the intensity distribution of laser induced fluorescence. As it turned out later, it required a correction. Using the IPA method, a potential energy curve was fitted to the observed energy levels with the vibrational numbering assumed in the paper [46]. The resulting curve reproduced the positions of most energy levels within the measurement uncertainty (<0.1 cm⁻¹). For a few levels, measured in Riga [46], there were deviations of the order of 0.2 cm⁻¹ due to local interactions with the energy levels of $c(2)^{3}\Sigma^{+}$ and $B(1)^{1}\Pi$ states. However, with this numbering of vibrational levels, it failed to reproduce the intensity distribution of the recorded lines in both experiments in the simulations performed with the resulting potential with the vibrational numbering assumed in Prof. R. Ferber's group. A correction to the vibrational numbering was made in the paper [A7]. By constructing a series of potential energy curves that reproduced with the same accuracy the energies of the vibrational levels with different vibrational numberings, the one was found that also reproduced the intensity distribution of the lines in both experiments. Consistency was obtained for the vibrational numbering shifted by $\Delta v'=-3$ with respect to that proposed in the paper [46]. After the correction, the numbering of the observed vibrational levels ranged from v'=3 to v'=18. Energy levels below v'=3 were inaccessible in the performed experiment due to the unfavourable distribution of Franck-Condon factors. On the other hand, spectral lines corresponding to transitions to vibrational levels v'>18 were masked by the lines, which corresponded to $B(1)^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ transitions, and were strongly intensity broadened. This was a consequence of the fact that the dipole moment of the $B(1)^1\Pi \leftarrow X^1\Sigma^+$ transitions in this region is about five times larger than for the transitions between the C(3)¹ Σ^+ and $X^{1}\Sigma^{+}$ states [37]. As a result, a potential energy curve of the C(3) $^{1}\Sigma^{+}$ state describing the positions of 390 energy levels with an average standard deviation of σ_{rms} = 0.04 cm⁻¹ was determined from the recorded spectroscopic data using the IPA method.

In later spectroscopic studies of the $C(3)^{1}\Sigma^{+}$ state, reported in [A8], the problem of masking of weaker spectral lines by stronger ones was minimised by controlling the light intensity of the pump beam and by selecting appropriately the labelled vibrational levels in the ground state. The ground state rovibrational levels were chosen in such a way that the Franck-Condon factors were maximal for the $C(3)^{1}\Sigma^{+} \leftarrow X^{1}\Sigma^{+}$ transitions and as small as possible for the $B^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ transitions in the investigated spectral range. During the measurements, for each labelled level in the ground state, the intensity of the pump beam was selected individually so that weak spectral lines corresponding to transitions to the $C(3)^{1}\Sigma^{+}$ state were observed at the lowest possible intensity broadening of the lines corresponding to the $B^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ transitions. During the analysis of the recorded spectra, 1300 additional spectral lines were identified for the $C(3)^{1}\Sigma^{+} \leftarrow X^{1}\Sigma^{+}$ transitions.

Combining the obtained results with those presented in Birzniece *et al.* [37] and Szczepkowski *et al.* [A7], allowed for the determination of the energies of 1436 rovibrational levels of the $C(3)^{1}\Sigma^{+}$ state in the range of quantum numbers: $v' \in <3;54>$ and $J' \in <38;127>$. Based on these data, about 55% of the depth of the potential well of the $C(3)^{1}\Sigma^{+}$ state was described experimentally. The experimental potential energy curve obtained using the IPA method allows to reproduce the measured energies of most rovibrational levels with experimental accuracy (<0.1cm⁻¹). For individual levels, differences of the order of 0.2 cm⁻¹ between the measured energy and the calculated

value were noted, indicating the presence of local perturbations. From the location of the perturbed levels in the direct vicinity of the energy levels of the B(1)¹ Π or c(2)³ Σ^+ or b(1)³ Π states, it can be concluded that the interactions between the C(3)¹ Σ^+ state and the mentioned states are the origin of the observed perturbations.

A full explanation of the mechanism responsible for the direct excitation from the ground state $X^1\Sigma^+$ to the $c(2)^3\Sigma^+$ state observed in [A7], and the level position perturbations in the $C(3)^1\Sigma^+$ state reported in [46][A8], requires a global deperturbation analysis using a model that takes into account all interacting states correlated with the first excited caesium atomic asymptote. Currently, in collaboration with Prof. A. Pashov's group (Sofia), we have started work on the construction of such a model.

The results of spectroscopic studies of electronic states correlated with the Cs(6s)+K(4p) atomic asymptote were presented in [A9]. The effects led to the observation, for the first time, of transitions to the $2^{3}\Pi$ and $3^{3}\Sigma^{+}$ states. Also a significant addition to the information on the positions of energy levels in the D(2)¹ Π state published in the work [48] was done. The experimental setup described in [A7,A8] was used for the measurements. In the spectral range from 15400 cm⁻¹ to 16700 cm⁻¹, almost 4500 spectral lines were recorded, the position of which was determined with an accuracy better than 0.05 cm⁻¹. After merging the Warsaw set of data with the data from the experiment performed by the group from Riga [48], the energies of 6039 rovibrational levels belonging to states correlated with the atomic asymptote Cs(6s)+K(4p) were analysed.

During the analysis, multi-state rotational perturbations of the energy levels of the D(2)¹ Π state were found. The electronic states responsible for the formation of the perturbations were also identified. For vibrational levels v'≤12 it was the 2³ Π state, and for v'>12 levels the 2³ Π and 3³ Σ ⁺ states.

A deperturbation analysis of the vibrational levels $0 \le v' \le 12$ in the $D(2)^1\Pi$ state was carried out for the first time. The main origin of the perturbation in the discussed range of vibrational levels was the spin-orbit interaction with the Ω =1 component of the $2^3\Pi$ state (abbreviated notation $2^3\Pi_1$). The position of some of the rovibrational levels of the $D(2)^1\Pi$ state was weakly perturbed by the L-uncoupling interaction with the rovibrational levels of the Ω =0⁺ component of the $2^3\Pi$ state. The experimental data allowed for the construction of a two-channel model describing positions of energy levels in the $D(2)^1\Pi \sim 2^3\Pi_1$ state system taking into account the spin-orbit interaction. The model was based on the Hamiltonian:

| T | ${}_{\Pi}(v_S=0,J)$ | 0 | 0 | $(H_{so})_{0,0}$ | | $(H_{so})_{0,6}$ | |
|---|---------------------|----|---------------------------|--------------------------|----|---------------------------|---|
| [| 0 | •. | 0 | : | | ÷ | |
| | 0 | 0 | $T_{^{1}\Pi}(v_{S}=12,J)$ | $(H_{so})_{12,0}$ | | $(H_{so})_{12,6}$ | |
| | $(H_{so})_{0,0}$ | | $(H_{so})_{0,12}$ | $T_{{}^3\Pi_1}(v_T=0,J)$ | 0 | 0 | ' |
| | : | | : | 0 | •. | 0 | |
| / | $(H_{so})_{6,0}$ | | $(H_{so})_{6,12}$ | 0 | 0 | $T_{3_{\Pi_1}}(v_T=6,J)/$ | / |

where: $T_{1_{\Pi}}(v_S, J)$ and $T_{3_{\Pi}}(v_T, J)$ denote the unperturbed energies expressed by Dunham coefficients [58], that describe the positions of rovibrational levels in the D(2)¹ Π and 2³ Π_1 states respectively, and $(H_{SO})_{v_S,v_T}$ coefficients describe the off-diagonal matrix elements of the spin-orbit interaction between the vibrational levels v_S and v_T of the D(2)¹ Π and 2³ Π_1 states. In the described model, the value of $(H_{SO})_{v_S,v_T} \neq 0$ is assumed only in the areas where the vibrational levels of the two states interact directly with each other, assuming that the influence of distant energy levels is global and causes a regular shift of all levels of a given state, and that this phenomenon is characterised by the effective values of the diagonal matrix elements. The above assumptions and the observed perturbation distribution resulted in a boxlike (2x2) arrangement of the Hamiltonian matrix. The values of the coefficients in the model were determined by the process of fitting the eigen values of the Hamiltonian to the experimental values of energies of the rovibrational levels. As a result of the deperturbation procedure, a fully analytical model describing the energies of more than 2000 rovibrational levels in the D(2)¹ $\Pi \sim 2^{3}\Pi_{1}$ system, with an average standard deviation of $\sigma_{rms} \sim 0.03$ cm⁻¹, was obtained. The main advantage of the presented approach is its simplicity which allows for easy determination of the energies of the observed rovibrational levels and interpolation of the energy values of the levels not observed in the experiment.

IV.6. Energetic structure of bipolar dimers build of a strontium and alkali metal atom

IV.6.1. Motivation and state of the art

In contrast to diatomic alkali metal molecules, spectroscopic studies of the electronic structure of dimers composed of alkali metal and strontium metal (Alk-Sr) atoms have been carried out for a relatively short time. Similar to the KCs molecule, their initiation was motivated by the development and needs of so-called "cold physics".

In 2010, the first results of electronic structure calculations for this group of molecules were published [59]. The publication of further theoretical papers on the energetic structure of alkali metal-strontium dimers [26,60,61] showed large discrepancies in the presented *ab initio* calculation results. This means that an accurate calculation of the electronic structure of alkali metal-strontium dimers is still a major challenge for theoreticians. This is due to the presence of the heavy strontium atom, in which there are strong interactions between valence electrons and closed shell electrons. The degree to which these correlations are taken into account makes a major contribution to the discrepancies between the results obtained by different quantum chemistry computational methods. For example, the values of the depth of the KSr ground state potential well differ by more than 20% depending on the calculation method used e.g. [B1] and [61].

Results of first experiments were published in 2014 [26]. They concerned lowresolution spectroscopic measurements of transitions from the ground state to several excited states in the RbSr molecule [26], and were performed by the Prof. W. Ernst's group (Graz). Results of the first high-resolution energetic structure studies of alkali metal-strontium dimers were published in 2017. This research was carried out in the Prof. E. Tiemann's group (Hannover), and concerned the electronic structure of the LiSr molecule [27]. In contrast to the experiment performed in Prof. W. Ernst's group, LiSr molecules were produced in a high-temperature spectroscopic cell of heat-pipe type. On the basis of spectroscopic measurements, Prof. E. Tiemann's group determined molecular constants for the ground state and the first excited states with symmetries ${}^{2}\Sigma^{+}$ and ${}^{2}\Pi$ in the LiSr molecule. Further analysis of the experimental data by Prof. E. Tiemann's group [29], provided information on the interactions between the $2{}^{2}\Sigma^{+}$ and ${}^{2}\Pi$ excited states.

Experimental work on the preparation of RbSr molecules [62] under ultra-low temperature conditions, started by Prof. F. Schreck (Insbruck/Amsterdam) in 2011, revealed the importance of further investigation of the energetic structure of these molecules. During my research stay (2011/2012) in Prof. F. Schreck's group, I took part in the work on the preparation of a mixture of Bose-Einstein condensates of rubidium and strontium atoms [62], serving as a starting point to obtain ultracold RbSr molecules. This stay inspired me to undertake spectroscopic studies of this group of molecules in the Warsaw laboratory.

IV.5.2. Experimental techniques

• Preparation of KSr and RbSr molecules - multi-zone heat-pipe oven

The start of the research on the energetic structure of a new group of molecules was associated with a number of challenges. One of these was the process of producing of such molecules at high temperature. In the case of the LiSr molecule, the boiling point of lithium (about 1600 K) is lower than the temperature at which experiments are carried out (about 1100 K). This allows a liquid mixture of strontium and lithium to be obtained, what is necessary for the correct operation of the spectroscopic cell of the heat-pipe type. For the heavier alkali metals, in particular potassium and rubidium, it is not possible to obtain such a mixture because of the fact that their boiling points are lower even than the melting point of strontium (approx. 1070 K). This problem was solved by building a heat-pipe oven with three heating zones (Fig. 7), and separated circulation of the liquid phase of alkali metals and strontium. The central part of the pipe was filled with 10 g of strontium and heated to a temperature of about 1100 K, while the outer part was filled with 10 g of potassium or rubidium and heated to a temperature 823 K. The inside of the oven was filled with 30 Torr of argon, serving as a buffer gas, which main role was to prevent the deposition of metal vapours on the spectroscopic windows.

• Thermally and laser induced fluorescence



Fig. 7 Distribution of temperatures in a three-zone heat-pipe oven for the production of RbSr molecules. The locations of metallic rubidium and strontium are shown with grey and yellow rectangles, respectively.

Two spectroscopic methods were used to study the energetic structure of bipolar molecules in the Warsaw laboratory:

1. Thermoluminescence spectroscopy is based on the thermal population of rovibrational levels of the excited state. Thermally excited fluorescence spectra were recorded using a Bruker Vertex v80 vacuum Fourier spectrometer. Thermoluminescence measurements of KSr and RbSr molecules provided spectra with several rotationally unresolved bands with prominent band heads, which correspond to transitions between different rovibrational levels of the excited and ground electronic states. In principle, this technique allows even to obtain information about the rotational structure of electronic states, as has already been demonstrated for the LiSr molecule [27]. However, the small value of the rotational constants for the investigated states in KSr and RbSr molecules resulted in overlapping of spectral lines for individual transitions between rovibrational levels with similar values of the rotational quantum number because of Doppler broadening.

2. In Laser Induced Fluorescence (LIF) spectroscopy, in which fluorescence to the ground state is recorded, and excitation to higher lying electronic states is a result of an absorption of laser light at a chosen wavelength. Due to this excitation scheme, the spectrum of fluorescence to the ground state is limited to transitions from selectively populated rovibrational levels of the excited state, what greatly simplifies the process of analysing of the spectra. In Warsaw the LIF spectra have been recorded using a Bruker Vertex v80 vacuum Fourier transform spectrometer with a spectral resolution of 0.16 cm⁻¹.

IV.6.2. Overview of the results

The paper [B1] presents the results of the first spectroscopic studies of the KSr molecule. As a result, fundamental spectroscopic constants and potential energy curves of the ground and excited $B(2)^{2}\Sigma^{+}$ states were determined. A comparative analysis was also carried out between the potential energy curves derived from the three quantum chemistry calculation methods and potentials determined basing on experimental data. It allowed for verification of the results of calculations performed with different *ab initio* methods.

Until this work, the electronic structure of the KSr molecule was known only from ab initio calculations. The results of the first comprehensive calculations of the ground state potential energy curve, excited states and the value of the transition dipole moment were presented by Pototschnig et al. [61]. This was done using the MRCI (Multireference Configuration Interaction) method. For comparative purposes, the Prof. O. Dulieu's group (Orsay) and Prof. P. Żuchowski's group (Toruń) performed calculations of the electronic structure of KSr by alternative methods: FCI+ECP+CPP and RCCSD(T), respectively. The results of these calculations were presented for the first time in the discussed paper [B1]. A direct comparison of the shapes of the potential energy curves calculated using the mentioned methods revealed a number of differences. The largest discrepancies concern the depth D_e of the ground state potential well, reaching more than 20% in the extreme case: $D_e \approx 1383 \text{ cm}^{-1}$ for MRCI and $D_e \approx 1139 \text{ cm}^{-1}$ for RCCSD(T). The smallest differences were for the equilibrium distance of atomic nuclei in the ground state ($\Delta R_e < 2\%$). Finally, the shapes of these curves were compared with the shapes of the potential energy curves obtained from the analysis of the thermally excited fluorescence spectrum.

KSr molecules were produced in a three zone heat-pipe oven, after heating strontium to 1100 K in the central part of the oven and potassium to 820 K in the outer parts. The high oven temperature caused thermal population of the excited states of the KSr molecule so the fluorescence resulting from spontaneous emission to the ground state could be observed. The fluorescence spectrum was recorded with a Fourier spectrometer at a resolution of 0.16 cm⁻¹.

Fourteen band heads were observed in the spectral range from 8850 cm⁻¹ to 9300 cm⁻¹. According to theoretical predictions [B1] [61], $A(1)^2\Pi \rightarrow X(1)^2\Sigma^+$ and $B(2)^2\Sigma^+ \rightarrow X(1)^2\Sigma^+$ transitions should be observed in this spectral range. In order to identify the states and the individual rovibrational energy levels from which fluorescence was observed, the recorded spectrum of thermally induced fluorescence was compared with its simulations based on three sets of theoretical potential energy curves. To simulate the spectrum of thermally excited fluorescence, my own program was used. Comparison of the simulation and experimental results led to a number of conclusions. Three of them turned out to be crucial in the interpretation of the experimental data:

- In the experiment, only fluorescence from the thermally excited B(2)²Σ⁺ state was observed, as the predicted line intensity for A(1)²Π→X(1)²Σ⁺ transitions is typically 2000 times lower than for B(2)²Σ⁺→X(1)²Σ⁺ transitions.
- Both the contour of the fluorescence spectrum and the arrangement of the vibrational band heads in the spectra resulting from the simulations are very similar to those observed in the experimental spectrum. This allowed the identification of the vibrational levels of the ground and excited states, between which transitions were observed, in thirteen out of the fourteen band heads observed in the B(2)²Σ⁺→X(1)²Σ⁺ experimental spectrum. The validity of this identification was confirmed by constructing the corresponding Deslandre's table.
- The spectral structure remained rotationally unresolved under the present experimental conditions, and each of the observed band heads comprised dozens of overlapping spectral lines corresponding to transitions between the rovibrational levels of the $X(1)^2\Sigma^+$ and $B(2)^2\Sigma^+$ states.

From the modelling of the positions of the groups of spectral lines forming the band heads, the spectroscopic constants for the ground state and the $B(2)^2\Sigma^+$ state were determined. In the model used, the position of each line was defined as the difference in the energies of rovibrational levels of the ground and excited states expressed by Dunham coefficients. The identification of the spectral lines forming each head was performed by simulating the spectrum separately for each of the three sets of theoretical potential energy curves, calculated with the methods MRCI, FCI+ECP+CPP, and RCCSD(T). Three sets of spectral lines were thus obtained. Modelling of the band head positions was performed for each identified set of lines, assuming theoretical values of the rotational constant of the ground state. Three sets of Dunham coefficients for each state were thus obtained, which were based on different theoretical values of the equilibrium distance of the nuclei in the ground state R_e . However, they remain in agreement with each other within the error of their determination. The Dunham coefficients describe the energy of the first five (v"=0-4) vibrational levels in the ground state, and the first eight (v'=0-7) in the B(2)² Σ^+ state.

Basing on the information about the rovibrational energy levels, calculated from the experimental Dunham coefficients, the potential energy curves of the $X(1)^2\Sigma^+$ and $B(2)^2\Sigma^+$ states were determined. Three sets of theoretical potential energy curves were used as a starting point for the IPA procedure. In each case, the shapes of the curves were optimised to match the experimental data. As it turned out, the resulting potentials have almost identical shapes, regardless of the curveing starting curve. Only the relative positions of the equilibrium distance of the nuclei R_e differ noticeably, which is related to the use of theoretical values of the rotational constant during the analysis. In order to verify the results, the molecular spectra were simulated again based on the experimental sets of potential energy curves. In each of the three simulated spectra, the position of the band heads overlapped with those observed in the experimental spectrum.

The best agreement between the experimental and simulated spectrum contours was found for the spectrum calculated with a set of experimental curves in the model basing on calculations performed using the FCI+ECP+CPP method. Also the values of the spectroscopic constants determined by this computational method are closest to the values determined from the spectroscopic data. This allowed for

conclusion, that among the three theoretical approaches analysed in this work, the FCI+ECP+CP method provides the best agreement with the experimental results. However, it should be noted that in the other cases the overall agreement with the obtained experimental data is also satisfactory.

The experimental potential energy curves presented in this work can be used to model possible schemes for the production of ultracold KSr molecules. The experimental method employed in this work and the methods of analysis of the data provide an alternative to other complex and often very time consuming experimental techniques, especially when rapid evaluation and coarse optimisation of theoretical potential energy curves are required.

The paper [B2] presents the results of an energetic structure study of the RbSr molecule using two-colour photoassociation spectroscopy of an ultracold $(T \sim 1 \,\mu\text{K})$ mixture of rubidium and strontium atoms and thermoluminescence and Laser Induced Fluorescence (LIF) spectroscopy of hot $(T \sim 1000 \text{ K})$ RbSr molecules. Measurements carried out at ultralow temperatures provided information on the energies of weakly bound rovibrational levels located near the dissociation limit of the ground state, described by the long-range part of the potential energy curve. In contrast, measurements performed at high temperatures provided information on deeply bound rovibrational energy levels located near the equilibrium nuclei distance of the ground $X(1)^2\Sigma^+$ and excited $B(2)^2\Sigma^+$ states, described by the short range part of the potential energy curve. Measurements at low temperature were performed in Prof. F. Schreck's group in the Amsterdam laboratory, and at high temperature in the Warsaw laboratory.

The spectroscopic studies performed in Prof. F. Schreck's group used strontium and rubidium atoms cooled to temperatures of the order of 1 µK, trapped in an optical trap. Technical details of the apparatus used in the experiment are described in the paper [E9]^{*}. Positions of weakly bound ground state energy levels were determined using the two-colour photoassociation method [B2] and magnetossociation [28]. In order to unambiguously determine the vibrational and rotational numbering of the observed levels, measurements were performed for three isotopic mixtures (⁸⁷Rb⁸⁸Sr, ⁸⁷Rb⁸⁷Sr, ⁸⁷Rb⁸⁸Sr). As a first approximation, the positions of the observed weakly bound ground state levels were described by the Lennard-Jones potential. This way, the values of the C_6 and C_8 dispersion coefficients, the vibrational and rovibrational numbering of the observed energy levels, and the number of ground state bound levels were determined. The validity of the assignment of quantum numbers to the observed energy levels was confirmed by achieving an agreement between the value of the s-wave scattering constant between cold rubidium and strontium atoms calculated using the fitted Lennard-Jones potential and its measured value.

Independently of the work performed in Amsterdam, I began spectroscopic studies of the energetic structure of RbSr molecules in the Warsaw laboratory. The molecules were produced in a high-temperature heat-pipe oven. As in the case of KSr molecules, the high temperature of the oven induced thermal population of the excited states of RbSr molecules, what made possible recording spectra of spontaneous emission from the excited states to the ground state using a Fourier spectrometer. In the recorded spectra, 24 rotationally unresolved band heads were

^{*} The paper is included in the list of publications resulting from research carried out outside the home institutions presented in chapter V.1

observed. To analyse them, the method described in [B1] was used, based on a comparison of the experimental spectrum with its simulations, performed on the basis of theoretical potential energy curves. As a result of this analysis, it was found that only band heads for transitions between the B(2)² Σ^+ and X(1)² Σ^+ states were observed in the spectrum. Unfortunately, it soon became clear, that the accuracy of the available ab initio calculations, performed using three different methods (MRCI [24], FCI+ECP+CPP [22] i RCCSD(T) [22]), was insufficient for unambiguous identification of the energy levels between which the observed transitions occurred. In order to establish the correct vibrational numbering of the energy levels in the ground state and in the B(2)² Σ^+ state, laser-induced fluorescence (LIF) measurements were additionally performed. By tuning the laser wavelength to the position of selected band heads, the fluorescence spectrum was recorded using a Fourier spectrometer. From the analysis of the combined results of the thermally excited luminescence and the laser-induced fluorescence techniques, the positions of the six lowest vibrational levels in the ground state $X(1)^2\Sigma^+$ (v"=0-5) and nine in the excited state $B(2)^{2}\Sigma^{+}$ (v'=0-8) were derived.

Due to the lack of rotational resolution of the obtained experimental results, as in the case of KSr, the rotational constant of the ground state resulting from theoretical predictions was used to model the positions of the energy levels with Dunham coefficients. Therefore, three sets of Dunham coefficients were generated to describe the observed set of energy levels in the $X(1)^2\Sigma^+$ and $B(2)^2\Sigma^+$ states, for the rotational constants determined basing on calculations with three *ab initio* methods: MRCI [24], FCI+ECP+CPP [22] i RCCSD(T) [22].

The main goal of the spectroscopic studies discussed here was to determine the shape of the ground state $X(1)^2\Sigma^+$ potential energy curve, so that it correctly describes all the experimental data. Information from both experiments was used to determine the shape of this potential, and in the energy range where experimental data were not available the results of *ab initio* calculations were used. In particular, this concerned the position of the equilibrium distance between nuclei R_e , which could not be determined from the experimental data. The energy ranges that relate to the individual data and the form of the model potential are schematically presented in Fig. 8.



Fig. 8 The ground state potential energy curve of the RbSr molecule described by the Morse Long-Range model $V_{MLR}(r)$. The energy ranges covered by the experimental data are marked in blue and red, while by *ab initio* data - in yellow. Symbol meanings: *r* - distance between nuclei of atoms, r_e - equilibrium distance, D_e - dissociation energy, C_m - dispersion coefficient, $d_m(r)$ - damping function, β_i - fitting coefficients

The derivation of the shape of the potential energy curve has begun with description of the results of *ab initio* calculations performed with the MRCI [24], FCI+ECP+CPP [22] and RCCSD(T) [22] methods, using the Morse Long-Range (V_{MLR}) analytical model. In the next step, an optimisation of the model potential coefficients with the IPA method was performed in order to describe the experimental energy levels, while preserving the theoretical values in the region not covered by the experimental data. The optimisation process resulted in three potential energy curves differing essentially only in the positions of the equilibrium distance of the nuclei. In Fig. 9, a comparison of the potential energy curves before and after optimisation procedure of their shapes is presented.



Fig. 9 Comparison of the ground state potential energy curves determined by *ab initio* methods (upper panel) and after fitting to experimental data (lower panel). The maximal values of the discrepancy in the depth of the potential well ΔD_e and the values of the vibrational constant $\Delta \omega_e$ are also indicated on the graphs.

By combining the results of measurements from both research groups and the results of ab initio calculations in a common analysis, the depth of the ground state $X(1)^{2}\Sigma^{+}$ potential energy curve was determined for the first time for alkali metalstrontium dimer. Moreover, the semiempirical ground-state potential energy curve derived in the analysis process describes with experimental accuracy the experimentally determined energies of the weakly and deeply bound rovibrational levels and the positions of the Fano-Feschbach resonances [28]. Based on the derived ground state potential energy curve, the positions and widths of other previously unobserved Fano-Feschbach resonances were calculated. Additionally, the molecular constants for the $X(1)^{2}\Sigma^{+}$ and $B(2)^{2}\Sigma^{+}$ states and the dispersion coefficients (C₆ and C₈) for the $X(1)^2\Sigma^+$ state were determined in the analysis process. Based on the experimental results, a comparative analysis of the potential calculated using three ab initio methods MRCI [24]. energy curves FCI+ECP+CPP [22] and RCCSD(T) [22] was also done. For both ground and $B(2)^{2}\Sigma^{+}$ excited states the best agreement with experimental results was obtained for curves calculated by the FCI+ECP+CPP method. The paper [B2] was acknowledged by the editors of Phys. Chem. Chem. Phys. as "Editor's choice".

IV.7. Summary

The research work that I have performed has allowed a comprehensive description of the energetic structure of the excited states of the KCs molecule and the ground and low excited electronic states in KSr and RbSr dimers. The research involved the development and use of complementary measurement techniques, a variety of data analysis methods and collaborations with groups performing advanced *ab initio* calculations.

The study of the properties of the KCs molecule, in addition to providing an accurate, in most cases a first characterisation of a number of excited electronic states, also allowed for the formulation of a few general conclusions:

- The spin-orbit interactions, causing mixing of the wavefunctions of the energy levels of singlet states with the wavefunctions of the levels of triplet states, allow the observation of nominally forbidden, intercombination transitions between the vibrational levels of the ground state and the levels of triplet states. A number of spectral lines corresponding to such transitions have been identified. Such transitions allow, for example, the transfer of ultracold KCs molecules to energy levels of states with different multiplicities, a phenomenon that is regarded as highly desirable for efforts to control chemical reactions at the quantum level at ultralow temperatures.
- In all investigated electronic states the spin-orbit interaction is, on the one hand, strong enough to cause the aforementioned effect of mixing of the wavefunctions of the rovibrational levels of states with different multiplicities and, on the other hand, it is not strong enough to cause a full splitting of the system of electronic states described by the Hund's coupling case (a) into the system described by the Hund's coupling case (c).
- I found that it is possible to observe direct transitions from the vibrational level v"=0 in the ground state to rovibrational levels located near the dissociation limit of excited states correlated with the K(4²S)+Cs(5²D) atomic asymptote. Such transitions are used to transfer weakly bound molecules produced by photo- or magneto-association to the absolute rovibrational electronic ground state.

The results of the study of the properties of KSr and RbSr bipolar molecules allowed the formulation of the following conclusions:

• The developed new data analysis method and the used measurement methods allow for relatively fast verification and optimisation of the results of *ab initio* calculations. Due to the large discrepancy in the results of *ab initio* calculations, their rapid verification is very important for the experiments, as it facilitates and speeds up the data analysis process. At the same time, the obtained experimental results may stimulate the development of quantum chemistry computational methods. It is also worth pointing out that, despite the improvements in computational methods, the accuracy of the information on the molecular energetic structure obtained from experiments is still significantly higher. However, in many cases, the information obtained from *ab*

initio calculations is essential, and often without them the analysis and interpretation of experimental results is not possible at all.

- Transitions between the $X(1)^2\Sigma^+$ and $B(2)^2\Sigma^+$ states in KrSr and RbSr molecules exhibit an almost diagonal distribution of Franck-Condon factor values between vibrational levels. Taking into account the literature data on such transitions in the LiSr molecule and the preliminary results of my spectroscopic studies of the NaSr molecule, it can be concluded that this is a characteristic feature of dimers composed of an alkali metal atom and a strontium atom. The diagonal distribution of the Franck-Condon factor values for the transitions between the vibrational levels of the $X(1)^2\Sigma^+$ and $B(2)^2\Sigma^+$ states may be used for the optical cooling of such molecules.
- In the RbSr molecule, the derived ground-state potential energy curve allowed for the calculation of the positions of previously unknown Fano-Feshbach resonances. The work is currently underway in Prof. F. Schreck's group to use selected resonances to produce ultracold RbSr molecules.

In conclusion, the obtained results are important for prospective "cold physics" experiments, providing new and unique data necessary for their planning, as well as for groups of theoreticians performing *ab initio* calculations, as they enable the verification and optimisation of their computational methods.

V. Presentation of significant scientific or artistic activity carried out at more than one university, scientific or cultural institution, especially at foreign institutions

In addition to the Institute of Physics of the Pomeranian Academy in Słupsk (from 2001 to 2009) and the Institute of Physics of the Polish Academy of Sciences in Warsaw (from 2009 to the present), I conducted research related to cold and ultracold gases in the following institutions:

- 09.2002-01.2004 Institut für Experimentalphysik (IEP) TU Graz (Austria), head of group Prof. L. Windholza,
- 2005-2013 National Laboratory of Atomic Molecular and Optical Physics (KL FAMO) UMK Toruń (Poland), head of group Prof. W. Gawlika,
- 11.2011-01.2012 Institut für Quantenoptik und Quanteninformation (IQQI) ÖAW Innsbruck (Austria), head of group Prof. F. Schrecka.

The experimental work I performed at the IEP TU Graz concerned the analysis of collisional processes between cold lithium and sodium atoms, which affect the escape of cold atoms from the magneto-optical trap. The results of the research are presented in the papers [E1, E2] and my PhD thesis.

At the National FAMO Laboratory (Nicolaus Copernicus University Toruń) I joined an interuniversity team investigating the properties of ultracold atomic gases. Experimental work performed by this team resulted, among other things, in obtaining of the first Bose-Einstein (B-E) condensate in Poland. The quantum degenerate state was obtained in a gas of ultracold rubidium atoms trapped in a magnetic trap. The experimental setup, the procedure of the experiment, and the hydrodynamic properties of the obtained rubidium B-E condensate are presented in the paper [E3]. Further studies conducted at KL FAMO resulted in the experimental confirmation of the interactions between the B-E condensate and the cloud of ultracold atoms surrounding the condensate [E4,E5]. This achievement was highlighted in Europhysics News [EPN, 40, 1, p.17 (2009)]. A major challenge during this research was to determine the percentage of condensed and non-condensed fractions in the observed cloud of atoms. The solution to this problem, involving the development of a method for analysing and calibrating the absorption image, was presented in the paper [E6]. Further experiments carried out in the Toruń laboratory focused on the formation of spinor condensates [E7] and the evolution of interference in spinor condensates [E8].

While I was in Prof. Florian Schreck's group at the IQQI ÖAW Innsbruck laboratory, I was involved in the construction of an experimental setup for obtaining a mixture of Bose-Einstein condensates of rubidium and strontium atoms [E9]. The construction of the experimental setup was part of a scientific project related to quantum simulations using B-E condensate formed by RbSr molecules.

One of the problems mentioned by Prof. F. Schreck, which was an obstacle in obtaining a molecular B-E condensate was the lack of precise information about the energy structure of the RbSr molecule. This inspired me to start studies on the energetic structure of a new class of molecules, i.e. dipolar dimers made of alkali

metal atoms and strontium atoms at the Institute of Physics of the Polish Academy of Sciences. The cooperation with Prof. F. Schreck's group is currently being continued. Its result is the determination, for the first time, the short- and long-range part of potential energy curve of the ground state in the RbSr molecule based on combined results of the spectroscopic studies performed under my supervision in the Warsaw laboratory and under the supervision of Prof. F. Schreck in Amsterdam. The article [B2] in which the results of the joint research were published was honoured by the editors of Phys. Chem. Chem. Phys. as "Editor's choice".

V.1. List of publications

- E1. L. Holler, G. Aubock, C. Binder, L. Windholz, J. Szczepkowski,
 E. Paul-Kwiek, *Heteronuclear cold collisions between lithium and sodium*,
 SPIE Proc. 5849, 203–205, 2004 (2005).
- E2. G. Auböck, C. Binder, L. Holler, V. Wippel, K. Rumpf, J Szczepkowski,
 W. E. Ernst and L. Windholz, *Trap loss collisions of ⁶Li and ⁷Li with ²³Na in a combined magneto-optical trap*, J. Phys B 39, 871-897, (2006)
- F. Bylicki, W. Gawlika, W. Jastrzebski, A. Noga, J. Szczepkowski,
 M. Witkowski, J. Zachorowski, M. Zawada, Studies of the hydrodynamic properties of Bose-Einstein condensate of ⁸⁷Rb atoms in a magnetic trap, Acta Phys. Pol. A 113, 691-705, (2008)
- E4. M. Zawada, R. Abdoul, J. Chwedeńczuk, R. Gartman, J. Szczepkowski,
 Ł. Tracewski, M. Witkowski, W. Gawlik, *Free-fall expansion of finite*temperature Bose–Einstein condensed gas in the non-Thomas–Fermi regime,
 J. Phys B 41, 241001, (2008)
- E5. W. Gawlik, W. Jastrzębski, J. Szczepkowski, M. Witkowski, J. Zachorowski,
 M. Zawada, *Experiments on the dynamics of the Bose-Einstein condensate at finite temperatures*, Phys. Scr. 135, 014028 (2009)
- E6. J. Szczepkowski, R.Gartman, M. Witkowski, L. Tracewski, M. Zawada,
 W. Gawlik, Analysis and calibration of absorptive images of Bose-Einstein condensate at nonzero temperatures, Rev. Sci. Instr. 80, 053103 (2009)
- E7. R. Gartman, M. Piotrowski, J. Szczepkowski, M. Witkowski, M. Zawada, W. Gawlik, Production of spinor condensates of ⁸⁷Rb released from a magnetic trap, Opt. App. 40, no.3, 565-570 (2010)
- E8. M. Witkowski, R. Gartman, B Nagórny, M. Piotrowski, M. Płodzien, K. Sacha, J. Szczepkowski, J. Zachorowski, M. Zawada, W. Gawlik, *Matter-wave interference versus spontaneous pattern formation in spinor Bose-Einstein condensates*, Phys. Rev. A 88, 025602 (2013)
- E9. B. Pasquiou, A. Bayerle, S.M. Tzanova, S. Stellmer, J. Szczepkowski,
 M. Parigger, R. Grimm, F. Schreck, *Quantum degenerate mixtures of strontium and rubidium atoms,* Phys. Rev A 88, 023601 (2013)

VI. Presentation of teaching and organizational achievements as well as achievements in popularization of science or art.

- 1. Member of the organising committee of the "International School & Conference on the Physics of Semiconductors "Jaszowiec", editions: 2021,2022, 2023.
- 2. Co-organise and lead a series of ten workshops on 'Quantum Key Distribution' for secondary school students during the 2022/2023 school year. Construction of a circuit to demonstrate quantum key distribution based on the BB84 protocol.
- 3. Presentation, within the framework of Cluster Q, of the demonstrator of quantum key distribution BB84 protocol during the Science Picnic of the Polish Radio and Copernicus Science Centre in Warsaw on 27.05.2023.
- 4. Co-teaching with dr. hab. K. Pawłowski (Prof. CFT) of the course "Outreach Lab" at the Warsaw Doctoral School in the summer semester 2021.
- 5. Co-supervisor of undergraduate thesis: "Investigation of the structure of diatomic molecules by sub-Doppler spectroscopy" completed at the IP PAS and successfully defended at the Institute of Experimental Physics, University of Warsaw (2015).
- 6. Supervising one year long research internships for students of Warsaw University and Warsaw University of Technology in the laser spectroscopy group of the IP PAS 2 internships.
- Supervising summer internships (180h-240h/person) in the laser spectroscopy team of the Institute of Physics of the Polish Academy of Sciences for students of the University of Warsaw and the Warsaw University of Technology - a total of 12 students
- 8. Reviewer of the Polish selection for the EU Contest for Young Scientists (EUCYS) (2014)
- 9. Teaching a C++ programming lab for physics students at Cardinal Stefan Wyszyński University in Warsaw 1 semester
- 10. Supervising workshops for gifted young people as part of the cooperation between IP PAS and the National Children's Fund 3 editions
- 11.Demonstrations of experiments and laboratories during the "IP PAS Open Day".
- 12. Organisation of over 30 sessions of demonstrations of experiments for preschool children, primary school pupils, secondary school pupils and students of the University of the Third Age as part of the ""Meeting with Physics" campaign held by the Institute of Physics at the Pomeranian Academy in Słupsk ("the campaign was submitted for the PTF Prize for Popularisation of Physics in 2007") (2005-2009)
- 13. Popular science lectures during the Baltic Science Festival::
 - "Cold, colder, BEC" 2004
 - "Physics in Art" 2005

- 14. Popular Science Lecture "Illusions" at the 3rd Gyorgy Kempes International Symposium on Science and Art at the University of Eger (Hungary) 14.XI.2005
- 15.Co-organising and running demonstrations of experiments at mass outdoor events:
 - "Physics at Bytów Castle": 20.V.2005, 27.V.2006, 1.VI.2007, 01.VI.2008
 - "Physics show" scene in front of the Richter Granary in Słupsk 26.V.2007, 31.V.2008
 - First Regional Science Festival of the Grammar School in Lubichów 31.V.2005
- 16. Teaching activities at the Pomeranian Academy in Słupsk (2001-2009):
 - Exercises:
 - Fundamentals of PhysicsI, II, IV
 - Atomic and molecular physics
 - Modern physics
 - Algorithms and programming
 - Mathematical analysis I
 - Introduction to discrete mathematics
 - Mathematical methods in physics
 - Repetitorium of mathematics for physicists
 - Laboratories:
 - Physics laboratory I, II
 - IT laboratories: programming languages; multimedia; computer networks.

VII. Apart from information set out in I-VI above, the applicant may include other information about his/her professional career, which he/she deems important

VII.1. Information on scientific activity before obtaining the PhD degree[†]

VII.1.1. Modelling of transport processes and materials properties

In 1996 I started my bachelor's studies in physics with computer science at the Institute of Physics of the Higher School of Pedagogy (now Pomeranian University) in Slupsk. During my first degree studies, I started my scientific work. Under the guidance of Prof. Vladimir Mitiyushev from the Institute of Mathematics, I participated in the work of an interdisciplinary team preparing a plan for the reclamation of the coastal lake Kopań. In this team, I worked on modelling the salinity distribution of the lake as a result of water inflow from the Baltic Sea. This issue was presented in my thesis entitled *Neumann's problem for the Laplace equation and its application* and publication [P43]. I completed my first-degree studies with a very good final mark and obtained a bachelor's degree in physics with a specialisation in computer science in 1999.

In the same year I started my master's studies in physics at the Institute of Physics of the Pomeranian Pedagogical Academy in Słupsk. During this studies I continued my scientific work under the supervision of Prof. V. Mityushev. I worked on the development of analytical models of effective thermal properties of fibrous composite materials. In 2001, I graduated with a very good final grade.

From graduation until 2003, I continued my research work on modelling the properties of composite materials at the Department of Mathematics Applications, Institute of Mathematics, Pomeranian Pedagogical Academy in Słupsk in Prof. V. Mityushev's group. The analytical model of the effective thermal conductivity of a fibrous composite material developed during this period was presented in a publication [P42].

VII.1.2. Properties of cold and ultracold atomic gases

From September 2002 to January 2004, I took part in research under the supervision of Prof. Laurentius Windholz at the Institut für Experimentalphysik TU Graz within the framework of a grant from the Fonds zur Förderung der wissenschaftlichen Forschung (FWF). The aim of my research was to analyse inelastic collision processes between cold lithium and sodium atoms in a magneto-optical trap (MOT). Collisions of this type are exoenergetic, and the amount of kinetic energy gained from the inelastic collision of two cold atoms depends on the quantum state the atoms are in before, after and during the collision process. This process contributes to an increase in the temperature of the atoms and, in the extreme case, to their escape from the trap when the kinetic energy gained by the atoms is greater than the depth of the trap. This results in the loss of trapped atoms and affects the

[†] Publications labelled [Pxx] are listed in appendix no.6 "List of scientific or artistic achievements which present a major contribution to the development of a specific discipline".

dynamics of the loading and unloading processes of atoms in the trap. By analysing the dynamics of the loading and unloading processes of the MOT, I determined the loss rate coefficients for collision processes in which, before the collision, one of the atoms was in the excited state, and the second in the ground state. The measurements were performed for collisions of isotopes of lithium (⁶Li or ⁷Li) with sodium atoms.

After returning from Graz, I continued my research work on cold collisions under the supervision of Prof. Ewa Paul-Kwiek at the Department of Experimental Physics of the Institute of Physics of the Pomeranian Academy in Słupsk. The model of the depth of the magneto-optical trap developed by me allowed a full interpretation of the results of the measurements performed in Graz. In particular, it allowed to determine the efficiency of two collision channels: when an atom in the excited state decay during the collision directly to the ground state (radiative escape) and when during the collision in the excited atom a transition between levels of the fine structure of the excited state takes place (fine structure changing collisions). The results of studies of inelastic collisions between cold atoms were presented in the articles [P39-P41] and in my PhD thesis entitled *The cold collisions of lithium isotopes and sodium atoms in the magneto-optical trap*, which I defended (*cum laude*) in September 2009 at the Faculty of Physics and Applied Computer Science of the Nicolaus Copernicus University in Toruń.

Since 2005, in parallel to the research performed in Słupsk, I have conducted research at the National Laboratory of Atomic, Molecular and Optical Physics in Toruń. A series of experiments performed at NL FAMO focused on studying the properties of ultracold atomic gases. As a result, a Bose-Einstein (B-E) condensate was obtained for the first time in Poland and the interactions between the B-E condensate and the surrounding cloud of cold atoms were analysed. The results of the studies carried out were presented in papers [P34, P35, P37, P38]. The results of the interaction studies presented in the paper [P37] were highlighted in Europhysics News [EPN, **40**, 1, p.17 (2009)].

VII.2. Information on scientific activity after obtaining the PhD degree[‡]

VII.2.1. Spectroscopy of diatomic molecules

In November 2009, I joined Prof. Włodzimierz Jastrzębski's research group at the Institute of Physics of the Polish Academy of Sciences in Warsaw. In this group, I specialised in the study of the energetic structure of diatomic molecules and the interactions between molecular electronic states on the basis of spectroscopic measurements. A series of experiments performed with the use of the laser polarisation labelling spectroscopy technique allowed to determine, in most cases for the first time, the potential energy curves of five excited states $(2^{1}\Sigma^{+}, 4^{1}\Sigma^{+}, 9^{1}\Pi, 10^{1}\Pi, 11^{1}\Pi)$ in the KLi molecule [P16, P29, P32, P36], D¹Π state in the NaLi molecule [P24], five excited states $(2^{1}\Sigma^{+}, 4^{1}\Sigma^{+}, 9^{1}\Pi, 10^{1}\Pi, 11^{1}\Pi)$ in the LiCs molecule [P19, P20, P23 P30], two states $(1^{1}\Pi, 3^{3}\Sigma^{+})$ in the NaCs molecule [P31], seven states $(5^{1}\Sigma^{+}_{u}, 7^{1}\Sigma^{+}_{u}, 8^{1}\Sigma^{+}_{u}, 5^{1}\Pi_{u}, 7^{1}\Pi_{u}, 8^{1}\Pi_{u})$ in the Rb₂ molecule [P2, P5, P12, P13, P14, P18] and the $3^{1}\Pi_{u}$ state in the Cs2 molecule [P4]. The results of

[‡] Publications labelled [Pxx] are listed in appendix no.6 "List of scientific or artistic achievements which present a major contribution to the development of a specific discipline".

my spectroscopic studies of the energy structure of the KCs molecule [P1, P3, P6, P7, P8, P11, P17, P21, P28] are described in details in section IV of this report.

During my research work on the electronic structure of Sr_2 molecules, I developed a method of producing these molecules that extended the operating time of the heat-pipe oven from a few hours to several months. This allowed for the application of the polarisation labelling spectroscopy technique to study the energy structure of this molecule. The first results obtained with this technique were presented in [P1] and addressed the interactions of rovibrational energy levels of the $2^{1}\Sigma^{+}_{u}$ state with rovibrational energy levels of the $1^{1}\Pi_{u}$ and $2^{1}\Pi_{u}$ states.

To extend the group's research field, I initiated spectroscopic studies of bipolar dimers composed with strontium and alkali metal atoms. The results of performed research of the energy structure of KSr [B1] and RbSr [B2] molecules have been described in detail in section IV of this report. Currently, in collaboration with Prof. M. K. Tey's group (Beijing), which is performing spectroscopic studies at ultralow temperatures, and groups of theoreticians, I have begun research on the energy structure of highly excited electron states of the LiSr molecule. The goal of this research is, among other things, to determine the optimal transfer path of weakly bound ultracold LiSr molecules to the absolute rovibrational ground state.

A further extension of the research field, introduced by me, is the realisation of studies on the energy structure of KAg and CsAg molecules within the framework of the NCN project *Spectroscopy, formation, and application of ultracold highly polar KAg and CsAg molecules: theory and experiment,* in progress since 2022 by the consortium of the Faculty of Physics of the Warsaw University and the Institute of Physics of the Polish Academy of Sciences.

VII.2.2. Investigation of the properties of ultracold atomic gases

After receiving a PhD degree, I continued my collaboration with NL FAMO in Toruń, where I performed research on the properties of the Bose-Einstein condensate. Results of this research were published in papers [P26,P33] and described in section V of this raport.

During my stay in Prof. F. Schreck's group (Insbruck/Amsterdam), I carried out research work on obtaining a mixture of atomic condensates of rubidium and strontium [P25].

Within the framework of the POIG programme *Fizyka u podstaw nowych technologii* carried out at the Faculty of Physics of the University of Warsaw, I provided scientific support for the creation of the Laboratory of Ultracold Molecules directed by Prof. Paweł Kowalczyk.

VII.2.3. Characterisation of the spectral properties of materials

In research collaboration with groups working at the Institute of Physics of the Polish Academy of Sciences, I performed optical characterisation materials.

In the work [P15], studies of the absorption spectrum of β -NaYF₄:20%Yb³⁺,2%Er³⁺ nanoparticles in SiO₂ coating was used to confirm the successful detachment of oleic acid from the nanoparticle. This is one of the stage of the chemical reaction that is required to functionalise the nanoparticles for fluorescence imaging of cancer cells.

In [P27], the results of far infrared absorption measurements of a ceriumdoped gadolinium garnet crystal were used to determine the structure of the Ce^{+3} centres formed in the crystal, as a consequence of the replacement of Gd^{+3} ions with Ce^{+3} ions.

Problem of elimination of the thermal background during spectroscopic measurements performed in high-temperature heat-pipe resulted in the development, in collaboration with Prof. M. Godlewski and Prof. B Witkowski's group, of optical high bandpass filter based on a ZnO:Al₂O₃ coating. The prototype of this filter is currently being used in spectroscopic studies of the energetic structure of the NaSr molecule. *An optical high-pass edge filter and a method of its production* is the subject of patent application P.442834.

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