Direct deperturbation analysis of the $A^1\Sigma^+ \sim b^3\Pi$ complex in LiCs based on polarization labelling spectroscopy and *ab initio* calculation

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For several years the mixed $A \sim b$ levels provided convenient windows to study the triplet manifold of excited states by perturbation-facilitated optical-optical double resonance transitions from the ground state of singlet symmetry $X^1\Sigma^+$ [1]. In more recent times the attention has been drawn to the fact that the same perturbation can facilitate transfer of ultracold molecules derived from Feshbach resonances to the absolute ground state (i.e. $v_X = 0$, $J_X = 0$) by a stimulated Raman process [2]. This motivates recent experimental efforts to characterize the $A \sim b$ complex in heavy (Rb and Cs) alkali atom molecules such as NaRb, NaCs, KCs, RbCs, Rb_2 or Cs_2.

The present analysis was undertaken to provide the rigorous coupled-channel (CC) deperturbation treatment of about 780 rovibronic term values of the strongly spin-orbit (SO) coupled $A^1\Sigma^+$ and $b^3\Pi$ states of the ^{7}Li^{133}Cs molecule recorded by polarization labelling spectroscopy technique. The explicit $A^1\Sigma^+ \sim b^3\Pi_{\Omega=0,1,2}$ coupled-channels treatment allowed us to reproduce 95% experimental term values with a standard deviation of 0.05 cm^{-1} which is close to the accuracy of the present experiment. The initial potential energy curves (PECs) of the mutually perturbed states and spin-orbit (SO) matrix elements were *ab initio* evaluated in the basis of the spin-averaged wave functions. Both interacting $A^1\Sigma^+$ and $b^3\Pi$ states are described by the analytical potentials defined by the "Expanded Morse Oscillator" (EMO) form. The direct SO coupling between the $b^3\Pi_0$ sub-state and $A^1\Sigma^+$ state as well as the spin-rotational mixing of different $b^3\Pi_{0,1,2}$ sub-states is explicitly taken into account using a semi-empirical, "morphed" form of the *ab initio* SO matrix elements.

The developed CC deperturbation model allowed us to assign more lines in the recorded spectra and to reproduce most of the experimental observations with an accuracy consistent with experimental uncertainties, thus considerably surpassing the accuracy of the previous study [3]. Furthermore, the achieved accuracy encouraged to imply the empirically refined PECs and SO functions as well as *ab initio* $A^1\Sigma^+ - X^1\Sigma^+$ and $b^3\Pi - a^3\Sigma^+$ transition moments to predict energy and radiative properties of the $A \sim b$ complex of both ^{6,7}LiCs isotoplogues. The information could be useful for perturbation-facilitated double resonance experiments as well as to optimize formation and detection of ultracold LiCs molecules in their absolute ground state [4].

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References

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