Spectroscopic study of the $4^1\Sigma^+$ state of LiCs and comparison with theory

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The $4^1\Sigma^+$ electronic state of ^{7}LiCs molecule was investigated experimentallly for the first time. Two colour polarization labelling experiment (see e.g. [1]) measuring the $4^1\Sigma^+ \leftarrow X^1\Sigma^+$ band system under rotaional resolution furnished energies of about 400 rovibronic levels in the $4^1\Sigma^+$ state with an accuracy better than 0.1 cm^{-1}. The observed vibrational progressions exhibited irregular intervals for two reasons. First, the potential curve of the $4^1\Sigma^+$ state was expected to be of irregular shape because of an anticrossing with the lower $3^1\Sigma^+$ state. Second, numerous strong, local perturbations of $4^1\Sigma^+$ by the neighbouring electronic states were evident. To aid the interpretation of the experiment, theoretical calculations of adiabatic potentials for excited states of LiCs including $4^1\Sigma^+$ were performed with the MOLPRO program package [2]. They confirmed the assumption of unusual shape of the $4^1\Sigma^+$ state potential and also provided a good starting point for the inverted perturbation approach (IPA) procedure [3], which allowed to construct the potential energy curve of this state from the experimental observations. A full deperturbation treatment of the $4^1\Sigma^+$ state was not attempted, but a robust weighting scheme [4] was used to reduce the influence of levels that cannot be properly represented by a single channel model. Parameters derived in a fit of the potential curve include term energy T_e=18848.4 cm^{-1}, well depth D_e=1931 cm^{-1} and equilibrium distance R_e=4.91 Å.

References

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