High resolution study and deperturbation analysis of the $A^1\Sigma^+ - b^3\Pi$ complex in KRb

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In heavy heteronuclear alkali diatomic molecules containing Rb and Cs atoms the lowest excited $A^1\Sigma^+$ and $b^3\Pi$ states ($A - b$ complex for short) are strongly coupled by spin-orbit (SO) interaction. An accurate description of such systems is a challenging task, which imposes a detailed experimental study and elaboration of a powerful deperturbation procedure. Recently this problem was successfully solved for NaRb [1], NaCs [2], KCs [3], RbCs [4] and Rb_2 [5] molecules. In these studies the term values of the $A - b$ complex were determined from laser induced fluorescence (LIF) spectra recorded by high resolution Fourier Transform (FT) spectrometer. The coupled-channel deperturbation analysis allowed to reproduce the obtained data with experimental accuracy 0.01 cm^{-1}.

The goal of the present work is to apply this approach for the KRb $A - b$ complex. In the experiment KRb molecules were produced in a linear stainless steel heat pipe. The laser beam was sent into the heat pipe through a pierced mirror. The backwards LIF was collected by the same mirror and focused on the input aperture of the FT spectrometer Bruker IFS-125HR and recorded with a resolution of 0.03-0.05 cm^{-1}. We used a direct $(A^1\Sigma^+ - b^3\Pi) \leftarrow X^1\Sigma^+$ excitation by diode lasers (980 - 1020 nm) and by Ti:Sph laser (Coherent MBR-110) followed by observation of the $(A^1\Sigma^+ - b^3\Pi) \rightarrow X^1\Sigma^+$ LIF. Overall more than 300 LIF spectra were recorded and 900 KRb progressions for $^{39}K^{85}Rb$ and $^{39}K^{87}Rb$ isotopologues were analyzed yielding more than 4000 term values of the $A - b$ complex, including the data from collisional rotational energy transfer. The data field contains rovibronic levels with rotational quantum numbers $J \in [3, 279]$ in the energy range $E \in [10927, 14250]$ cm^{-1}.

A direct deperturbation treatment of the experimental rovibronic term values of both isotopologues of the mutually perturbed $A^1\Sigma^+$ and $b^3\Pi$ states was accomplished in the framework of inverted coupled-channel approach by means of the 4x4 Hamiltonian constructed in Hund's (**a**) coupling case basis functions. The Expanded Morse Oscillator model was used to describe potential energy curves while for the SO coupling functions we adopted the "morphed" form of the relevant *ab initio* spin-orbit matrix elements. As a result, 44 mass-invariant fitting parameters of the corresponding functions have been required to reproduce 96% of experimental term values of the $A - b$ complex with a standard deviation of 0.004 cm^{-1}. The energy-based deperturbation analysis was additionally confirmed by a calculation of relative intensity distributions in the $A - b \rightarrow X$ LIF progressions.

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