DIRECT-POTENTIAL-FIT ANALYSIS FOR $Li_2(a\,^3\Sigma_u^+)$ AND EXTENSIONS OF THE 'MLR' POTENTIAL FUNCTION MODEL

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While a number of studies of the weakly bound $a\,^3\Sigma_u^+$ state of $^{6,6}Li_2$ and $^{7,7}Li_2$ have been reported, the only potential functions obtained for these systems were based on point-wise semiclassical RKR curves generated from Dunham or near-dissociation expansions for the vibrational energies and B_v constants.[a] Moreover, to date the data for $^{6,6}Li_2$ and $^{7,7}Li_2$ have always been treated independently, so the effect of Born-Oppenheimer breakdown in this system is unknown.

The present work reports a combined-isotopologue direct-potential-fit analysis of all available fluorescence and PAS data for the $1\,^3\Sigma_g^+ - a\,^3\Sigma_u^+$ and $2\,^3\Pi_g - a\,^3\Sigma_u^+$ systems of $^{6,6}Li_2$ and $^{7,7}Li_2$. The analytic potential energy functions used to characterize the $a\,^3\Sigma_u^+$ and $1\,^3\Sigma_g^+$ states are extended versions of the 'Morse-Long-Range' (MLR) potential model which explicitly incorporates the theoretically-known inverse-power long-range behaviour within a unified potential function form.[b] 'Adiabatic' Born-Oppenheimer breakdown functions are required to yield a consistent analysis of the data for the two isotopologues, and they yield isotopologue-dependent well depths for these two states. The $-C_3/r^3$ limiting long-range behaviour of the $1\,^3\Sigma_g^+$-state potential presented a challenge to the use of the MLR potential function form with two or more long-range terms, and this led to better understanding and a significant extension of the MLR model.

[a](a) F. Martin *et al., Spectrochim. Acta* **44A**, 1369 (1988); (b) C. Linton *et al., J. Chem. Phys.* **91**, 6036 (1989); (c) W.T. Zemke and W.C. Stwalley, *J. Phys. Chem.* **97**, 2053 (1993); (d) A.J. Moerdijk *et al., Phys. Rev. Lett.* **72**, 40 (1994); (e) C. Linton *et al., J. Mol. Spectrosc.* **196**, 20 (1999).

[b]R.J. Le Roy, Y. Huang and C. Jary, *J. Chem. Phys.* **125**, 164310 (2006); R.J. Le Roy and R.D.E. Henderson, *Mol. Phys.* **105**, 663 (2007).