Fourier transform spectroscopy of the $A^1\Sigma^+$ and $b^3\Pi$ states in RbCs: observation of "dark" $b^3\Pi_0^+$ levels below the $A^1\Sigma^+$ state

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The $A^1\Sigma^+$ and $b^3\Pi$ states in RbCs are strongly mixed due to spin – orbit (SO) interaction, which is larger than the vibrational intervals in these states. The description of this very complicated system is based on multichannel deperturbation model involving several mutually interacting electronic states. First qualitative high resolution study of the $A^1\Sigma^+$ and $b^3\Pi$ states (A-b in short) in RbCs [1] covers energy range from 10070 to 12420 cm $^{-1}$, and, derived from these data, deperturbation parameters reproduce satisfactory observed term values, however, with typical uncertainty larger than experimental one.

The goal of the present study was to extend the energy range of the experimental data of the $A^1\Sigma^+$ and $b^3\Pi$ states and to perform improved global deperturbation analysis to be able to reproduce rovibronic level structure with experimental accuracy 0.01 cm⁻¹. Experiment was based on combination of Fourier transform (FT) spectroscopy and laser induced fluorescence (LIF) detected either from directly excited A-b rovibronic levels, or from excited the (4) $^1\Sigma^+$ state to A-b. The LIF from the (4) $^1\Sigma^+$ to A-b appeared to be very suitable at the final stage of the present A-b study for observation of "dark", weakly perturbed, $b^3\Pi_0^+$ vibrational levels below A – state.

RbCs molecules were produced in a stainless steel heat pipe. LIF spectra were recorded by FT spectrometer Bruker IFS - 125HR with a resolution of 0.03-0.05 cm⁻¹. Direct excitation of the A-b complex was performed by several diode lasers (laser diodes covered the range from 830 nm to 1060 nm). The (4) $^1\Sigma^+$ state was excited by a single mode ring dye laser with Rhodamin6G dye. The LIF was detected by two InGaAs detectors to cover the spectral range from 4500 to 11000 cm⁻¹. Excitation of the (4) $^1\Sigma^+$ state around v'=25 allowed us to observe in LIF a number of very weak transitions to the $b^3\Pi_0^+$ levels, the lowest reached level is $v_{b0}^+=3$. On the other hand, for observation of high rovibronic levels with energy over 13000 cm⁻¹, the (4) $^1\Sigma^+$ state was excited at the range of v' around 55. Overall 5700 term values in energy range from 9000 to 13150 cm⁻¹ were determined for 85 Rb 133 Cs and included in the fit. As a result improved empirical potential energy curves of $A^1\Sigma^+$ and $b^3\Pi$ states and SO functions were obtained. Reliability of the deperturbation model is confirmed by comparison of predicted and measured 1450 term values of 87 Rb 133 Cs.

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[1] O. Docenko, M. Tamanis, R. Ferber, T. Bergeman, S. Kotochigova, A. V. Stolyarov, Andreia de Faria Nogueira, and C. E. Fellows, *Physical Review A*, 2010, **81**, 042511.