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Scientific Curriculum Vitae

Contents:

I. Curriculum Vitae

Personal information

Surname: Grochola
Name: Anna
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Scientific career

M.Sc: 2001, University of Warsaw, Faculty of Physics
Supervisor: Prof. T. Stacewicz,
Title: Collisions of electrons with lithium atoms in the 2p state
PhD: 2004, University of Warsaw, Faculty of Physics
Supervisor: Prof. P. Kowalczyk,
Title: Investigation of the electronic structure of alkali metal dimers using the polarization spectroscopy technique

09.2004 - 01.2005 - technician in Optics Division, Institute of Experimental Physics, UW
since 02.2005 - adiunkt in Optics Division, Institute of Experimental Physics, UW
09.2007 - 02.2009 - Alexander von Humboldt Foundation fellowship, in Institute of Physics, University of Freiburg, Germany

II. Scientific work before receiving PhD

I began studying in 1996 and completed my study in 2001 in Faculty of Physics at the University of Warsaw. During my fourth year of study I chose optics as specialization. In Optics Division of the Institute of Experimental Physics I began my scientific work under the supervision of prof. Tadeusz Stacewicz. My Master Thesis concerned collisions between electrons and lithium atoms in excited states in low temperature plasma. The main goal of my work was to find rate coefficients for collisions, which lead to population of higher excited states in lithium. The chosen experimental method was to analyze the fluorescence light during spontaneous emission to lower energetic states after excitation process. Results of my work were published in two papers (number 1 and 4 on the paper list). In 2001 I received the M.Sc. degree in physics, defending the thesis "Collisions of electrons with lithium atoms in the 2p state".

In the same year I started my Ph.D. studies in Optics Division at the Institute of Experimental Physics, finished in 2004. Under the supervision of prof. Paweł Kowalczyk I investigated excited electronic states of alkali metal dimers. In series of experiments several excited electronic states of both homo- and heteronuclear diatomic molecules were examined, using the modern laser spectroscopy technique called polarization labeling method. The main goal of each experiment was to construct a potential energy curve for a given electronic state, using a few different numerical methods. Particularly in case of irregular shapes of potential energy curves the Inverted Perturbation Approach (IPA) method was used, a technique which was also developed in our laboratory.

First experiments performed in Optics Division of our Institute, concerned high excited states of K_2 molecule, which were not examined experimentally to that moment: $6^1\Sigma^+_u$ and $7^1\Pi_u$ (paper no. 6 on the publication list). The next group of experiments allowed to examine $6^1\Pi$ and $7^1\Pi$ states in NaK molecule (paper no. 5). Next work included the construction of potential energy curves for several states of Na_2 molecule and the results were published in a set of publications (numbers 8, 9 , 11-14 on the list of publications).

At the same time I participated in a series of experiments concerning KLi and NaK molecules at the Institute of Physics of Polish Academy of Sciences, since the experimental apparatus in this Institute was complementary to the one existing in our laboratory. Those experiments resulted in construction of potential energy curves for three excited states of KLi, namely $D^1\Pi$, $C^1\Sigma^+$ and $4^1\Pi$ (papers no. 2, 3 and 10), and $C^1\Sigma^+$ state of NaK (paper no. 7). In the case of $C^1\Sigma^+$ state of NaK part of the work was also done in Lyon (France) in cooperation with a group of dr. Amanda Ross.

The results of experiments were compared with the newest theoretical calculations, what allowed for verification of the used theoretical models. In summary, my results were published in twelve papers in widely known scientific journals, and seven of them were a basis for my Ph.D. thesis. They were also presented during international conferences. On 7th June 2004 I defended the Ph.D. thesis "Investigation of the electronic structure of alkali metal dimers using the polarization spectroscopy technique", getting the highest grades during exams.

III. Scientific work after receiving PhD

The next group of experiments, started after receiving my Ph.D. degree, concerned excited states of Li_2 and NaLi molecules. Particularly the work on NaLi molecules was a challenge, since this molecule is extremely difficult to create. Molecular states chosen for experimental investigation were not examined experimentally to that time. Our investigations allowed for construction of potential energy curves for a set of excited states in Li_2 molecule: $C^1\Pi_u$, $2^1\Sigma^+{}_u$, $5^1\Pi_u$, $6^1\Pi_u$, and a group of Rydberg states. Also for NaLi molecule experimental potentials were built for a few excited electronic states: $3^1\Pi$, $4^1\Pi$, $5^1\Sigma^+$ and $6^1\Sigma^+$. Results of our work were published in nine papers (numbers 15-19, 22, 26, 28 and 31 on the list of publications).

Since September 2007 till February 2009 I was a fellow of the Alexander von Humboldt Foundation and I was working at the University of Freiburg in the group of prof. Matthias Weidemüller. The aim of the work was to find an effective method of creating ultracold LiCs molecules in photoassociation process and to transfer such molecules to an absolute (electronic, vibrational and rotational) ground state. Trapping molecules in such a state is an important step towards creation of molecular BEC as well as a basis for a set of further experiments on a degenerate gas of dipolar molecules. The main goal was achieved and, as a first group in the world, we observed heteronuclear molecules in the absolute ground state: v”=0, J”=0.

Simultaneously we also started the spectroscopic investigation of ultracold LiCs molecules to gather a new knowledge concerning molecular features and energetic structure, since photoassociation experiments have precision and resolution which exceed by far typical spectroscopic experiments. Excited electronic states of LiCs were investigated using REMPI (Resonant-Enhanced Multi-Photon Ionization) technique. We showed that, in specific conditions, photoassociation of molecules is possible not only to energy levels which are close to the asymptote, but it is also possible to create ultracold molecules directly in deeply bound vibrational levels, even v’=0, as it happens in the case of $B^1\Pi$ state of LiCs. This set of experiments allowed to investigate the energetic structure of $B^1\Pi$ state with the highest possible precision, from the bottom of the potential well to the asymptote. To that time it was the only state examined in this way and, due to this fact, known so well. The next important result was to find an experimental value of the permanent electric dipole moment of LiCs molecule in the ground state, using the Stark effect. Previously only theoretical predictions of this value existed. Results were published in a set of papers in important international journals (positions: 20, 23-25, 27 and 34 on the paper list). These investigations are the part of my work being a basis for the habilitation procedure and are described in next chapters in more details.

Experiments performed in Freiburg allowed to increase my knowledge concerning different experimental techniques, particularly spectroscopic methods. Due to this fact I could continue the work on energetic structure of diatomic molecules containing heavy alkali atoms like cesium after my return to Warsaw. This knowledge is crucial in the field of “ultracold physics”, since spectroscopic data are necessary for correct planning and analyzing of experiments.

Since spring 2009 I investigate molecular structure of either the same molecule as in Freiburg (LiCs) or another heteronuclear alkali dimer also containing cesium atom NaCs, similar to LiCs from the point of view of ultracold experiments. Results of this work are presented in detail in three publications, being the second part of my habilitation (29, 32 and 33 on the list of publications). They are also described in the next chapters of this review. Molecules containing heavy alkali metal atoms like Cs, have typically very rich spectra, due to the fact that one may observe nominally forbidden singlet-triplet transitions. Apart from general information about energetic structure of molecules, performed experiments allow to correct theoretical models used to describe shapes of molecular potential energy curves and predict other molecular features. That is why our results are always compared with theoretical calculations.

As it was mentioned before, our spectroscopic investigations are important from the point of view of experiments performed in conditions of very low temperatures. It was directly shown by our cooperation with prof. Bigelow's group from University of Rochester (USA). But at the same time we took the effort, together with prof. Paweł Kowalczyk, to built a new laboratory in Warsaw within a frame of the project "…". Our main goal is to produce and investigate ultracold KCs molecules, and, in the long term, to approach experimentally so called "ultracold chemistry", i.e. controlling simple chemical reactions at ultracold environment.

Results of experiments were presented at international conferences:

- EGAS (European Group for Atomic Systems) Conference, in years: 2002, 2009, 2011;
- ECAMP (European Conference on Atoms, Molecules and Photons) in years 2004 and 2010;
- HRMS (High Resolution Molecular Spectroscopy) Colloquium in years: 2003, 2010, 2011;
- Deutsches Physikalisches Gesellschaft Tagung in years 2008 and 2009;
- Faraday Discussion 2009.

I had three oral presentations: at EGAS 2009 and both DPG Tagung (2008 and 2009).

I took part in several research projects:

- „Fizyka u podstaw nowych technologii - rozwój nowoczesnej infrastruktury badawczej na Wydziale Fizyki Uniwersytetu Warszawskiego"
  Project number: POIG.02.01.00-14-122/09-02
- „High resolution investigation of an electronic structure of diatomic molecules"
  Project number: N202 203938
- „Spectroscopic characterization of electronic states of alkali dimers, important for creation and detection of ultracold molecules"
  Project number: N202 103 31/0753
- „Spectroscopic investigation of heteronuclear alkali metal dimers"
  Project number: 2 P03B 063 23
- „Investigation of the $4^1\Pi$ and $6^1\Sigma^+$ states of the KLi molecule"
  Project number: 1 P03B 080 26
- „Theoretical and experimental investigation of heteronuclear alkali metal dimers"
  Polish-French project POLONIUM

Since December 2011 I am also a project leader in the project: „Investigation of Hund's coupling cases in alkali metal diatomic molecules", financed within the program Iuventus Plus.

Work in international groups:

- In POLONIUM program: 09.2003 in Lyon, France
- Alexander von Humboldt Fellowship: 07. 2007 – 02.2009 at the Freiburg University, Germany

Awards:

- Prof. Stefan Pieńkowski Award for investigation of diatomic molecules of alkali metals in 2011
- University of Warsaw Rector Award in 2006 and 2011

IV. List of publications

1. N. A. Gorbunov, A. Grochola, P. Kruk, A. Pietruczuk, T. Stacewicz, "Studies of electron energy distribution in plasma produced by a resonant laser pulse", Plasma Sources Sci. Technol. **11**, 492 (2002)

2. A. Grochola, W. Jastrzębski, P. Kowalczyk, P. Crozet, A.J. Ross, "The $C^1\Sigma^+$ state of KLi studied by polarisation labelling spectroscopy technique", Acta Phys. Pol. **102**, 729 (2002)

3. A.Grochola, W.Jastrzębski, P.Kowalczyk, A.Ross, P.Crozet "The molecular constants and potential energy curve of the $D^1\Pi$ state in KLi", Chem.Phys.Lett. **372**, 173 (2003)

4. N. A. Gorbunov, A. Grochola, P. Kruk, A. Pietruczuk, T. Stacewicz, "Investigation of electron – excited atom collisions", Phys. Chem. News **17**, 1 (2004)

5. A.Grochola, W.Jastrzebski, P.Kortyka and P.Kowalczyk, "Experimental study of the $6^1\Pi$ and $7^1\Pi$ states of NaK by polarization labeling spectroscopy technique", J.Mol.Spectrosc **221**, 279 (2003)

6. A.Grochola, W.Jastrzebski, P.Kowalczyk, S.Magnier and M.Aubert-Frecon, "Experimental and theoretical investigation of the $6^1\Sigma^+_u$ and $7^1\Pi_u$ states of K_2", J.Mol.Spectrosc. **224**, 151 (2004)

7. A.J.Ross, P.Crozet, I.Russier-Antoine, A.Grochola, P.Kowalczyk, W.Jastrzebski and P.Kortyka, "On the $C^1\Sigma^+$ state of NaK", J.Mol.Spectrosc. **226**, 95 (2004)

8. A.Grochola, W.Jastrzebski, and P.Kowalczyk, "The $3^1\Pi_u$ state in Na_2", Chem.Phys.Lett. **394**, 383 (2004)

9. A. Grochola, P. Kowalczyk, W. Jastrzebski and A. Pashov, "A regularized inverted perturbation approach method: potential energy curve of the $4^1\Sigma^+_u$ state in Na_2", J.Chem.Phys. **121**, 5754 (2004)

10. A. Grochola, W. Jastrzebski, P. Kortyka and P. Kowalczyk, "Polarization labelling spectroscopy of the $4^1\Pi$ state in the KLi molecule", Mol.Phys. **102**, 1739 (2004)

11. A. Grochola, W. Jastrzebski and P. Kowalczyk, "The $C^1\Pi_u$ state of Na_2 revisited: a comprehensive study by polarization labeling spectroscopy technique", J.Mol.Spectrosc. **232**, 291 (2005)

12. A. Grochola, W. Jastrzebski, P. Kowalczyk, "New analysis of the $D(4)^1\Pi_u$ state of Na_2 using polarization labelling spectroscopy", Mol. Phys. **104**, 2569 (2006)

13. A. Grochola, P. Kowalczyk, W. Jastrzebski, M. Głódź, "On the $6^1\Pi_u$ state of Na_2", Chem. Phys. Lett. **430**, 247 (2006)

14. A. Grochola, M. K. Kubkowska, W. Jastrzebski, P. Kowalczyk, "The $6^1\Pi_u$ state of Na_2 molecule", Opt. Appl. **36**, 469 (2006)

15. Nguyen Huy Bang, A. Grochola, W. Jastrzebski, P. Kowalczyk, H. Salami, "Investigation of a highly excited electronic $^1\Pi$ state of NaLi molecule", Opt. Appl. **36**, 499 (2006)

16. M. K. Kubkowska, A. Grochola, W. Jastrzebski, P. Kowalczyk, "The $C^1\Pi_u$ and $2^1\Sigma^+_u$ states in Li_2: Experiment and comparison with theory", Chem. Phys. **333**, 214 (2007)

17. Nguyen Huy Bang, A. Grochola, W. Jastrzebski, P. Kowalczyk, " First observation of the $3^1\Pi$ and $4^1\Pi$ states of NaLi molecule", Chem. Phys. Lett. **440**, 199 (2007)

18. Z. Jędrzejewski-Szmek, A. Grochola, W. Jastrzebski, P. Kowalczyk, "Molecular constants and potential energy curve for the $5^1\Pi_u$ state of Li_2", Chem. Phys. Lett. **444**, 229 (2007)

19. A. Grochola, W. Jastrzebski, P. Kowalczyk, "Spectroscopic study of the $6^1\Pi_u$ state in Li_2", Mol. Phys. **106**, 1375 (2008)

20. J. Deiglmayr, A. Grochola, M. Repp, K. Mörtlbauer, C. Glück, J. Lange, O. Dulieu, R. Wester, M. Weidemüller, „Formation of ultracold polar molecules in the rovibrational ground state“, Phys. Rev. Lett. **101**, art. no. 133004 (2008)

21. N. H. Bang, A. Grochola, W. Jastrzebski, P. Kowalczyk, "Spectroscopy of mixed alkali dimers by the polarisation labelling technique: application to NaLi and NaRb molecules", Opt. Mat. **31**, 527 (2009)

22. Nguyen Huy Bang, A. Grochola, W. Jastrzebski, P. Kowalczyk, "Polarization labeling spectroscopy of highly excited $^1\Pi$ and $^1\Sigma^+$ states in NaLi", J. Chem. Phys. **130**, art. no. 124307 (2009)

23. J. Deiglmayr, P. Pellegrini, A. Grochola, M. Repp, R. Côté, O. Dulieu, R. Wester, M. Weidemüller, „Influence of a Feshbach resonance on photoassociation of LiCs“, New J. Phys. **11**, art. no. 055034 (2009)

24. J. Deiglmayr, M. Repp, A. Grochola, K. Mörtlbauer, C. Glück, O. Dulieu, J. Lange, R. Wester, M. Weidemüller, „Photoassociation of ultracold dipolar molecules in the lowest vibrational states”, Faraday Discussions **142**, 335 (2009)

25. A. Grochola, A. Pashov, J. Deiglmayr, M. Repp, E. Tiemann, R. Wester, M. Weidemüller, „Photoassociation spectroscopy of the $B^1\Pi$ state of LiCs”, J. Chem. Phys. **131**, art. no. 054304 (2009)

26. I. D. Petsalakis, G. Theodorakopoulos, A. Grochola, P. Kowalczyk, W. Jastrzebski, "Theoretical study of highly excited $^1\Sigma^+$ and $^1\Pi$ states of NaLi and experimental observation of the interacting $5^1\Sigma^+$ and $6^1\Sigma^+$ states", Chem. Phys., **362**, 130 (2009)

27. J. Deiglmayr, A. Grochola, M. Repp, O. Dulieu, R. Wester, M. Weidemüller, “Permanent dipole moment of LiCs in the ground state”, Phys. Rev. A **82**, art. no. 032503 (2010)

28. A. Grochola, P. Kowalczyk and W. Jastrzebski, „Rydberg states of the Li_2 molecule studied by polarization labelling spectroscopy”, J. Phys. B **43**, art. no. 155102 (2010)

29. A. Grochola, P. Kowalczyk, W. Jastrzebski, “Investigation of the $B^1\Pi$ state in NaCs by polarisation labelling spectroscopy”, Chem. Phys. Lett. **497**, 22 (2010)

30. J. Szczepkowski, A. Grochola, W. Jastrzebski, P. Kowalczyk, „The $4^1\Sigma^+$ electronic state of KLi molecule”, Chem. Phys. Lett. **499**, 36 (2010)

31. Z. Jędrzejewski-Szmek, A. Grochola, W. Jastrzębski, P. Kowalczyk, „Analysis of the mutually perturbed $(3^1\Pi_u, 4^1\Pi_u) \leftarrow X^1\Sigma^+_g$ band system in Li_2”, Opt. Appl. **40**, 577 (2010)

32. A. Grochola, P. Kowalczyk, J. Szczepkowski, W. Jastrzebski, A. Wakim, P. Zabawa, N. P. Bigelow, "Spin-forbidden $c^3\Sigma^+ (\Omega = 1) \leftarrow X^1\Sigma^+$ transition in NaCs: Investigation of the $\Omega = 1$ state in hot and cold environments", Phys. Rev. A **84**, art. no. 012507 (2011)

33. A. Grochola, J. Szczepkowski, W. Jastrzebski, P. Kowalczyk, "Experimental investigation of electronic states of LiCs dissociation to $Li(2^2S)$ and $Cs(5^2D)$ atoms", J. Chem. Phys. **135**, art. no. 044318 (2011)

34. J. Deiglmayr, M. Repp, A. Grochola, O. Dulieu, R. Wester and M. Weidemüller, “Dipolar effects and collisions in an ultracold gas of LiCs molecules”, Journal of Physics: Conference Series **264**, art. no. 012014 (2011)

35. A. Grochola, J. Szczepkowski, W. Jastrzebski, P. Kowalczyk, „The $A^1\Sigma^+$ electronic state of KLi molecule”, Chem. Phys. Lett. **535**, 17-20 (2012)

36. J. Szczepkowski, A. Grochola, W. Jastrzebski, P. Kowalczyk, „On the $4^1\Sigma^+$ state of the KCs molecule”, J. Mol. Spectrosc., **276-277**, 19-21 (2012)

V. Overview of the publications contributing to habilitation

1. Introduction

During the last years one could observe a tremendous progress in ultracold matter physics, particularly in the field of laser cooling and trapping. It made possible, for example, creation of an atomic Bose-Einstein condensate (BEC). So far two Nobel Prizes were awarded for the achievements from this field: in 1997 and 2001 [1]. Since that time this discipline was divided into many separate branches. The subject of theoretical or experimental works may be investigation of basic properties of BEC [2-4] as well as using ultracold atoms in metrology [5], modern electronics [6, 7] or quantum information [8]. One of the most exciting subjects, opening new possibilities, is switching from ultracold atoms to ultracold molecules. The problem is complicated because of a very complex energetic structure of molecules in comparison to atoms. Direct cooling to ultralow temperatures (of nanoKelvin range) using techniques developed for atoms is impossible. Alternative methods of direct cooling of molecules like using Stark or Zeeman decelerators [9-11] allow to reach temperatures only of miliKelvin range. So far only two methods (both indirect) allow to cool molecules down to the micro- or even nanoKelvin temperatures: photoassociation [12] or a technique taking advantage of so called Feshbach resonances (magnetoassociation) [13].

Since the very beginning one of the main goals in "cold" experiments was to create molecular Bose-Einstein condensate. Producing ultracold molecules in an absolute electronic and rovibrational ground state is the first step in this direction. This step is particularly important because of possible inelastic collision between molecules, which may cause big losses from the trap. Only if molecules are in the absolute ground state, heating due to inelastic collisions is impossible. So far a few groups managed to get molecular BEC, but only for homonuclear molecules: Li_2 [14, 15] and K_2 [16]. However much more effort is directed to obtain heteronuclear BEC, since such molecules have permanent electric dipole moment and are susceptible to manipulation by external electric or magnetic fields. First attempts towards heteronuclear molecular BEC were already performed [17, 18].

Experimental techniques, which were successfully used so far for producing ultracold molecules, photoassociation and magnetoassociation, require a precise knowledge of molecular energetic structure. This knowledge is also important for planning further experiments, which concern getting control over population of chosen molecular energetic states. It involves a knowledge of energies of molecular rovibrational levels, transition probabilities, Franck-Condon factors and all possible perturbations, which may affect the molecular states and energy levels. That is why the usual first step is performing a spectroscopic investigation. The results should make possible correct planning of "ultracold experiments". Properly planned experiments on ultracold molecules may, on the other hand, bring complementary knowledge concerning molecular structure.

Present experiments from the ultracold matter domain belong to the most demanding in the sense of knowledge needed for correct planning as well as very complicated apparatus necessary to get into ultracold regime. Usually a cooperation of a few different groups, experimental and theoretical, is necessary. But such experiments allow to achieve a new level of understanding and control over the matter, particularly concerning transition between classical and quantum world.

This overview consists of two main parts. The first one summarizes experiments performed in the ultracold regime for LiCs molecules. Papers P1 and P2 refer to photoassociation of LiCs molecules and the main goal, which was achieved – producing the molecules in the absolute ground state, achieved for the first time for heteronuclear molecules. In publications P3 – P5 investigation of the molecular properties and energetic structure in ultralow temperatures is described, including measurements of the value of LiCs permanent electric dipole moment. The subject of the second part are spectroscopic experiments performed on LiCs and NaCs molecules in conditions of high temperatures. The paper P6 presents the first experimental observation of triplet electronic states of LiCs molecule, excited directly from the singlet ground state. Publications P7 and P8 concern similar experiments performed for the NaCs molecule. The main goal was to investigate excited states which are important for the ultracold physics experiments. One of the achievements was an interpretation of photoassociation spectra, obtained by prof. Bigelow's group, who works on NaCs molecules in the ultracold regime.

A basis of habilitation procedure are eight publications entitled „Investigation of alkali metal dimers containing cesium atoms in high and ultralow temperatures", being a scientific achievment according to 16th article of the act from 14th March 2003 and Dz. U. no 65, position 595:

[P1] J. Deiglmayr, A. Grochola, M. Repp, K. Mörtlbauer, C. Glück, J. Lange, O. Dulieu, R. Wester, M. Weidemüller, „Formation of ultracold polar molecules in the rovibrational ground state", Phys. Rev. Lett. **101,** art. no. 133004 (2008)

[P2] J. Deiglmayr, M. Repp, A. Grochola, K. Mörtlbauer, C. Glück, O. Dulieu, J. Lange, R. Wester, M. Weidemüller, „Photoassociation of ultracold dipolar molecules in the lowest vibrational states", Faraday Discussions **142**, 335 (2009)

[P3] A. Grochola, A. Pashov, J. Deiglmayr, M. Repp, E. Tiemann, R. Wester, M. Weidemüller, „Photoassociation spectroscopy of the $B^1\Pi$ state of LiCs", J. Chem. Phys. **131,** art. no. 054304 (2009)

[P4] J. Deiglmayr, P. Pellegrini, A. Grochola, M. Repp, R. Côté, O. Dulieu, R. Wester, M. Weidemüller, „Influence of a Feshbach resonance on photoassociation of LiCs", New J. Phys. **11**, art. no. 055034 (2009)

[P5] J. Deiglmayr, A. Grochola, M. Repp, O. Dulieu, R. Wester, M. Weidemüller, "Permanent dipole moment of LiCs in the ground state", Phys. Rev. A **82**, art. no. 032503 (2010)

[P6] A. Grochola, J. Szczepkowski, W. Jastrzebski, P. Kowalczyk, "Experimental investigation of electronic states of LiCs dissociation to Li(2^2S) and Cs(5^2D) atoms", J. Chem. Phys. **135**, art. no. 044318 (2011)

[P7] A. Grochola, P. Kowalczyk, W. Jastrzebski, "Investigation of the $B^1\Pi$ state in NaCs by polarisation labelling spectroscopy", Chem. Phys. Lett. **497**, 22 (2010)

[P8] A. Grochola, P. Kowalczyk, J. Szczepkowski, W. Jastrzebski, A. Wakim, P. Zabawa, N. P. Bigelow, "Spin-forbidden $c^3\Sigma^+$ ($\Omega = 1$) $\leftarrow$ $X^1\Sigma^+$ transition in NaCs: Investigation of the $\Omega = 1$ state in hot and cold environments", Phys. Rev. A **84**, art. no. 012507 (2011)

2. Investigation of the properties and electronic structure of LiCs molecule at ultralow temperatures

2.1 Motivation

One of the main goals of physics of the ultracold molecules physics is to create a stable quantum-degenerate gas of molecules, in which all molecules populate the ground state of the system, comprising motional and internal degrees of freedom. Such a system provides unique possibilities in terms of further control and manipulation and may serve as a starting point for many further applications, like measurements of fundamental constants [19] or ultracold chemical reactions [20]. Polar molecules are of particular interest, because dipolar interactions may be exploited to study the quantum many-body phenomena [21, 22] or quantum information processing [23-26].

The most promising way to create a quantum-degenerate gas of molecules in the absolute ground state is to associate ultracold atoms using either magnetic or oscillatory electric fields. In magnetoassociation molecules are formed through magnetically induced Feshbach resonances, which couple a pair of free atoms into the weakly bound molecule. A transfer to the absolute internal ground state may be accomplished due to the STIRAP (Stimulated Raman Adiabatic Passage) technique, which uses a combination of two pulsed laser fields. This scheme was successfully used to produce deeply bound molecules: Rb_2 [27], Cs_2 [28] and KRb [29]. An alternative approach is a direct photoassociation of molecules from an ultracold gas of atoms followed by spontaneous emission. In this case second, bound-bound excitation and transfer of molecules to the vibrational ground state may be a next step. This method has led to the formation of vibrational ground state molecules: K_2 [30], RbCs [31], Cs_2 [32], LiCs [P1] and LiK [33].

Magnetoassociation combined with STIRAP has an advantage of being a fully coherent process, which preserves the phase-space density of the initial gas, while photoassociation followed by spontaneous emission leads to smaller phase-space densities. But photoassociation can be driven as a continuous process, allowing for accumulation of molecules, e.g. in an optical trap.

Among the ground state ultracold molecules listed above the only dipolar ones are heteronuclear molecules: RbCs, KRb, LiCs and LiK. They all have a permanent dipole moment, and the biggest predicted value is for LiCs molecule: $\mu = 5.5$ Debye [34]. Since present efforts of scientists are concentrated on the effects related to the polar nature of ultracold molecules, the interest in the LiCs molecule is fully justified.

2.2 Creation of LiCs molecules in the absolute ground state

- **Photoassociation**

One of the two most popular techniques, which are used for creation of ultracold diatomic molecules at temperatures in microKelvin or lower range is photoassociation (PA), and it was chosen for formation of ultracold LiCs molecules. As it was already mentioned, a very rich and complicated energetic structure of molecules makes direct cooling by methods developed for atoms impossible (ineffective). In the case of LiCs molecule, lithium and cesium atoms were evaporated in a double species oven and decelerated in a single Zeeman slower [35] and trapped in two overlapping magneto-optical traps (MOT) [36]. A detailed description of the experimental setup may be found in papers [P1-P3].

In overlapped magneto-optical traps for different atomic species, high loss rates due to inelastic interspecies collisions provide a well known experimental difficulty. The dominant loss channel has been identified as collisions between excited cesium and ground state lithium atoms. These losses were reduced by implementation of a dark magneto-optical trap, also called „dark spontaneous force optical trap" or "dark SPOT" [37]. In the center of such a trap the repumping light is blocked, so cold atoms are pumped by the cooling light off-resonantly into the lower hyperfine ground state, which is now a dark state. The large number of atoms in a dark hyperfine ground state reduces interspecies loss rates.

In order to form ultracold molecules, colliding pairs of ultracold atoms are transferred into a bound molecule by photoassociation. Two colliding atoms may absorb a photon from a photoassociation laser and form an excited bound molecule [12]. The necessary condition is that a sum of kinetic energy of colliding atoms and the absorbed photon energy is equal to energy of a bound molecular level. The second condition to form a molecule is that distances between atoms should be small enough to make the absorption process efficient, so the atomic clouds should have proper (high) density. In all experiments LiCs molecules were photoassociated into the chosen rovibrational levels of the $B^1\Pi$ state, since it was the only excited state with a well known energetic structure [38]. The energies of its levels were known experimentally for vibrational levels $v' = 0$ to $v' = 26$, the last one lying approximately 80 cm^{-1} below the asymptote. The experimentally determined potential energy curve of the $B^1\Pi$ state allowed to predict positions of rovibrational levels in this range of v' with an accuracy better than 0.1 cm^{-1}. In the photoassociation process one usually gets molecules in rovibrational levels of excited states lying close to atomic asymptote, since good overlap between scattering wavefunction and a wavefunction of a chosen energetic level is a basic condition for effective molecule formation. That is why the long-range states, states with a broad potential energy well (like the $B^1\Pi$ state) or double-minimum states, in which a second well is used, are particularly preferred for photoassociation of molecules.

- **Photoassociation spectroscopy**

In the first part of experiments with ultracold LiCs molecules the $B^1\Pi$ state was experimentally examined, particularly in the region close to the asymptote, using photoassociation spectroscopy. The excitation and detection scheme of the experiment is shown in Fig. 1. A photoasociation laser was scanned in chosen spectral regions, around expected positions of resonant transitions. Whenever the laser wavelength hit a resonance, created molecules decayed spontaneously to the ground state. The next step was two-photon ionization of molecules and $LiCs^+$ ions were then detected in a high resolution time-of-flight mass spectrometer and counted in a single ion counting setup [39].

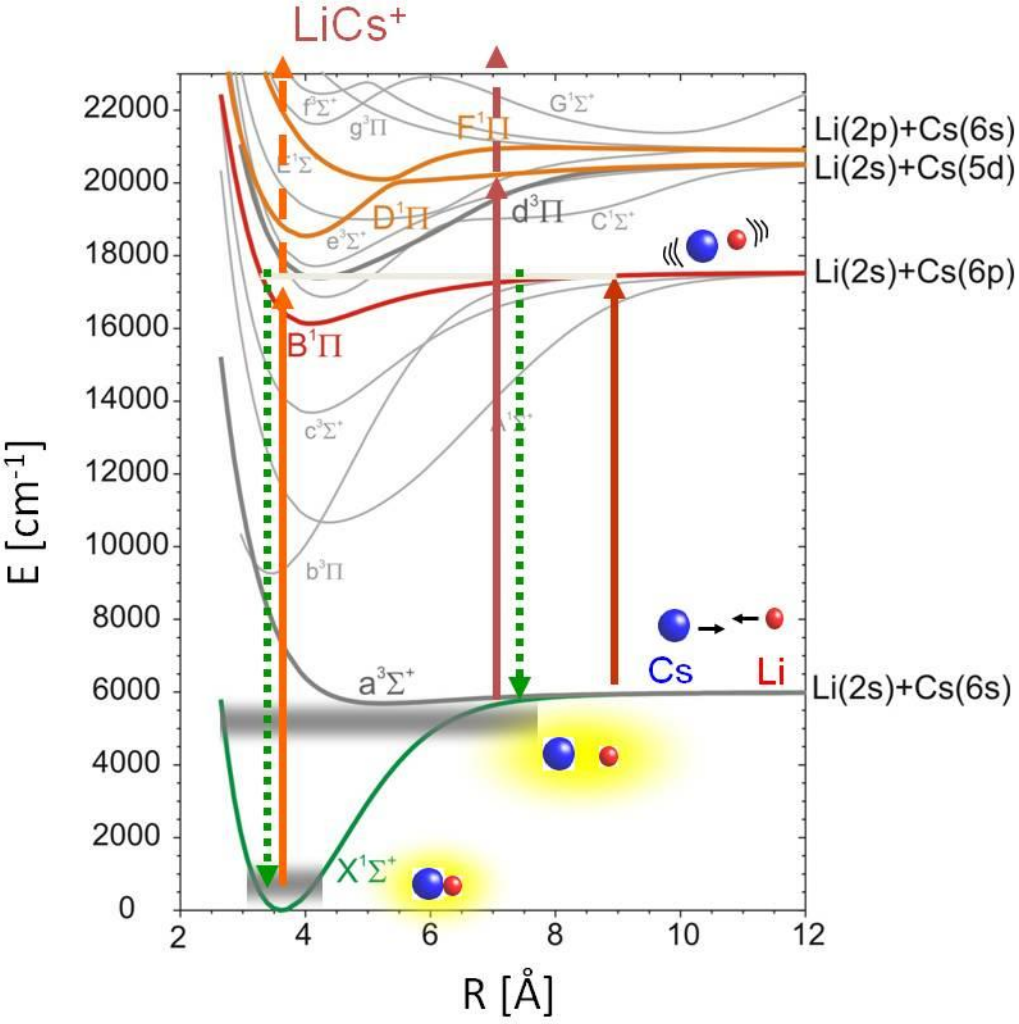

Fig. 1 The excitation and detection scheme used in photoassociation spectroscopy: red colour – photoassociation, green colour – spontaneous emission, orange colour – two photon ionization.

The first important conclusion resulting from the experiment was that in case of the $B^1\Pi$ of LiCs state the photoassociation process is possible and efficient not only to rovibrational levels lying close to the asymptote, but to almost all, even deeply bound energy levels, including v' = 0. This is a unique feature which plays an important role in the process of creating LiCs molecules in an absolute ground state, what was the main goal of our experiments.

The knowledge of the shape of potential energy curves for the ground state of LiCs [40] and the $B^1\Pi$ state [38] allowed us to find an optimal rovibrational level for photoassociation process. The main criterion was the biggest value of transition probability between $B^1\Pi$ state levels and v"=0 level of the $X^1\Sigma^+$ state, to make population of the vibrational ground state as big as possible after spontaneous emission from the $B^1\Pi$ state. At the same time the PA process should be also efficient. For further set of experiments the vibrational level v'=4 of the $B^1\Pi$ state was chosen, because of high efficiency of PA and good overlap between its wavefunction and the wavefunction of v"=0 level in $X^1\Sigma^+$ state.

- **REMPI spectroscopy**

The next important experimental step was an identification which rovibrational levels of the LiCs ground state were most populated due to the spontaneous emission following photoassociation. The main goal was to check if population of the levels agrees with theoretical predictions. We used a so called REMPI (Resonance Enhanced Multi-Photon Ionization) spectroscopy technique. As it was mentioned above, the detection process involved two-photon ionization. The REMPI spectroscopy is based on the enhancement of the ionization efficiency, whenever an energy of the absorbed photon allows for transition to a real intermediate rovibrational level, while in general ionization takes place through a virtual one.

The experimental scheme comprised two main steps: the photoassociation laser was fixed on a resonance with transition to a specific level in the excited $B^1\Pi$ state. Then the frequency of the ionization laser was tuned in a relatively broad range, to induce transitions of molecules from the ground state to energy levels of some intermediate state. If the laser frequency was tuned to a real resonance, the number of detected ions increased dramatically. The next step was an identification of the resonances in the recorded spectra, in order to take control over the population of the ground state levels after spontaneous emission by choosing a proper resonance for photoassociation. As an intermediate state the same $B^1\Pi$ state was used, since it was the only excited state in LiCs known experimentally at that time, what made possible an identification of the resonances in the REMPI spectra. The spectrum recorded with the REMPI technique after photoassociation to the v'=4 vibrational level of the $B^1\Pi$ state confirmed that in this case population of the v"=0 level in the ground state by spontaneous emission was the highest in comparison to the other cases, when different photoassocition resonances were chosen for the first step.

- **Depletion spectroscopy**

Population of the lowest vibrational level of the ground electronic state was a success, but only a partial one. For future experiments, including creation of molecular BEC, the particularly important was to have a group of molecules in the absolute ground state including rotation (J"=0). So a depletion spectroscopy was used to confirm (or deny) the existence of such molecules in our trap. In this technique an additional laser beam of a very narrow bandwidth is employed to pump out molecules from specific rotational sublevels of the v"=0 vibrational level. The reduction of the observed ion signal confirms that such process takes place and a latter identification of the lines of depletion spectra allows to check the population of rotational levels of molecules in the trap.

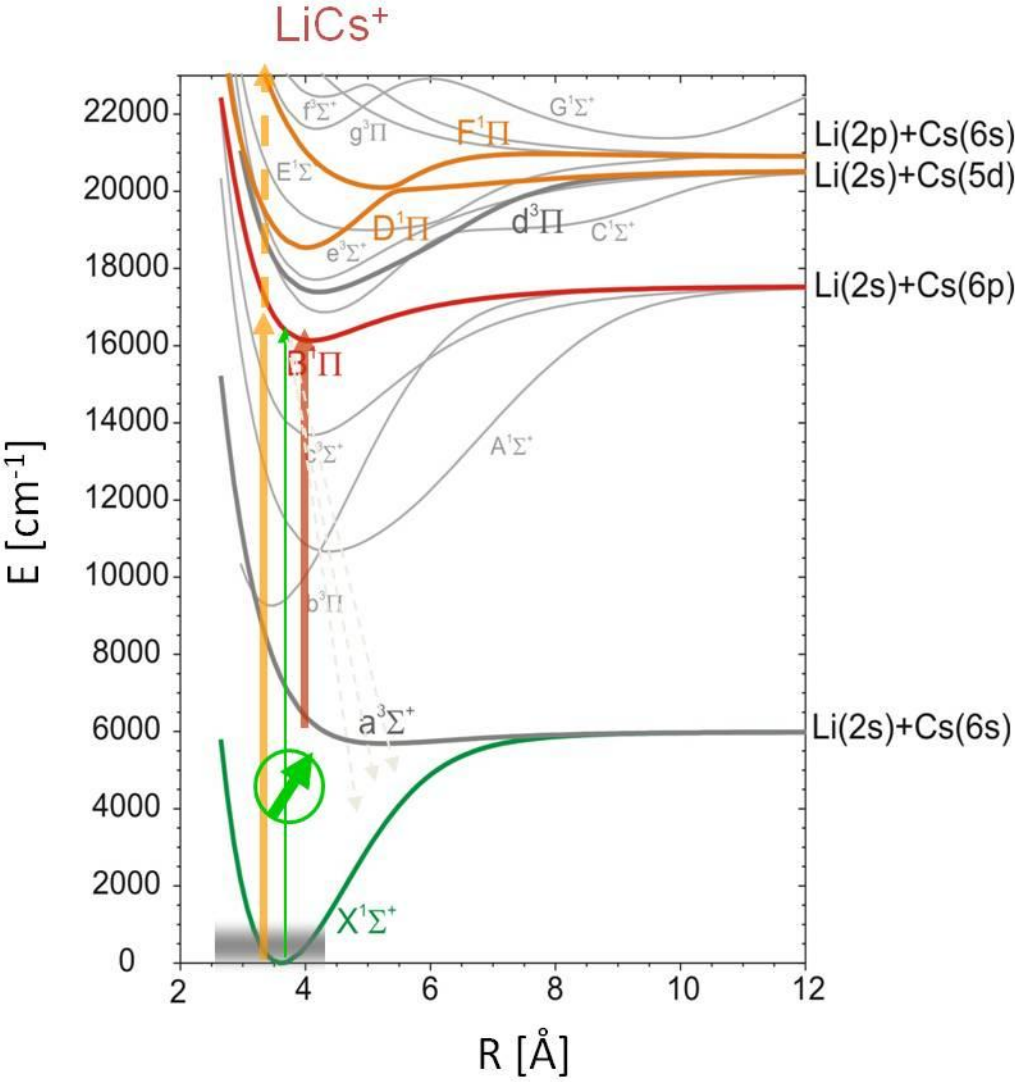

Fig. 2 The excitation and detection scheme for depletion spectroscopy: red colour – photoassociation, orange colour – two photon ionization, green colour – depletion.

The excitation and detection scheme for this part of experiment is shown in Fig. 2. For photoassociation the v'=4 vibrational level of the $B^1\Pi$ state was chosen to provide the highest population of the v"=0 level in the ground state after spontaneous emission. One of the characteristic features of photoassociation process is that only creation of molecules in the lowest rotational levels (usually J'=0-3) is possible. For higher J values a rotational barrier is too high for this process to occur. In the case of v'=4 level it turned out that only two rotational levels were available: J'=1 and 2. Experiments were performed for these both resonances, however the case of J'=1 was much more important, since only then the selection rules allow for transition to J"=0 in the process of spontaneous emission. So the photoassociation laser was locked to the chosen resonance and also the ionization laser had a fixed frequency, corresponding to the energy of the transition between v"=0 level in the ground state and v'=14 in the $B^1\Pi$ state (because of relatively high value of Franck-Condon factor for this transition). With such selection of laser frequencies the ion signal had a constant and high value, proportional to the high number of produced $LiCs^+$ ions. The wavelength of the depletion laser was scanned around the transition v"=0, J"=0,1,2 → v'=12, J'=0-3 (because of relatively broad line the ionization laser covered transitions from all three rotational levels). If a resonance was hit when scanning the laser frequency, one of the rotational levels was depleted and the ion signal was reduced, proportionally to the lower number of the atoms in the v”=0 state and (consequently) the lower number of produced $LiCs^+$ ions. This experiment allowed to confirm that, for the first time in case of heteronuclear molecules, their creation in an absolute ground state has been achieved.

2.3 Investigation of properties and energetic structure of LiCs molecule

- **Characterisation of the potential energy curve of the $B^1\Pi$ state**

The experiments discussed in the previous section showed that creation of heteronuclear molecules in the absolute ground state is possible. But this was not their only result. An extra knowledge was acquired, concerning the energetic structure and properties of the examined LiCs molecule. Because of unique property of the $B^1\Pi$ state, the photoassociation was possible to almost all vibrational levels of this state, from v’=0 to the asymptote (“almost”, because for a few of these levels the value of the overlap integral between the scattering wavefunction and the vibrational wavefunction of the particular level was close to zero). The last observed rovibrational level, coresponding to v’=35, lies less than 1 cm^{-1} below the asymptote. In previous spectroscopic experiments [38] the $B^1\Pi$ state was examined only to the level v’=26 and the inability of observation of higher lying levels was explained by possible predissociation of the LiCs molecule.

The photoassociation spectroscopy showed that this explanation was incorrect. Predissociation would result in broadening of corresponding spectral lines, due to very short lifetimes of high vibrational levels involved in transitions. No such broadening was observed. Additionally photoassociation experiments provided complementary data concerning energies of rovibrational levels of the $B^1\Pi$ state, particularly for the region close to the asymptote, what made the complete description of the potential energy curve for this state possible. Also a new, more accurate value of the potential well depth of the $X^1\Sigma^+$ ground state was found, which is one of the key parameters for theoretical calculation of positions of the Feshbach resonances [13]. A further profit from the photoassociation spectroscopy was a very high resolution of the spectra, allowing for observation of the hyperfine structure of molecular lines. In the paper [P3] a qualitative description and explanation of the observed line structure is presented.

- **Investigation of the properties of the $B^1\Pi$ state**

The possibility of photoassociation of molecules directly to deeply bound rovibrational levels of the $B^1\Pi$ state was an unusual property, but potentially opening new possibilities. The crucial point was to find an explanation for this surprising fact and to decide whether this may be a universal feature, or it is a unique attribute of this particular state or this molecule.

The attempt to find an explanation for this problem was made together with a group of theoreticians. The first, simplified calculations, based only on values of overlap integrals for proper wavefunctions, suggested that creation of ultracold molecules in deeply bound levels directly from the gas of ultracold atoms should be impossible. The values of overlap integrals were practically equal to zero and, consequently, the efficiency of such process should be negligible. Some phenomenon (or phenomena), not taken into account during calculations of Franck-Condon factors, increased dramatically the probability of the process of molecule formation. Although in the region close to the asymptote energy levels of the singlet B state mix with energy levels of other, triplet states, dissociating to the same asymptote, and take some of the triplet character, the deeply bound levels of this state have a pure singlet character. This means that only a singlet component of the scattering wavefunction should be taken into account while trying to estimate the efficiency of the photoassociation of molecules in the B state levels. The overlap integral for the singlet scattering wavefunction and deeply bound levels of the $B^1\Pi$ state is indeed close to zero. One may notice however, that the same overlap integral, calculated for the triplet component of the scattering wavefunction, would give much bigger efficiency of the photoassociation process, if only it would be allowed according to selection rules. This observation resulted in a hypothesis, that a singlet component of the scattering wavefunction must be somehow perturbed by a closely lying bound level of a triplet character (particularly one of the levels of the triplet ground state $a^3\Sigma^+$). This suggested a presence of a Feschbach resonance in this region. Such problem was already theoretically examined as a potential way to enhance an efficiency of photoassociation [41]. The perturbation introduced by a Feshbach resonance may leave an "echo" of the triplet wavefunction somehow "imprinted" on a singlet one, what may in consequence change dramatically the values of the overlap integrals for the deeply bound levels of the $B^1\Pi$ state.

First results of theoretical calculations, performed by the theoretical group from University of Connecticut in Storrs, suggested indeed the presence of a Feshbach resonance, which could allow to explain the experimental results, what was described in details in the paper [P4]. However the work on an exact explanation of this problem is not finished yet and full model of this phenomenon is not completed. But the importance of the problem is obvious, as well as the necessity to build the model which could allow to predict effects of this kind in case of other energetic states and other molecules.

- **Experimental determination of the electric dipole moment of the LiCs molecule**

One of the reasons why physicists started to work with heteronuclear diatomic molecules at ultracold conditions was a fact that these molecules have a permanent electric dipole moment (EDM). Many proposed experiments among already mentioned, concerning exploration of quantum phases in dipolar gases [42], development of quantum computation techniques [23], or precision measurements of fundamental constants [19], require a non-zero value of the electric dipole moment. LiCs is predicted to have the largest permanent EDM of all alkali metal dimers [34], and thus is very advantageous for such schemes.

In the paper [P5] a series of experiments is described, leading to experimental determination of the permanent EDM of deeply bound levels of LiCs molecules. The experimental sequence for formation, detection and high resolution spectroscopy of ground state molecules was similar to the one described in the previous section. Ultracold LiCs molecules were formed by photoassociation of laser cooled Li and Cs atoms in chosen rovibrational levels of the $B^1\Pi$ state. The excited LiCs molecules decayed spontaneously into different ground state levels. Molecules in given vibrational ground state levels were then ionized by resonant enhances multiphoton ionization (REMPI) and the resulting ions were detected in a time-of-flight mass spectrometer. Rotationally resolved spectroscopy of ground state molecules was achieved by depletion spectroscopy technique: a narrowband laser pumped population out of a selected rovibrational ground state level leading to a reduction in the detected ion signal from this level. This technique allows to achieve the resolution up to 5 MHz for determination of frequencies of spectral lines.

For experimental determination of the EDM of LiCs molecules the Stark effect was employed. Strong electric field of controlled value was applied to the molecular samples by two round electrodes inside the vacuum chamber. In order to determine the permanent EDM of a given vibrational level of the $X^1\Sigma^+$ state the electric field-induced shift in the transition frequency between the J”=0 component of the level and the excited $B^1\Pi$ level was measured. However, as the $B^1\Pi$ state is predicted to have a smaller EDM than the ground state, one could expect a significantly smaller Stark effect for the upper level than for the ground state level. In order to determine this experimentally a simple photoassociation spectroscopy for chosen levels of the $B^1\Pi$ state was performed and the influence of the strong electric field on the energy of photoassociation resonances was examined. The result confirmed that the photoassociation lines centers did not experience any significant shift, so one could presume that any change in the transition frequency of a depletion resonance can be exclusively attributed to the Stark shift of the ground state level.

The final experiment was performed for a few different vibrational levels of the LiCs ground state. The differences in spectral line positions as a function of an electric field applied to the molecular sample allowed to determine the LiCs permanent EDM for the ground state levels: $\mu = 5.5 \pm 0.2$ D for v”=2 and $\mu = 5.3 \pm 0.2$ D for v”=3. This result agrees with theoretical predictions [34], despite the fact that in theoretical calculations results are given as averaged values over many vibrational levels. But the dependence of the EDM value on the vibrational quantum number is so weak, that one cannot expect any significant change. Particularly EDM value for v”=0 level should be the same as for v”=2 or 3. Unfortunately, relatively weak population of the v”=0 level made impossible direct experimental determination of the EDM in the current experimental setup. But the confirmed large permanent EDM value of deeply bound LiCs molecules makes this molecule a promising candidate for realization of an ultracold gas with strong dipolar interactions.

3. Investigation of alkali dimer structure at high temperatures

3.1 Motivation

To investigate molecular properties at conditions of very low temperatures one needs previous information about energetic structure of molecules, to properly plan an experimental scheme and setup. This was the case also for LiCs molecule. Available data concerning potential curves of electronic states and positions of rovibrational levels made possible correct planning of photoassociation experiments and was very helpful in analyzing and interpretation of REMPI spectra, depletion spectra, etc.

A knowledge about energetic structure of molecules is generally important, not only in case of investigation of ultracold molecules, but also in other types of experiments. It is crucial particularly for testing theoretical models, in which physicists try to calculate shapes of potential energy curves and energies of molecular levels in particular electronic states. Presently experimental results are still a few orders of magnitude more accurate than those provided by theory. They serve as a reference point for theoretical calculations and allow to make further corrections of theoretical models.

3.2 Spectroscopy techniques and methods of data analysis

- **Polarization labeling spectroscopy**

A polarization labeling spectroscopy technique was used to investigate energetic structure of diatomic molecules. This method is described in details in [43, 44]. The excitation scheme is presented in Fig. 3. Polarization labeling spectroscopy is a pump-probe experimental technique, in which properly set polarization of the two laser beams allow to observe rovibrational molecular spectra only from a few chosen ("labeled") levels of the ground state. Both laser beams cross at small angle in the molecular sample. The strong pump laser beam creates an optical anisotropy in the sample, which changes the polarization of the second, weak, probe laser beam, but only in the case, when transitions induced by both laser beams originate from the same rovibrational level in the ground state. This change in polarization is detected and allows to limit the number of observed spectral lines. Due to this limitation in the recorded rotational structure is fully resolved, because spectral lines do not overlap. Usually only one or few levels are labeled by the probe laser beam of fixed, precisely chosen wavelength and their vibrational (v") and rotational (J") quantum numbers are known.

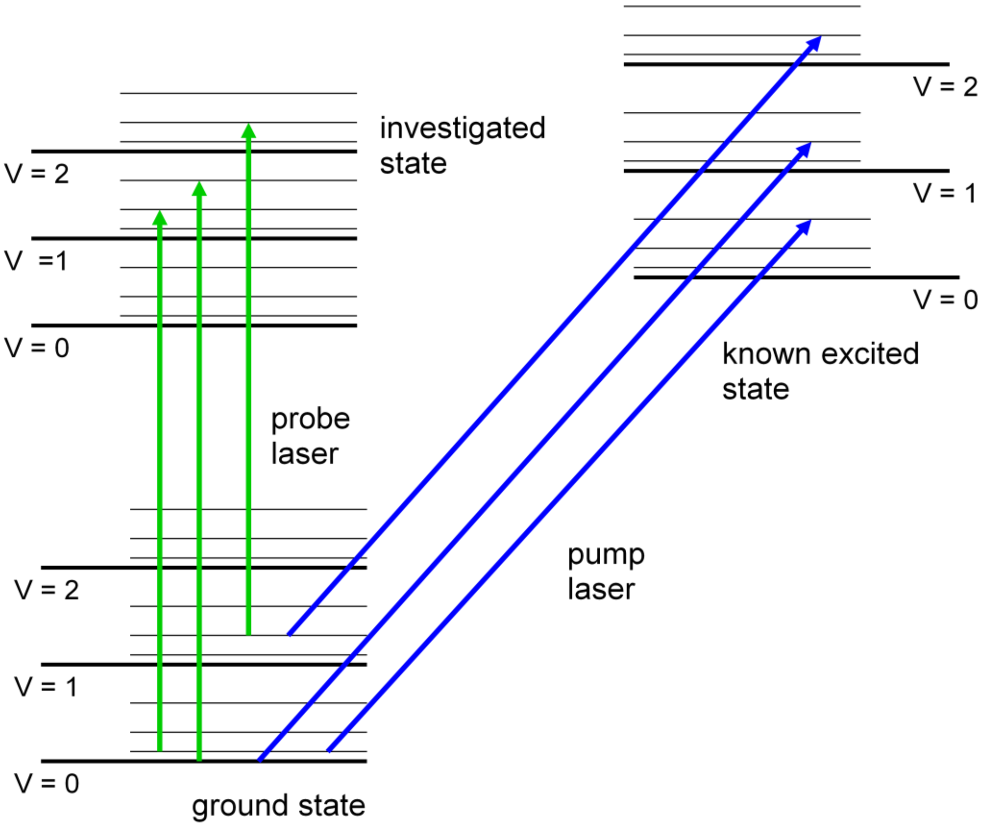

Fig.3 Excitation and detection scheme in the polarization labeling spectroscopy technique

- **RKR method**

The Rydberg-Klein-Rees (RKR) method [45] is a widely known technique, used for construction of potential energy curves for diatomic molecules, when molecular constants (Dunham coefficients) of a given electronic state are known [46]. These coefficients come from analysis recorded molecular spectra. In case of our experiments spectra were recorded using the polarization labeling spectroscopy technique. The RKR method is based on semi-classical quantization condition. The RKR potential is calculated in pairs of classical turning points for consecutive vibrational quantum numbers, starting from v=0 to the highest experimentally known vibrational level. Calculated potential may be interpolated to the minimum of the potential energy curve of investigated electronic state as well as extrapolated to the area above the last experimentally known energy level, usually using polynomial fit.

Since the RKR potential is based on a semi-classical model, one may expect that it is only an approximation of a real molecular potential energy curve. That is why the next step is to solve numerically the Schrödinger equation with the calculated RKR potential to check, if found eigenenergies are equal to experimental values. Usually discrepancies do not exceed typical experimental uncertainties (in our experiment: 0.1 cm^{-1}), what means that the representation of a given electronic state with the RKR potential energy curve is correct. However for regions close to the asymptote, where semi-classical approximation may not work correctly, such discrepancies become bigger. Also in case of electronic states with “irregular” shape of potential energy curve, which is not similar to the Morse curve, one cannot use the RKR method, particularly for potentials with double minima, where for some vibrational levels corresponding wavefunctions penetrate classically forbidden regions.

- **IPA method**

A fully quantum technique called Inverted Perturbation Approach (IPA) [47-49] is much more accurate than the RKR method for describing shapes of real molecular potentials. The main goal in this technique is to find a correction $\delta U(R)$ to the initial, approximate potential $U_0(R)$. A set of eigenenergies obtained by numerical solving of Schrödinger equation with the potential $U_0(R)+\delta U(R)$ should reproduce experimental values of molecular energies. It is an iterative procedure, treating the improved potential $U_0(R)+\delta U(R)$ as a next, better approximation, which serves as an initial potential in the subsequent step of calculation. Such procedure should be repeated untill the discrepancies between calculated and experimental values of eigenenergies will be small enough, where “small enough” is an arbitrary condition.

Finding an “ideal” correction $\delta U(R)$ would make possible a calculation of its influence on the energies of molecular levels, using the well known perturbation approach. Usually in such an approach the correction to the potential is known and corrections to eigenenergies values are sought. This case is opposite – the goal of the method is to find an “ideal” correction $\delta U(R)$ to the potential, basing on known differences (corrections) to the energies of molecular levels, what explains the name of the method.

The potential $U_0(R)$ as well as the corrections to the potential $\delta U(R)$ may be defined as a set of points, connected with spline functions [49]. This form is versatile and allows for an accurate and smooth approximation of potential energy curves in case of many different, even exotic shapes of potentials, for example functions with more than one minimum or with shelves. In case of more complicated functions only a larger number of points describing the potential is needed. Additionally in our version of the IPA method the values of potential corrections δU(R) for each point are at the same time fitting parameters. Defining of uncertainties of the fit is much easier in this case.

3.3 Investigation of the LiCs excited states

Experiments performed at the ultralow temperatures for LiCs molecules showed the importance and strong need for the knowledge of molecular energetic structure. Till that time only a few electronic states were examined experimentally: singlet $X^1\Sigma^+$ and triplet $a^3\Sigma^+$ ground states [40], and two excited states: $B^1\Pi$ state, known within very broad range of energies [38], and $D^1\Pi$ state, known in very limited range of vibrational quantum numbers [38]. The main goal of a set of experiments performed in Warsaw was to examine the experimentally unknown electronic states of LiCs molecule, correlating to the low lying atomic asymptotes, since these state are of particular importance for experiments on ultracold diatomic molecules.

Molecules were created in a three-section heat-pipe oven [50]. Its construction was specially designed for this particular molecule, because one should heat lithium and cesium atoms to very different temperatures to get similar partial pressures of atomic gases of both elements [P6]. The polarization labeling spectroscopy technique, described in the previous section, was used in a series of experiments. Either an optical parametrical oscillator or a dye laser served as a pump laser. An additional dye laser was used as a probe laser. Both pump and probe lasers were pumped with the same YAG or excimer laser. The probe laser frequency was set to a value equal to the energy of a known transition between the LiCs ground state level and a level of partially known $D^1\Pi$ state. The pump laser wavelength was tuned in a broad spectral range, selected to record absorption spectra corresponding to transitions from the ground state to excited electronic states, dissociating to the asymptote Li(2s)+Cs(5d). This range was chosen basing on theoretical calculations and taking into account a possible margin of error.

Theoretical calculations [51, 52] suggested that in the case of direct excitation from the ground $X^1\Sigma^+$ state one should observe transitions to the $C^1\Sigma^+$ state and, for a slightly higher energies, also to the $D^1\Pi$ state. For other electronic states from this energy range, direct optical transitions are forbidden by selection rules [46], since they are triplet states. But even a very rough analysis of registered absorption spectra showed that spectral lines correspond to transitions to four different electronic states. Two of them exhibit properties characteristic for transitions of $^1\Pi \leftarrow {}^1\Sigma$ type and two other of $^1\Sigma \leftarrow {}^1\Sigma$ type. Since there are not as many singlet electronic states within the examined energy range, the experimental spectra can be explained only if in that in the LiCs molecule a Hund's case c coupling of angular momenta is valid, instead of expected Hund's case a [46], which was used to describe electronic states of LiCs so far. Even though the lithium atom is very light, apparently the spin-orbit coupling between orbital and spin angular momenta of electrons is stronger than coupling between orbital angular momentum and the molecular axis. This leads exactly to the Hund's coupling case c. Electronic states of symmetries $^1\Sigma$, $^3\Sigma$, $^1\Pi$ and $^3\Pi$, split into several states with well defined quantum number Ω (a quantum number describing projection of resultant angular momentum of electrons on molecular axis), as it is presented on the scheme below:

Hund's case a coupling	Hund's case c coupling
$^1\Sigma$	$\Omega = 0^+$
$^3\Sigma$	$\Omega = 0^-, 1$
$^1\Pi$	$\Omega = 1$
$^3\Pi$	$\Omega = 0^+, 0^-, 1, 2$

The selection rules for electric dipole transitions in the Hund's case a allow for transitions from $^1\Sigma^+$ state only to states of symmetries $^1\Sigma^+$ and $^1\Pi$. But in Hund's case c transitions from $\Omega=0^+$ state to $\Omega=0^+$ or $\Omega=1$ states are allowed. Analyzing theoretical calculations of potential energy curves [51] one may see, that within the energy range of interest, two $\Omega=0^+$ states, resulting from $C^1\Sigma^+$ and $b^3\Pi$ states, and two $\Omega=1$ states, resulting from $b^3\Pi$ and $e^3\Sigma^+$ states, are present. Since $\Omega=0^+ \leftarrow \Omega=0^+$ transitions give spectra of the same appearance as the case $^1\Sigma^+ \leftarrow {}^1\Sigma^+$, and $\Omega=1 \leftarrow \Omega=0^+$ transitions give spectra like in case of $^1\Pi \leftarrow {}^1\Sigma^+$ transitions, this conclusion explains observations in our experiment.

Further analysis confirmed that recorded spectra indeed correspond to transitions to all states mentioned above. For all four electronic states potential energy curves were determined using either RKR or IPA method. Results were compared with theoretical calculations. Although during last several years one could notice a substantial progress in accuracy of theoretical models and resulting calculations, one could also see that experiment is still necessary, whenever exact values of molecular energy levels are needed.

Described experiments provided the first observations, that one has to use Hund's coupling case c to describe electronic states for a molecule, which contains atom as light as lithium, not only in the region close to the asymptote (when $R \to \infty$), but in the whole range of internuclear distances R. This fact has serious consequences. The number of states which are available in direct transition from the ground state changes dramatically. Also in the case of spontaneous emission the number of possible final states is much bigger than predicted before, what has to be taken into account in all planned experiments on LiCs molecule. This fact may also explain very rich spectra recorded with the REMPI technique in experiments performed on ultracold LiCs.

3.4 Investigation of the NaCs excited states

Results of investigations of LiCs molecule were so important, that experiments were continued for another diatomic alkali metal molecule, also containing cesium atom: NaCs. This molecule is also interesting from the point of view of ultracold physics [53, 54], what means that the knowledge about its energetic structure is crucial. So far only a few electronic states of this molecule were investigated experimentally: singlet $X^1\Sigma^+$ and triplet $a^3\Sigma^+$ ground states [55, 56], and first three excited states of $^1\Pi$ symmetry: $B(1)^1\Pi$ [57], $D(2)^1\Pi$ [58] and $3^1\Pi$ [59]. What's more, two of these excited states, B and D, were investigated within a very limited energy range. In case of NaCs theoretical calculations of potential energy curves of its electronic states exist for both Hund's coupling cases: a [60] and c [61].

Experiments were performed in the energy range corresponding to transitions from the $X^1\Sigma^+$ ground state to excited states dissociating to the first excited asymptote: Na(3s)+Cs(6p), since this region is crucial for photoassociation of NaCs molecules. The experimental setup was similar to that used in case of LiCs molecules. NaCs molecules were formed in a heat-pipe oven, and the pump-probe laser setup was identical. The pump laser was tuned within the energy region corresponding to transitions to energy levels of states lying below the Na(3s)+Cs(6p$_{3/2}$) asymptote, while the probe laser was fixed on transitions between ground state rovibrational levels and chosen rovibrational levels of the D$^1\Pi$ state, known from [58].

In the chosen energy region one may find two electronic states, namely the B$^1\Pi$ and c$^3\Sigma^+$ states. In the case of NaCs molecule, because of its mass, even bigger than of LiCs, one should expect that Hund's coupling case c is valid. Therefore labeling electronic states with the Ω quantum number is more adequate. Observed spectra correspond mainly to transitions between the ground state and the Ω=1 (B$^1\Pi$) state. But increasing the laser power to the level, when the spectra corresponding to B←X transitions were strongly saturated, allowed to observe and record spectral lines corresponding to transitions to the second state of the same symmetry: the Ω=1 (c$^3\Sigma^+$) state. No transitions to any Ω=0$^+$ state were found, what probably means that transition probability in such case is even smaller than for Ω=1 (c$^3\Sigma^+$) state and bellow the sensitivity of experiments described in this section.

In the paper [P7] experimental results concerning the Ω=1 (B$^1\Pi$) state were presented. To that moment only the lower part of the potential energy well of this state was experimentally investigated, up to the v'=25 vibrational level [57]. As it was shown in the paper [P7], we also found that in [57] some spectral lines were incorrectly assigned. Because of that the existing potential energy curve did not allow to find correct values of energies of rovibrational levels. In case of our experiment the investigated energy region included vibrational levels from the bottom of the state up to v'=52, and the last recorded level was less than 8 cm^{-1} from the asymptote. Experimental potential energy curve was constructed using the IPA method and supplemented by the analytic description of the long-range part. Our results were compared with theoretical calculations [61]. This experiment allowed to correct the value of the potential energy well depth of the Ω=1 (B$^1\Pi$) state as well as the value of the equilibrium internuclear distance R_0 for this state. Our experimental description of the Ω=1 (B$^1\Pi$) state made also possible correct identification and interpretation of photoassociation spectra, recorded by the group of prof. Bigelow from the University of Rochester [62]. One of the main features of photoassociation is that, in most cases, only observation of highly lying vibrational levels, particularly levels lying close to the asymptote, is possible. Such situation does not allow for correct numbering of the observed rovibrational levels. The full interpretation of recorded spectra is usually possible only when photoassociation results are supplemented by results of another experiment, taken with more "classical" spectroscopic technique. In the case of the Ω=1 (B$^1\Pi$) state this absolute numbering of the energetic levels was found by us, and it allowed to choose from many spectral lines recorded in the photoassociation experiment those, which indeed correspond to transitions to Ω=1 (B$^1\Pi$) state levels. The remaining lines must correspond to other states dissociating to the Na(3s)+Cs(6p$_{3/2}$) asymptote and this assumption was cleared up in our next experiment.

In case of Ω=1 (c$^3\Sigma^+$) state the cooperation with the group from Rochester was even closer. The results of the experiments from Warsaw (~93%), employing polarization labeling spectroscopy method, and from Rochester, obtained with photoassociation and depletion spectroscopy, were joined to construct the final potential energy curve. Photoassociation experiment from prof. Bigelow's group gave very accurate information concerning ten rovibrational levels of the Ω=1 (c$^3\Sigma^+$) state lying very close to the asymptote. The results from depletion spectroscopy had very low accuracy, the error in line positions was up to a few cm^{-1}, thus inacceptable in modern spectroscopy, but they allowed to find the absolute vibrational numbering for this state. It was one of very rare cases, when low values of Franck-Condon factors did not allow to observe the two lowest vibrational levels of this state using the polarization labeling spectroscopy method. The potential energy curve of the Ω=1 ($c^3\Sigma^+$) state was constructed, as in previous cases, using the IPA method.

This experiment showed advantages and disadvantages of all three spectroscopy techniques used to collect data for Ω=1 ($c^3\Sigma^+$) state:

- The polarization labeling spectroscopy technique allows to get a data set containing energies of rovibrational levels within a broad range of vibrational and rotational quantum numbers, determined with high accuracy of about 0.1 cm^{-1}. However, this technique does not allow to investigate the region close to the asymptote. In particular experiment on the Ω=1 ($c^3\Sigma^+$) state in NaCs also observation of the very bottom of this state was not possible.

- Photoassociation spectroscopy is very accurate, the resolution allows to observe the hyperfine structure of the spectral lines. But observed resonances correspond only to very low rotational quantum numbers (usually J=0-3) and very high vibrational quantum numbers (limited to the region close to the asymptote), what makes this method complementary to the previous one.

- In case of depletion spectroscopy the sensitivity is very high. This technique allows to observe transitions even from very weakly populated rovibrational levels. But its resolution and accuracy strongly depend on the used depletion laser, particularly its bandwidth. A laser with a very narrow bandwidth allows for rotational resolution, but still the uncertainty of results is much bigger than in case of photoassociation.

A connection of the data recorded with all three techniques mentioned above allowed for full description of the Ω=1 ($c^3\Sigma^+$) state, from the bottom to the asymptote, in very broad range of vibrational and rotational quantum numbers and, in particular, enabled assignment of several remaining photoassociation resonances. It is a perfect example, how important is to use complementary experimental techniques to get a full information about energetic structure of the molecule.

4. Summary

The performed experiments showed the importance of comprehensive investigations of molecular properties and structure. It is necessary to use a few complementary experimental techniques. The spectroscopic knowledge makes possible a better planning of experiments performed at very low temperatures. It was particularly striking in the case of investigations of ultracold LiCs molecules, when all experimental schemes were based on the only one experimentally known excited state ($B^1\Pi$ state). On the other hand the experiments on ultracold molecules provide a knowledge about molecular properties and energetic structure, which is not available from other techniques, what also was shown in experiments on both LiCs and NaCs molecules.

Particularly investigations of LiCs molecule allow to discover a few crucial properties and formulate some important (also from the point of view of future experiments) conclusions:

- The possibility of photoassociation of LiCs directly to the deeply bound rovibrational levels of $B^1\Pi$ state opened a way to create these molecules in the absolute ground state, what, consequently, opens new chances for experiments on a degenerate gas of dipolar molecules.

- Particularly necessary are further investigations to explain the reason of the above possibility, since the importance of predictions of such behavior for other molecules and different energetic state is obvious.

- A discovery that strong spin-orbit coupling in case of LiCs molecule causes that the Hund's coupling case c is very important, since this knowledge is necessary for correct description of allowed transitions between molecular states in this molecule. The consequence of this fact is that a direct optical transition from the ground state is possible to bigger number of electronic states than it was expected. This is a crucial information for planning further experiments on LiCs molecule.

- The same fact proves indirectly that one should expect similar behavior in case of all diatomic molecules heavier than LiCs, what was also shown for the case of NaCs molecule.

To continue this type of experiments a new laboratory is built in the Institute of Experimental Physics of University of Warsaw, in which experiments on ultracold molecules will be performed in the near future.

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