

STUDIES OF ALKALI DIATOMIC MOLECULES USING FOURIER TRANSFORM SPECTROSCOPY AND OPTIMISATION OF POTENTIAL ENERGY CURVE RECONSTRUCTION

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Summary of the Project results

In spectroscopy of diatomic molecules molecular electronic states are characterised by potential energy curves (PEC). Accurate knowledge of PEC allows controlling chemical reactions, opens possibilities for isotope separation, formation of cold molecules from cold atoms, etc. Existing *ab initio* methods of calculating PECs do not allow for such accuracy sufficient for performing the above mentioned experiments, therefore PECs based on the experimental data are necessary. For construction of experimentally based PEC $U(r)$ its analytical form is inserted into Schrödinger equation (SE) for obtaining of eigenvalues, which are experimentally measurable. It is also essential to elaborate algorithms for accurate and fast solving of SE for interacting potentials. Another complicated task is to construct $U(r)$ in the near-dissociation region.

1. Improvement of numerical methods (in collaboration with mathematicians)

1.1 Optimisation of solution of radial Schrödinger equation

For efficient solution of the main task of molecular spectroscopy, namely construction of a molecular potential energy curve (PEC) using a large set of experimental energy values, it is essential to elaborate and test efficient mathematical methods for solving of radial motion equations, which means to propose and develop fast algorithms for solution of one-dimensional radial Schrödinger equation (SE).

In the framework of this Project we have developed a new method for solving of SE. It can be shown that replacing the usual integration variable $r \in [0, \infty)$ by a reduced radial variable $y \equiv y(r; \bar{\alpha})$ defined analytically on a finite domain $y \in [a, b]$ transforms the conventional radial SE into an equivalent form in which treatment of levels lying close to dissociation becomes as efficient as a coupled channels approach.

Let's consider the familiar radial or effective one-dimensional Schrödinger equation, which is defined on the infinite domain $r \in [0, \infty)$:

$$\frac{d^2 \psi(r)}{dr^2} = -Q(E; r) \psi(r) \equiv - \left\{ \frac{2\mu}{\hbar^2} [E - U(r)] \right\} \psi(r). \quad (1)$$

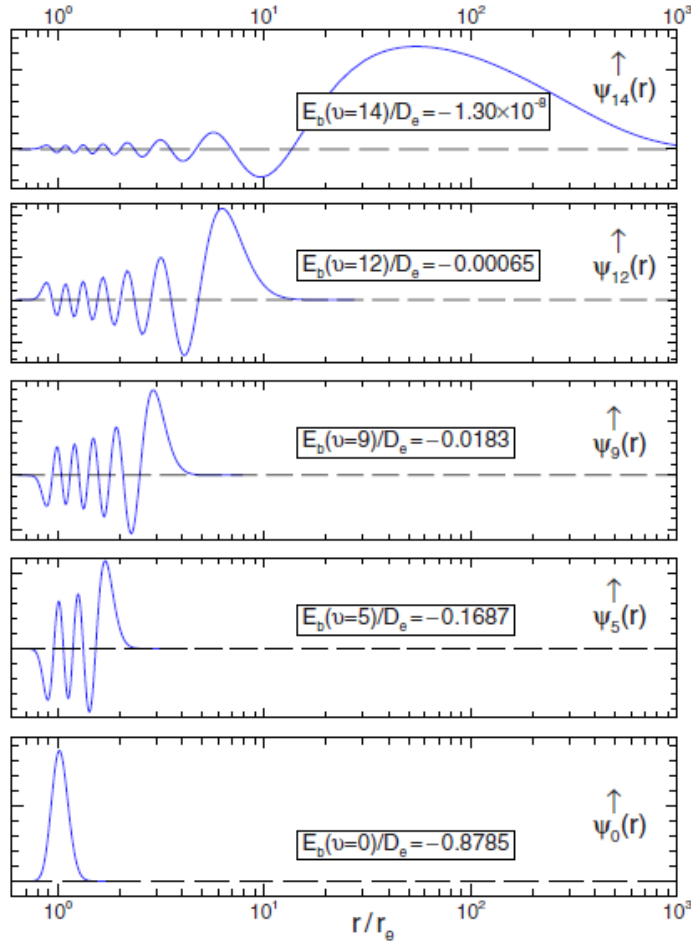


Fig. 1. Radial eigenfunctions $\psi(r)$ for different vibrational levels starting with $v = 0$ (strongly bound level) up to levels in the near-dissociation region.

The problem of solution of such an equation appears when one needs to simulate spectra or calculate a scattering length, which determines an efficiency of cold molecule formation. Existing methods of solving radial SE allow fast and efficient solution when energy levels of interest are much lower (more than 50-100 cm^{-1}) than a dissociation limit of potential $U(r)$. Problems arise when level energy is in the near-asymptotic region which means that r region where wave function has non-zero value tends to infinity. The nature of the problem is illustrated by Fig. 1.

For solution of such a problem let's introduce a new radial coordinate function $y(r)$, which is a smooth, monotonically increasing function of r , and our initial radial equation (1) becomes:

$$\left[\frac{d^2}{dy^2} - \left(\frac{g'}{g} \right) \frac{d}{dy} + g^2 Q \right] \psi = 0, \quad (2)$$

in which $g(y) \equiv \frac{dr(y)}{dy} = 1$, $\frac{dy(r)}{dr} > 0$ and $r(y)$ is defined on the interval $y \in [a,b]$ as the inverse function of $y(r)$ while a prime (') denotes differentiation with respect to the new variable y . The substitution $\psi(r) = \sqrt{g}\phi(y)$ then transforms Eq. (2) into the conventional form:

$$\frac{d^2\phi}{dy^2} = -\tilde{Q}(E, y)\phi(y) \quad (3)$$

in which $\tilde{Q}(E, y) \equiv g^2(y)Q(E, r(y)) + F(y)$ and the additive term

$$F(y) = \frac{g''}{2g} - \frac{3}{4}\left(\frac{g'}{g}\right)^2 \text{ depends only on the definition of the new radial coordinate.}$$

Equation (3) may also be rewritten in the equivalent form:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dy^2} + g^2\tilde{U} \right] \phi = g^2 E \phi \quad (4)$$

in which $\tilde{U} \equiv U - \frac{\hbar^2 F(y)}{2\mu g(y)^2}$ is the effective potential. The advantage of the chosen substitution is that it allows applying existing codes for solving of SE (e.g. Numerov method), simply replacing $Q(E, r)$ by $\tilde{Q}(E, y)$ and appropriately transforming the normalization conditions.

It is now necessary to introduce an explicit definition for the new radial variable $y(r)$. A particularly convenient choice is a two-parameter version of the Šurkus variable:

$$y(r; \alpha, \bar{r} > 0) = \frac{(r/\bar{r})^\alpha - 1}{(r/\bar{r})^\alpha + 1}; \quad y \in [-1, 1].$$

Then $r(y) = \bar{r} \left(\frac{1+y}{1-y} \right)^{1/\alpha}$. For this case

$$g(y) \equiv \frac{dr(y)}{dy} = \frac{2\bar{r}}{\alpha} \frac{(1+y)^{1/\alpha-1}}{(1-y)^{1/\alpha+1}} = \frac{(r^\alpha + \bar{r}^{-\alpha})^2}{2\alpha\bar{r}^{-\alpha} r^{\alpha-1}}, \text{ and the function } F(y) \text{ has the}$$

$$\text{form } F(y) = \frac{1 - 1/\alpha^2}{(1 - y^2)^2}.$$

To illustrate how integration boundaries have changed for wave functions after substitution, the same wave functions from Fig. 1 are plotted in Fig. 2 dependent on variable $y(r)$.

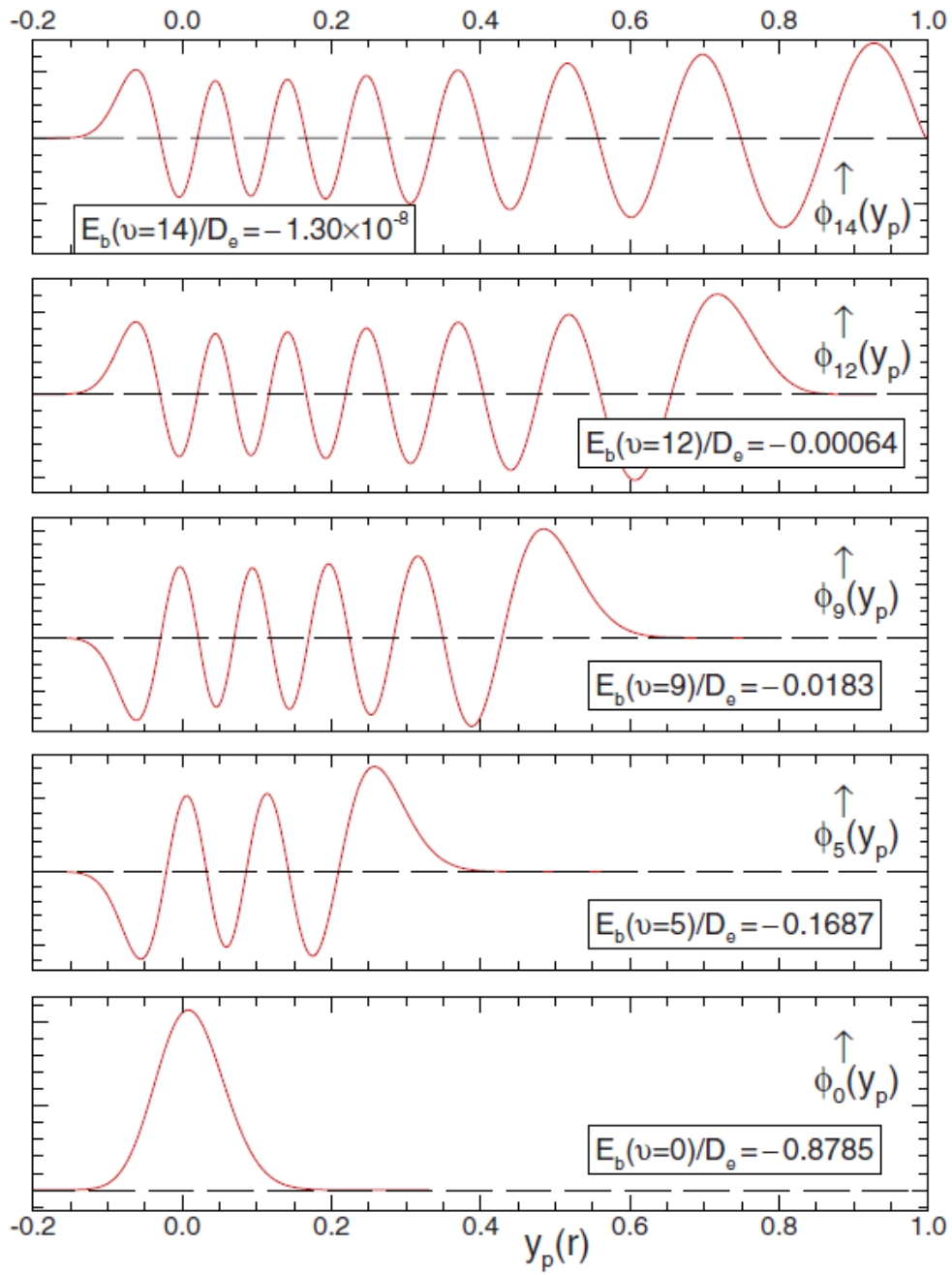


Fig. 2. Radial eigenfunctions $\phi(y)$ for the same five levels, in the same potential, as in Fig. 1.

The above described method is applied for calculation of wave functions in the paper [1].

1.2. Improvement of PEC approximation

In experiment we obtain energies for different rovibronic levels $E(v, J)$, and the task is to obtain a potential energy curve (PEC) using mathematical methods. Our purpose is to construct such a PEC which using a limited experimental data set, would possess the following properties: (a) the method should not be crucially dependent on the choice of initial potential, (b) PEC would allow to reproduce all experimental data with experimental accuracy, (c) PEC would allow to predict energies of the levels outside the experimental data field with the necessary accuracy (usually experimental accuracy), i.e. PEC should have good extrapolation properties. For modern applications (e.g. experiments with cold molecules) it is essential that PEC would provide an accurate description of the near-asymptotic region when $r \rightarrow \infty$. There is a variety of existing methods but each has advantages and disadvantages.

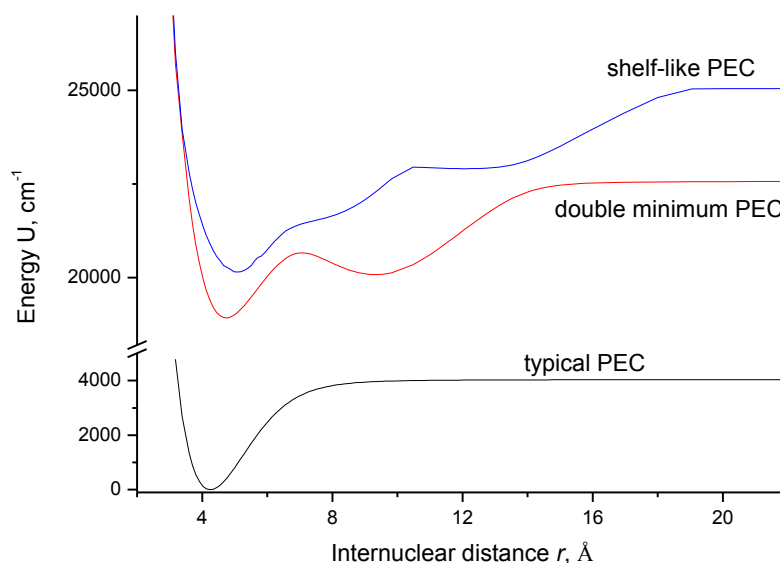


Fig. 3. Examples of different forms of PECs.

Historically the first method was a Morse-type potential $U(r) = D_e [1 - e^{-\alpha(r-r_e)}]^2$, where D_e is dissociation energy, r_e – equilibrium internuclear distance, Λ – unharmonicity parameter. SE with Morse potential has an analytical solution, but this model is not capable to reproduce a large set of vibrational levels with an experimental accuracy. A correct asymptotic behavior is also lacking. The analytically determined form of Morse potential also allows one not to describe shelf-like states or double minimum states.

Another approach is to describe experimental data with Dunham coefficients Y_{ik} , namely $E(v, J) = \sum_{i,k} Y_{ik} (v + 1/2)^i [J(J + 1) - \Lambda^2]^k$, where $E(v, J)$ is rovibronic energy, v – vibrational quantum number, J – rotational quantum number, Λ – projection of resulting electron orbital momentum on the internuclear axis. Rydberg-Klein-Rees method allows one to restore PEC using Dunham coefficients. But due to the polynomial character of the Dunham expansion PEC doesn't possess good extrapolation properties.

An alternative approach is to introduce PEC as a set of points connected with cubic spline function. This approach is very flexible and allows description of any form potentials. At the same time this flexibility is a reason for bad extrapolation properties, because PEC can describe data only inside the experimental data field.

Recently introduced Morse and Lennard-Jones (MLJ) potential modification provides good extrapolation properties and correct asymptotic behavior at $r \rightarrow \infty$, but is inflexible and is not able to describe shelf-like or double minimum states.

In the paper [9] a new method is suggested which would fulfill all described demands. Let's define a potential $U(r)$ on the interval $r \in [r_{\min}, +\infty)$ with analytical continuous function

$$U(r) = D_e - \frac{\sum_{k=0}^m c_k T_k(y_p)}{(r/r_{ref})^n + 1}$$

where $T_k(y)$ are Chebyshev polynomials of the first kind which are dependent on the reduced radial variable $y_p(r) \in [-1, 1]$. It is dependent on r as following:

$$y_p(r; r_{\min}; r_{ref}) = \frac{r^p - r_{ref}^p}{r^p + r_{ref}^p - 2r_{\min}^p}.$$

Here $p \in [1, 2, \dots]$ is a small natural number, $r_{ref} > r_{\min} \geq 0$ and r_{ref} is a reference distance chosen as the center of expansion. Introduced PEC has a correct asymptotic behavior at $r \rightarrow \infty$, namely $U(r \rightarrow \infty) \rightarrow D_e - \frac{C_n}{r^n} + \dots$, where a leading

dispersion coefficient C_n is dependent on coefficients c_k as $C_n = r_{ref}^n \sum_{k=0}^m c_k$. In the proposed model the dissociation energy D_e , the leading degree of long-range expansion n , the degree of the reduced variable p are considered to be the fixed parameters. So, excluding r_{ref} , the only variables are Chebyshev polynomial coefficients c_k and PEC is a linear function with respect to them. Chebyshev expansion is closely related to a conventional polynomial expansion, but contrary to the last one, Chebyshev orthogonal polynomial base functions provide very good convergency properties. This in turn diminishes the number of necessary polynomials m and provides decreasing of $|c_k|$ values as k increases.

The described method is applied for construction of PECs in the papers [4, 9].

2. Construction of experimental PECs

For performing of the introduced tasks we have measured and analysed high-resolution Fourier transform spectra of KCs and RbCs molecules. Using the obtained experimental data there were constructed PECs which allowed one (a) to reconstruct experimental data for strongly mixed states, as well as for states with local perturbations; (b) to test accuracy of quantum chemistry calculations; (c) to model and optimize optical cycles for production of cold molecules; (d) to model spin-orbit interaction effects using the studies of the strongly mixed $A^1\Sigma^+ - b^3\Pi$ states.

In Fig. 4 and 5 one can see electronic states which have been investigated in KCs (Fig. 4) and RbCs (Fig. 5) molecules in the framework of this Project. A detailed description of the Project results is given below.

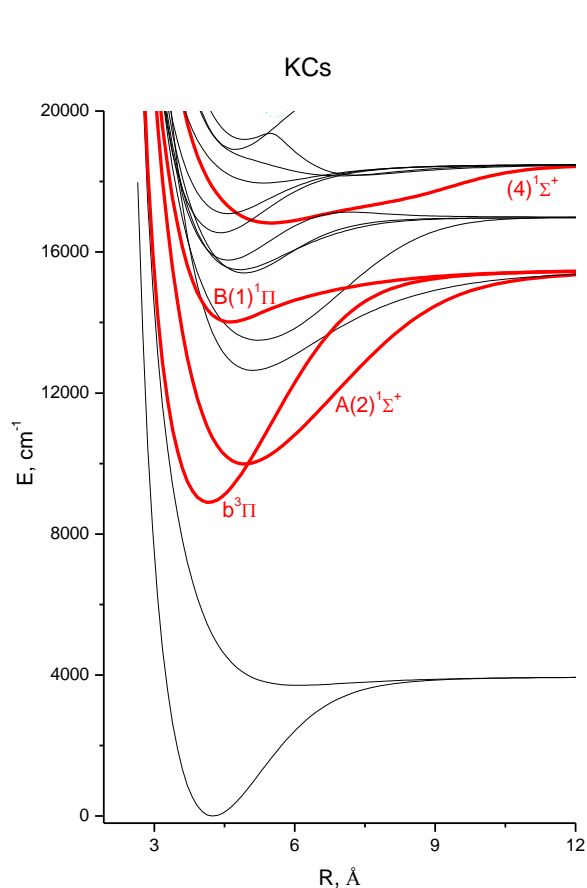


Fig. 4. Electronic states of KCs molecule. The states which PECs were constructed in the framework of this project are shown in red.

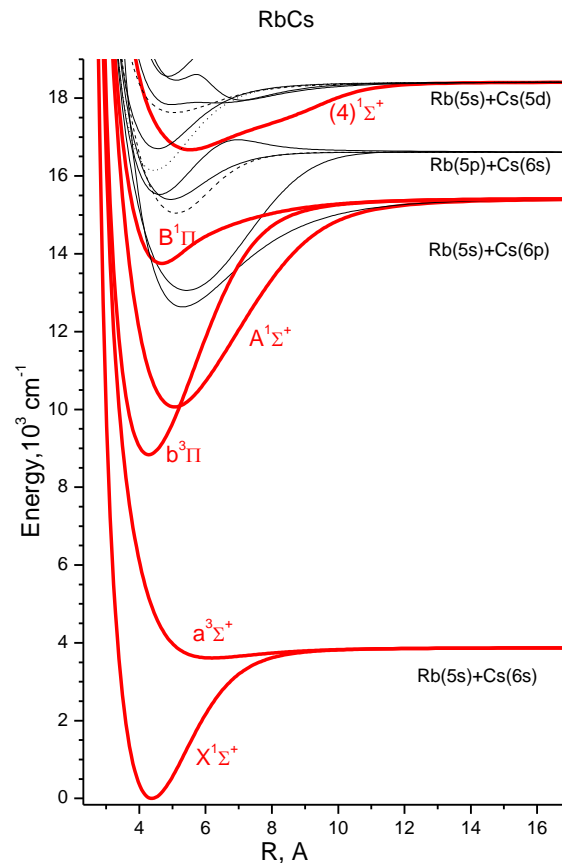


Fig. 5. Electronic states of RbCs molecule. The states which PECs were constructed in the framework of this project are shown in red.

2.1. Studies of the $X^1\Sigma^+$ and $a^3\Sigma^+$ states in RbCs molecule

In the course of work PECs of the $X^1\Sigma^+$ and $a^3\Sigma^+$ states of RbCs have been substantially improved and extended to the larger internuclear distances. Abundant spectroscopic data for transitions to the $X^1\Sigma^+$ (15709 transitions) and $a^3\Sigma^+$ (4549 transitions) states were obtained. It should be noted that it was the first observation of RbCs $a^3\Sigma^+$ state. Potential energy curves were constructed simultaneously for the $X^1\Sigma^+$ and $a^3\Sigma^+$ states in a coupled-channels fitting routine. This was necessary because approaching dissociation limit (3836.373 cm^{-1}) hyperfine mixing between the X and a states begins to play an important role and it becomes impossible to reproduce rovibronic level energy using only one state PEC. The obtained PECs allow one to reproduce experimental energies with a standard deviation of 0.006 cm^{-1} . Accurate knowledge of PECs provides opportunity to calculate positions and widths of Feshbach resonances which is essential for cold molecule formation experiments. Results are published in the article [6] and are presented in the 10th international conference on atoms, molecules and photons (10th ECAMP) in 2010.

2.2. Studies of the $A^1\Sigma^+ \sim b^3\Pi$ complex

2.2.1. KCs molecule

We have improved and tested the model description of the strongly mixed $A^1\Sigma^+ \sim b^3\Pi$ states. In order to extend substantially the energy range of the studied A-b complex, a new thermoelectrically cooled InGaAs detector for Fourier spectrometer IFS-125HR was acquired. Using this detector it became possible to observe fluorescence from the $4^1\Sigma^+$ state to the A-b complex thus substantially extending the preceding data set. A new data field contains 5800 points and is shown in Fig. 6.

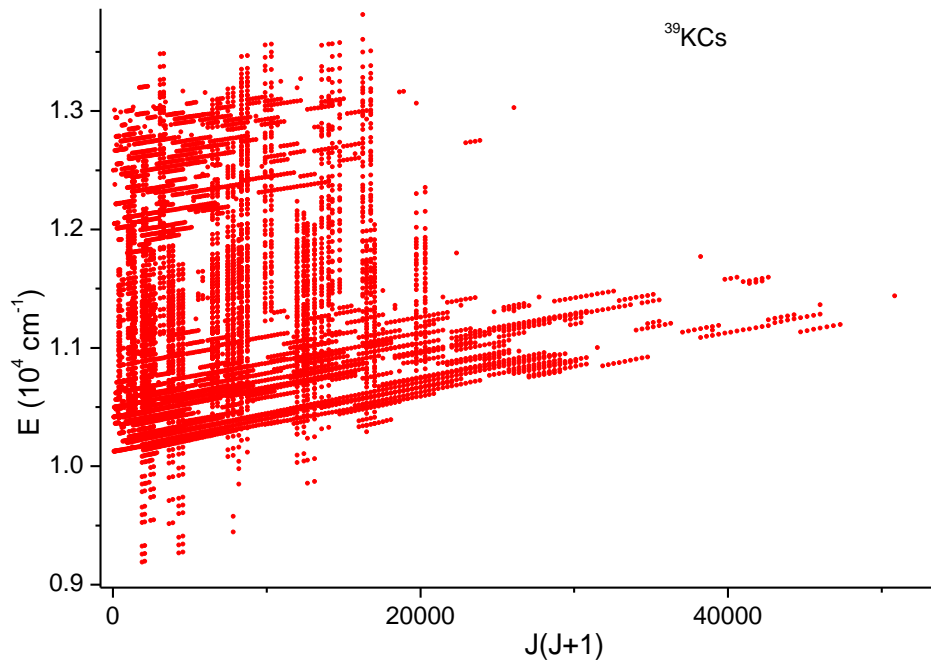


Fig. 6. Experimental data field for the KCs $A^1\Sigma^+ \sim b^3\Pi$ complex.

For all 5802 terms shown in Fig. 6 energies were calculated using coupled-channels approach. In this case four interacting channels are in consideration: $A^1\Sigma^+$ state and three $b^3\Pi$ state components. Experimental data were used to adjust the following parameters: $A^1\Sigma^+$, $b^3\Pi_0$, $b^3\Pi_1$, $b^3\Pi_2$ state PECs, as well as their spin-orbit interaction functions. Difference between experimental and calculated values is shown in Fig. 7.

Fig. 7 shows that more than 90% of points are described with accuracy 0.015 cm^{-1} (experimental uncertainty) or better, nevertheless the model needs to be improved in order to allow for better reproducing of data with energies higher than 13200 cm^{-1} . This implies that probably the number of the considered channels should be increased by including the $c^3\Sigma^+$ state components. For description of energies higher than 14000 cm^{-1} $B^1\Pi$ state and its interaction with $b^3\Pi$ and $c^3\Sigma^+$ states should be taken into account.

Part of the obtained data is published in the paper [9], the rest will be published as soon as the model description will be improved. Research results were presented in the 43rd Conference of the European Group for Atomic Systems (EGAS) and in the 22nd Colloquium on High-Resolution Molecular Spectroscopy (HRMS).

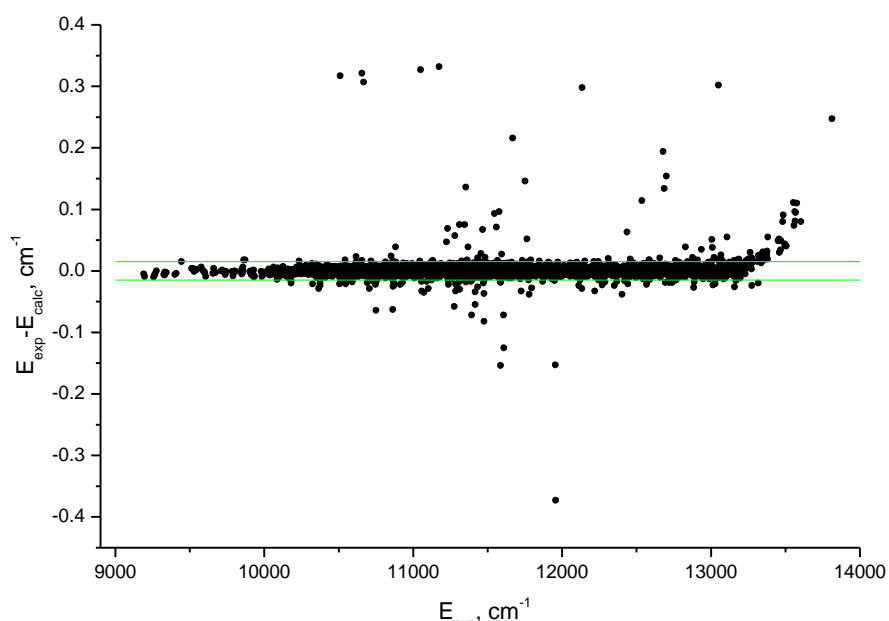


Fig. 7. Difference between experimental and calculated $A^1\Sigma^+ \sim b^3\Pi$ energy values for KCs. Green horizontal lines mark experimental uncertainty $\pm 0.015 \text{ cm}^{-1}$.

2.2.2 Cs_2 molecule

In the framework of the project we have performed studies of the $A^1\Sigma_u^+ \sim b^3\Pi_u$ complex of Cs_2 in order to improve the existing description. For this purpose laser induced fluorescence from the A-b complex to the ground state was measured using high resolution Fourier spectrometer. Part of Cs_2 data was obtained from Cs_2 spectra, which were excited simultaneously with KCs or RbCs fluorescence spectra. Apart of this a glass cell filled with Cs was made. Experiments in a cell allowed us to get “pure”, i.e. without lines of other molecules, Cs_2 spectra. Overall 2066 energy values were obtained. About 70 points were already included in the paper [7] together with the data of other groups for adjusting of the following parameters: $A^1\Sigma_u^+$, $b^3\Pi_0$, $b^3\Pi_1$, $b^3\Pi_2$ state PECs, as well as their spin-orbit interaction functions. Results are published in the paper [7]. In Fig. 8 one can see differences between experimental and calculated (according to the model in [7]) $A^1\Sigma_u^+ - b^3\Pi_u$ energy values for Cs_2 as a function of vibrational level number. One can notice that the differences till $N=130$ are mostly positive, whereas between 130 and 170 they are mostly negative. This implies a systematic deviation of the model calculations [7] from the experimental values, which points out a necessity to improve the model.

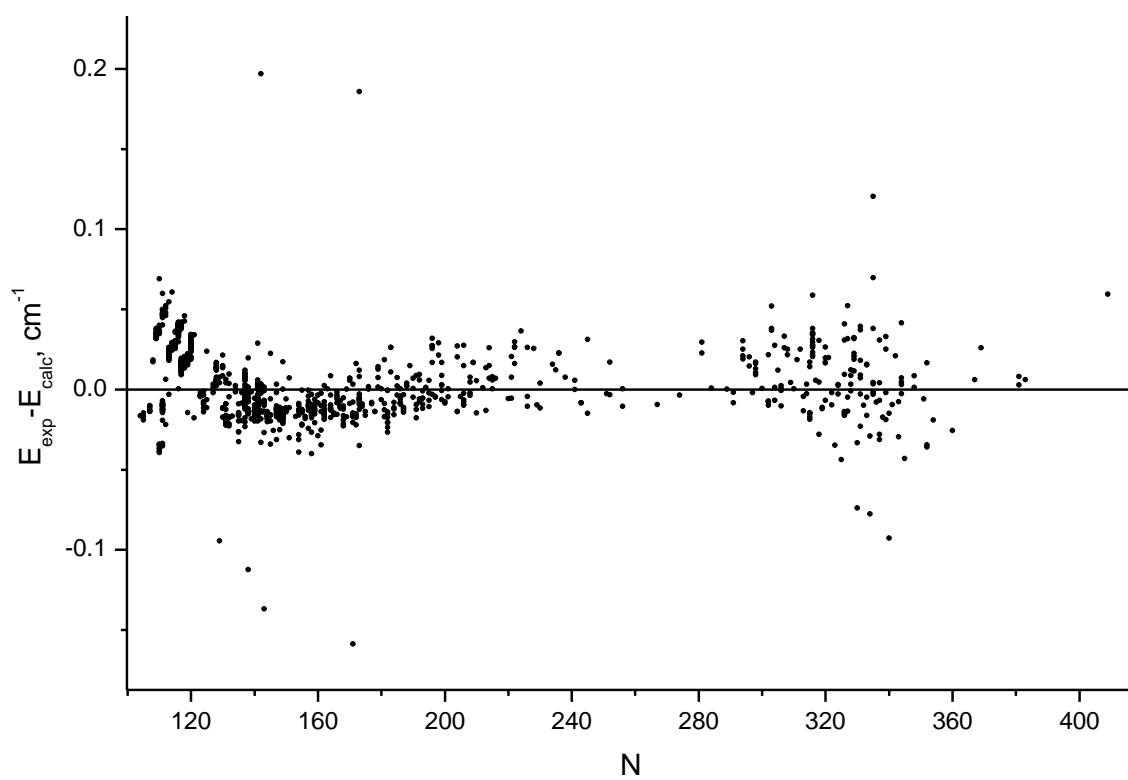


Fig. 8. Difference between experimental and calculated $A^1\Sigma_u^+ - b^3\Pi_u$ energy values for Cs_2 as a function of vibrational level number.

2.2.3. Rb_2 molecule

Investigations of the Rb_2 A-b complex have been also performed. Rb_2 LIF was recorded simultaneously with $RbCs$ LIF, performing $RbCs$ A-b complex studies. The obtained data together with the data of collaboration partners from Moscow and Lyon and the data of other groups were used for adjusting of the following parameters: $A^1\Sigma^+$, $b^3\Pi_0$, $b^3\Pi_1$, $b^3\Pi_2$ states PECs, as well as their spin-orbit interaction functions. Comparison and tests of experimental and calculated data have been performed. All obtained term energies for $^{85}Rb_2$ and $^{85}Rb^{87}Rb$ molecules dependent on $J(J+1)$ are shown in Figs. 9 and 10.

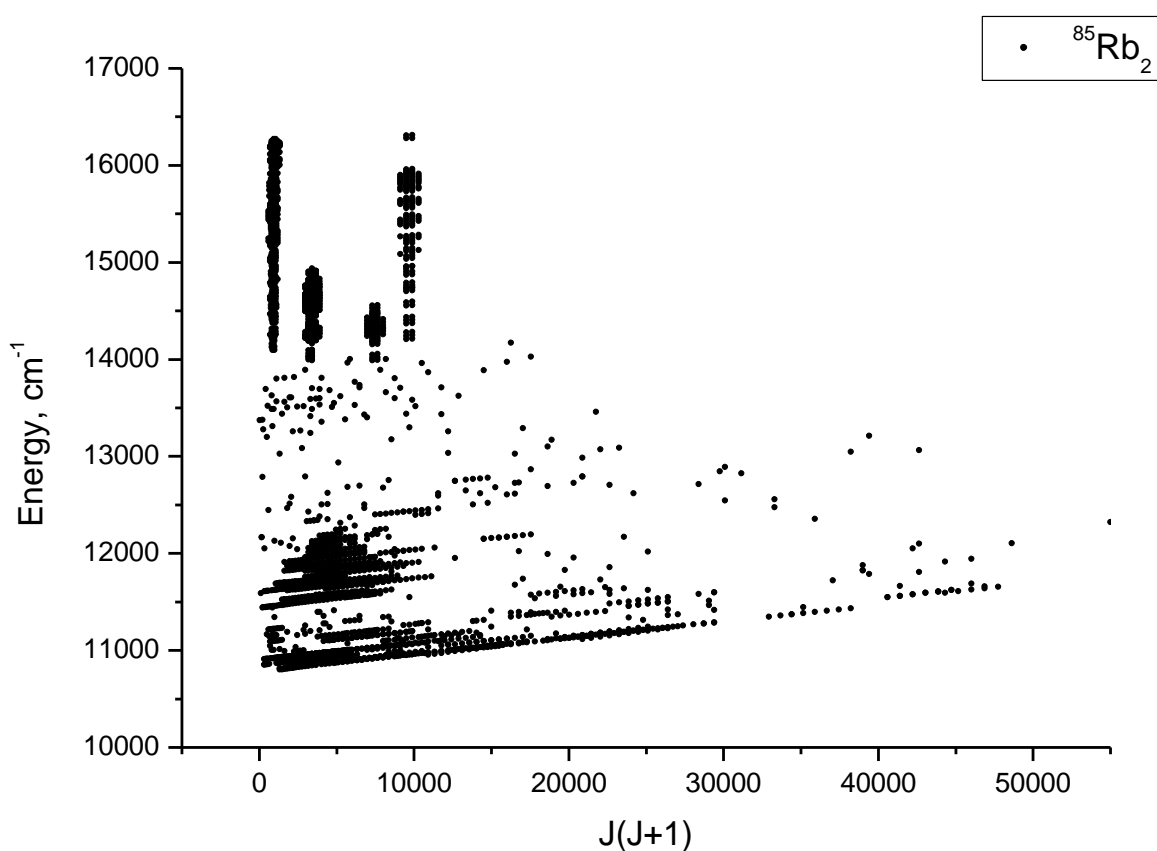


Fig. 9. Obtained $^{85}Rb_2$ A-b complex energies as dependent on $J(J+1)$.

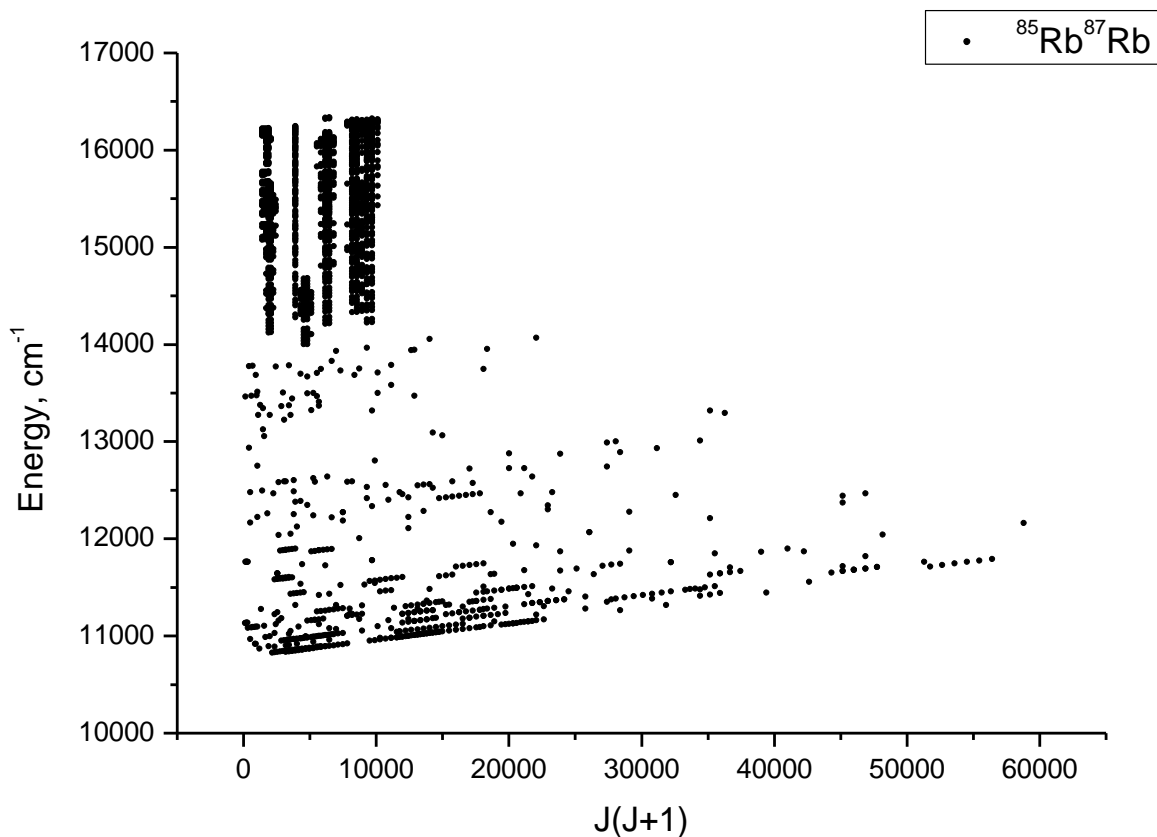


Fig. 10. Obtained $^{85}\text{Rb}^{87}\text{Rb}$ A-b complex energies as dependent on $J(J+1)$.

2.2.4. *RbCs and KRb molecules*

A new heat-pipe containing K and Rb metals has been prepared. For the first time high-resolution measurements of the KRb A-b complex have been performed and first original results about term values have been obtained. The derived data are important for cold molecule formation and stabilization experiments. Primary data analysis shows that the lowest vibrational levels $\nu = 0$, $\nu = 1$ and $\nu = 2$ were observed which is essential for further data identification and construction of PEC.

An adjustment of the experimental set-up and new experiment series have been realized for observing high vibrational levels of the RbCs A-b complex. For this purpose methodology was improved, namely applicability of TE-InGaAs detector for RbCs measurements was tested. A series of experiments which allowed observing transitions from the $4^1\Sigma^+$ state to the A-b complex were performed. Analysis of spectra showed that for reaching the uninvestigated region of the A-b complex one needs to excite the $4^1\Sigma^+$ state in the $\nu=60-70$ range. The preceding data set should be critically analysed in order to use the same method for obtaining the data field.

2.3. *B¹Π state studies*

2.3.1. *KCs molecule*

Measurements of the KCs LIF from the $B^1\Pi$ state to the ground state have been performed for the first time. The obtained $^{39}\text{K}^{133}\text{Cs}$ $B^1\Pi$ state energies were used to construct

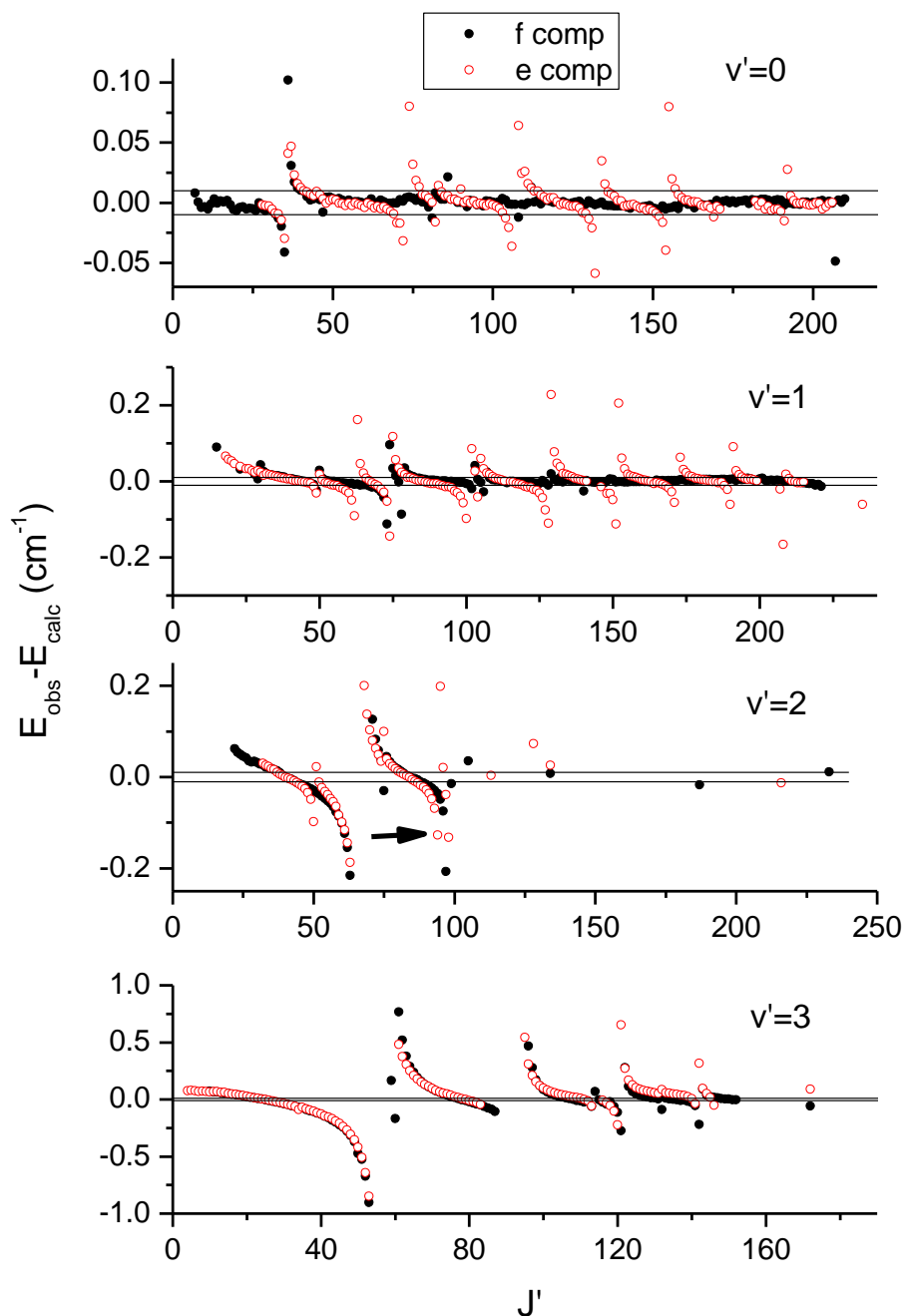


Fig. 11. Differences between experimental (E_{obs}) and calculated (E_{calc}) using the obtained PEC and q-factors energies as dependent on rotational quantum number J' for the $^{39}\text{K}^{133}\text{Cs}$ isotopologue.

a PEC using an Inverted Perturbation Approach (IPA) method. Rotational constant plots gave an opportunity to select points which could be perturbed by the $C^1\Sigma^+$ state as well as by the $b^3\Pi$ and $c^3\Sigma^+$ states. 520 unperturbed levels with $v' \in [0; 3]$ and $J' \in [7; 233]$ were incorporated into the IPA fit. The obtained PEC contains 23 points and reproduces experimental energies with a standard deviation of 0.02 cm^{-1} . Dunham coefficients were also fitted for the same unperturbed data set. q -factors were obtained for vibrational levels $v=0-3$. In order to test the derived PEC and q -factors, energies of 17 $^{41}\text{K}^{133}\text{Cs}$ levels were calculated and compared with the experimental ones. Fig. 11 shows comparison of the observed (E_{obs}) and calculated (E_{calc}) energy values as dependent on J' for the first four vibrational levels ($v' \in [0; 3]$) in $^{39}\text{K}^{133}\text{Cs}$. Molecular constants corresponding to the present potential have been also calculated. Molecular constants (E_v , B_v) for several $C^1\Sigma^+$ levels have been also derived. All obtained data are published in the paper [2]. Research results were also presented in the 43rd Conference of the European Group for Atomic Systems (EGAS) and in the 22nd Colloquium on High-Resolution Molecular Spectroscopy (HRMS).

2.3.2. RbCs molecule

A construction of the RbCs $B(1)^1\Pi$ state PEC using Fourier transform (FT) spectroscopy data on the vibrational levels $v = 0, 1$ un 2 has been accomplished. Overall about 160 FT spectra have been recorded and identified, including 98 rotation relaxation patterns. The whole data set is shown in Fig. 12 as dependent on J' . The obtained data provided the values of q -factors and rotational constants B_v for vibrational levels $v=0, 1, 2$ un 3, which allowed to determine perturbation-free regions that could be incorporated into the fit. Using this limited data set a $B^1\Pi$ state PEC for the $^{85}\text{RbCs}$ isotopologue was obtained. 358 unperturbed term energies of vibrational levels $v' \in [0; 2]$ and rotational levels $J' \in [6; 313]$ were included in the fit.

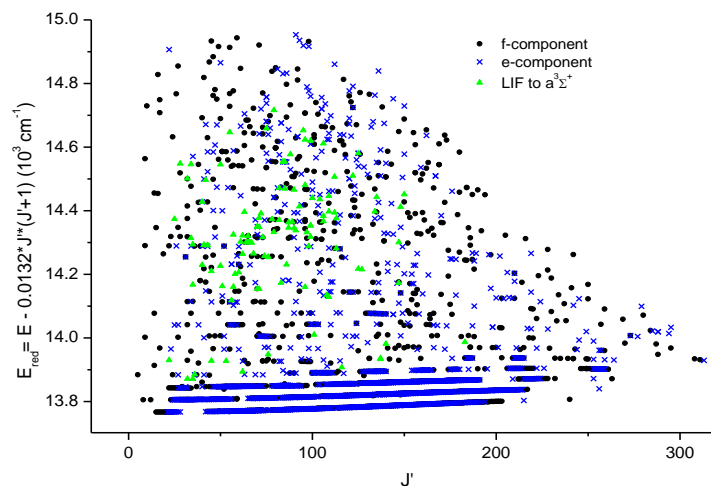


Fig. 12. Experimentally determined $^{85}\text{Rb}^{133}\text{Cs}$ $B^1\Pi$ state level energies dependent on J' .

The resulting IPA PEC includes 27 grid points. It reproduces the fitted term values with a standard deviation of 0.07 cm^{-1} .

We have also fitted a selected data set to Dunham coefficients, as well as obtained molecular constants for separate v' levels. We concluded that level $v' = 2$ is strongly

perturbed, because a systematic shift of this level can be observed. In order to test the derived PEC we have identified 15 rotational relaxation patterns for $^{87}\text{RbCs}$. We have calculated the differences between the measured (E_{exp}) and calculated by means of PEC (E_{calc}) energies for the first 3 vibrational levels ($v' \in [0; 2]$) in $^{85}\text{RbCs}$ and $^{87}\text{RbCs}$. J' dependencies of rotational constant allowed us to select points which are probably perturbed by the $\text{C}^1\Sigma^+$ state.

Research results are presented in the paper [3]. Results were also presented in the DOC-2012 conference ("High resolution spectroscopy and description of low-lying energy levels of RbCs $\text{B}^1\Pi$ state"), in the 44th Conference of the European Group for Atomic Systems (EGAS), as well as in the 22nd Colloquium on High-Resolution Molecular Spectroscopy (HRMS).

2.4. $(4)^1\Sigma^+$ state studies

2.4.1. KCs molecule

For the first time measurements of the KCs LIF from the $(4)^1\Sigma^+$ state to the ground state $\text{X}^1\Sigma^+$ using dye laser excitation were performed. Overall about 1650 rovibronic term values of the $(4)^1\Sigma^+$ state of $^{39}\text{K}^{133}\text{Cs}$ and $^{41}\text{K}^{133}\text{Cs}$ levels with vibrational quantum number v' from 2 till 74, and rotational quantum number J' from 1 to 188 were obtained. The derived energies were incorporated in both IPA and Chebyshev polynomial fitting routines. The obtained PEC reproduces experimental term values with a standard deviation of 0.005 cm^{-1} . PEC showed that KCs $(4)^1\Sigma^+$ state is a shelf-like state (see Fig. 4). In experiments it was established that $(4)^1\Sigma^+$ levels fluoresce not only to the ground state $\text{X}^1\Sigma^+$, but also to the triplet ground state $a^3\Sigma^+$ (see Fig. 13). This implies that $(4)^1\Sigma^+$ state has an admixture of a triplet state. In spite of this it became possible to accurately represent the whole data set with one PEC. The obtained PEC is published in the paper [8]. Triplet admixture to the $(4)^1\Sigma^+$ state means also that transitions from the $a^3\Sigma^+$ state to the $(4)^1\Sigma^+$ state and then to the $\text{X}^1\Sigma^+$ state are possible. This opportunity is essential for stabilization of cold molecules in the lowest ground rovibronic state. We have performed numerical simulations of such optical cycle in order to determine from which near-dissociation level of the $a^3\Sigma^+$ state it is better to excite the 4 state for efficient subsequent transfer of the molecules into the ground state with $v = 0$. Simulation results are presented in paper [1]. Research results are also presented in the 10th international conference on atoms, molecules and photons (10th ECAMP).

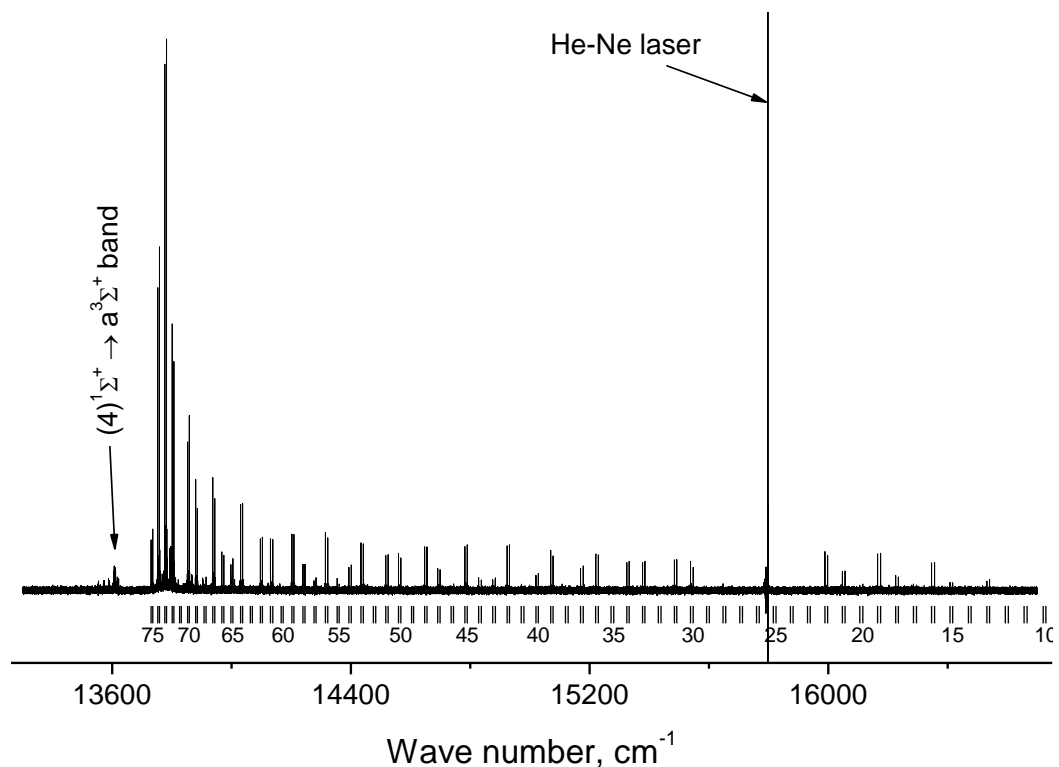


Fig. 13. Example of LIF from the $(4)^1\Sigma^+$ state in KCs. Around 13600 cm^{-1} one can see fluorescence to the $a^3\Sigma^+$ state.

2.4.2. RbCs molecule

We have performed experiments for obtaining of high-resolution RbCs $(4)^1\Sigma^+ - X^1\Sigma^+$ spectra which allowed us to extend significantly information about the $(4)^1\Sigma^+$ state high ($v > 83$), and low ($v < 5$) vibrational levels. This improved a PEC which was constructed using a Chebyshev polynomial expansion (CPE). 2317 term energies were incorporated into the fit and allowed for reproducing of experimental data with a standard deviation of 0.005 cm^{-1} . Similar to the case of KCs molecule RbCs $(4)^1\Sigma^+$ state has also a triplet admixture which opened possibility for performing simulation of the optical cycle $a^3\Sigma^+ \rightarrow (4)^1\Sigma^+ \rightarrow X^1\Sigma^+ (v = 0)$. Example of such simulation is shown in Fig. 14. Results are presented in paper [4].

2.5. KCs ground state studies in the near-dissociation region

Information about the ground state in the near-dissociation region is of great importance for cold molecule formation experiments using Feshbach resonances. PEC behavior near the asymptote determines the positions and widths of Feshbach resonances. During the studies of the $(4)^1\Sigma^+$ state we have observed LIF to the $X^1\Sigma^+$ state levels only few cm^{-1} from the asymptote therefore we have made improvements of our experimental set-up (acquired new optical filters) in order to increase signal-to-noise ratio (SNR) for weak signals in the near-asymptotic region. After narrowing

the detected optical range and many hours of signal acquisition we were able to increase SNR substantially and thus to identify LIF to levels which have binding energy of 0.3 cm^{-1} . An example of such spectrum is shown in Fig. 15. New data allowed us to extend PEC description till 20 \AA . Publication preparation is in progress.

2.6. Other activities in the framework of the Project

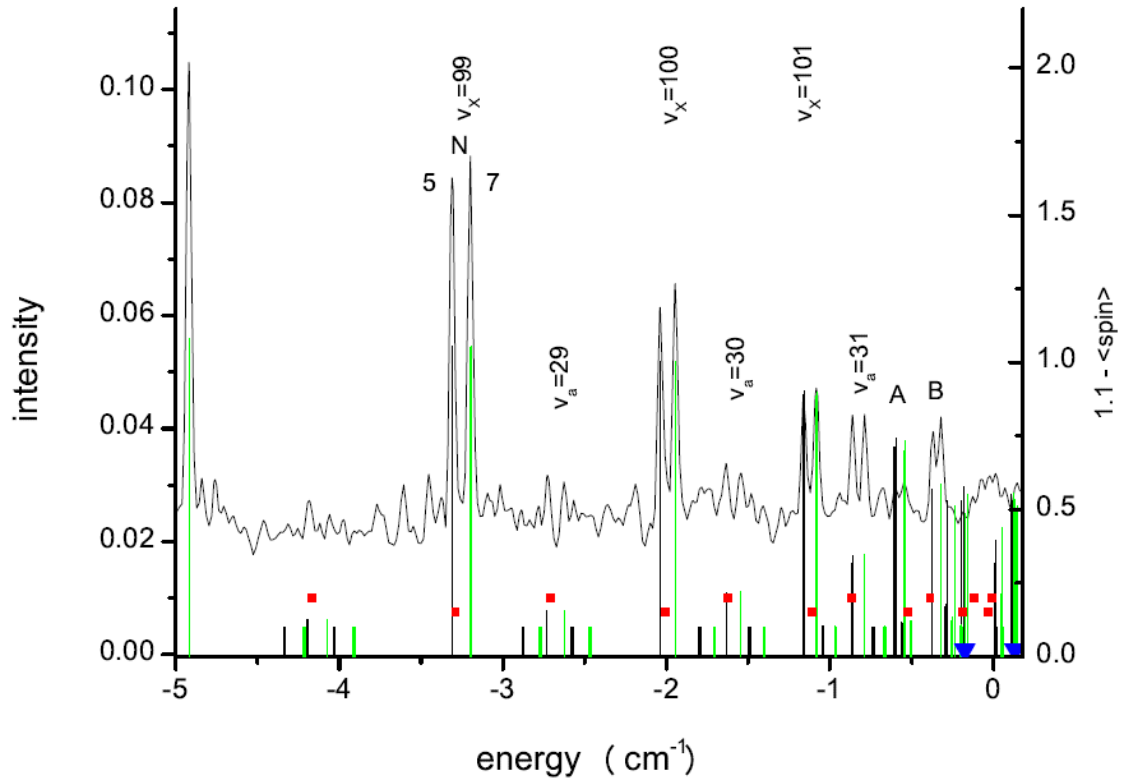


Fig. 15. Vibrational-rotational pattern for rotational quantum numbers $N=5$ un 7 in the vicinity of the $(4s)K+(6s)Cs$ asymptote compared with the coupled-channel calculations (vertical coloured lines) using improved PEC. Energies are relative to the $(4s)K+(6s)Cs$

We have measured high-resolution Fourier spectra in the hollow cathode lamp for La, Nb, V in order to obtain hyperfine structure constants (HFS) for new levels. Atomic transition spectra were recorded for La, Nb, V in a wide energy range, including the first observations in the infrared region till 1600 nm , Vanadium spectra are identified and the results are published in [5].

Publications

1. **I. Klincare, O. Nikolayeva, M. Tamanis, R. Ferber, E. A. Pazyuk, and A. V. Stolyarov**, Modeling of the $X^1\Sigma^+; a^3\Sigma^+ \rightarrow E(4)^1\Sigma^+ \rightarrow X^1\Sigma^+$ ($v = 0; J = 0$) optical cycle for ultracold KCs molecule production, *Phys. Rev. A* **85**, 062520 (2012).
2. **I. Birzniece, O. Nikolayeva, M. Tamanis, and R. Ferber**, $B(1)^1\Pi$ state of KCs: High-resolution spectroscopy and description of low-lying energy levels, *J. Chem. Phys.* **136**, 064304 (2012).
3. **I. Birzniece, O. Docenko, O. Nikolayeva, M. Tamanis, and R. Ferber**, $B(1)^1\Pi$ state of RbCs: high resolution spectroscopy and description of low-lying energy levels, *submitted to J. Chem. Phys.*
4. **V. Zutters, O. Docenko, M. Tamanis, and R. Ferber**, Spectroscopic studies of the $(4)^1\Sigma^+$ state in RbCs and modeling of the optical cycle for ultracold $X^1\Sigma^+$ ($v=0, J=0$) molecule production, *submitted to Phys. Rev. A*
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6. **O. Docenko, M. Tamanis, R. Ferber, H. Knöckel, E. Tiemann**, Singlet and triplet potentials of the ground-state atom pair Rb+Cs studied by Fourier-transform spectroscopy, *Phys. Rev. A* **83**, 052519 (2011).
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8. **L. Busevica, I. Klincare, O. Nikolayeva, M. Tamanis, R. Ferber, V.V. Meshkov, E.A. Pazyuk, and A.V. Stolyarov**, Fourier transform spectroscopy and direct potential fit of a shelflike state: Application to $E(4)^1\Sigma^+$ KCs, *J. Chem. Phys.* **134** 104307 (2011).
9. **M. Tamanis, I. Klincare, A. Kruzins, O. Nikolayeva, and R. Ferber, E. A. Pazyuk and A. V. Stolyarov**, Direct excitation of the “dark” $b^3\Pi$ state predicted by deperturbation analysis of the $A^1\Sigma^+-b^3\Pi$ complex in KCs, *Phys. Rev. A* **82**, 032506 (2010).
10. **P. Zabawa, A. Wakim, A. Neukirch, C. Haimberger, N. P. Bigelow, A. V. Stolyarov, E. A. Pazyuk, M. Tamanis, and R. Ferber**, Near-dissociation photoassociative production of deeply bound NaCs molecules, *Phys. Rev. A* **82**, 040501 (2010).

Conference theses

1. **Artis Kruzins, Kalvis Alps, Olga Docenko, Ilze Klincare, Maris Tamanis, Ruvin Ferber, Andrei V. Stolyarov** “High Resolution Spectroscopic Study of the $A^1\Sigma^+-b^3\Pi$ Complex in RbCs Molecule”, *The 23rd International Conference on Atomic Physics (ICAP) 2012*, July 23-27, 2012 Ecole Polytechnique, Palaiseau, France, Book of Abstracts, p.299.
2. **Inese Birzniece, Olga Docenko, Olga Nikolayeva, Maris Tamanis, and Ruvin Ferber**, "High resolution spectroscopy and description of low-lying energy levels of $B(1)^1\Pi$ state in RbCs", *The 22nd International Conference on High Resolution Molecular Spectroscopy*, September 4 – 8, 2012 Prague, Czech Republic.
3. **I. Birzniece, O. Docenko, O. Nikolayeva, M. Tamanis, and R. Ferber**, „Fourier Transform Spectroscopy of $B^1\Pi$ State in RbCs”, *44th Conference of the European Group for Atomic Systems (EGAS)*, July 9 - 13, 2012, University of Gothenburg, Gothenburg, Sweden, *Europhysics Conference Abstracts*, **36C**, p.157.

4. **I. Birzniece, O. Nikolayeva, M. Tamanis, and R. Ferber** "Fourier transform spectroscopy and potential construction for low vibrational levels of $B^1\Pi$ state in KCs", *43rd Conference of the European Group for Atomic Systems (EGAS)*, University of Fribourg, Fribourg, Switzerland, June 28 - July 2, 2011, Europhysics Conference Abstracts, **35C**, p.165.
5. **A. Kruzins, I. Klincare, O. Nikolayeva, M. Tamanis, R. Ferber, E.A. Pazyuk, and A.V. Stolyarov** „Novel study of the $A^1\Sigma^+ \sim B^3\Pi$ complex in KCs and refinement of deperturbation analysis”, *43rd Conference of the European Group for Atomic Systems (EGAS)*, University of Fribourg, Fribourg, Switzerland June 28 - July 2, 2011, Europhysics Conference Abstracts, **35C**, p.172.
6. **V. I. Pupyshev, E. A. Pazyuk, A. V. Stolyarov, O. Nikolayeva, I. Klincare, M. Tamanis, R. Ferber** „Insight into nodal structure of non-adiabatic diatomic states”, *22nd Colloquium on High Resolution Molecular Spectroscopy*, Dijon, France, August 29 – September 2, 2011, Program and Abstracts, p.260.
7. **I. Birzniece, O. Nikolayeva, M. Tamanis, R. Ferber** „Fourier Transform Spectroscopy and Molecular Constants for Low Vibrational Levels of $B^1\Pi$ State in KCs”, *22nd Colloquium on High Resolution Molecular Spectroscopy*, Dijon, France, August 29 – September 2, 2011, Program and Abstracts, p.234.
8. **O. Nikolayeva, M. Tamanis, R. Ferber** „KCs Ground State Revisited: Observation of Vibrational Levels Close to Atomic Asymptote Through $(4)^1\Sigma^+ \rightarrow X^1\Sigma^+$ Transition”, *22nd Colloquium on High Resolution Molecular Spectroscopy*, Dijon, France, August 29 – September 2, 2011, Program and Abstracts, p.261.
9. **M. Tamanis, L. Busevica, R. Ferber, I. Klincare, V. V. Meshkov, O. Nikolayeva, E. A. Pazyuk, A. V. Stolyarov** „Potential energy curve construction of the $(4)^1\Sigma^+$ state of KCs based on $(4)^1\Sigma^+ - X^1\Sigma^+$ transition study”, *10th European conference on atoms molecules and photons (ECAMP X)*, Spain, Salamanca, July 4-9, 2010, Conference Abstracts.
10. **M. Tamanis, O. Docenko, R. Ferber, H. Knockel, E. Tiemann** „Fourier transform spectroscopy of the $a^3\Sigma^+$ and $X^1\Sigma^+$ states in RbCs”, *10th European conference on atoms molecules and photons (ECAMP X)*, Spain, Salamanca, July 4-9, 2010, Conference Abstracts.
11. **A. Stolyarov, E. Pazyuk, M. Tamanis, L. Busevica, R. Ferber, I. Klincare, O. Nikolayeva** "Experimental and computational study of the spin-orbital coupling effect in $(2)^1\Pi$ KCs", *10th European conference on atoms molecules and photons (ECAMP X)*, Spain, Salamanca, July 4-9, 2010, Conference Abstracts.