DIRECT-POTENTIAL-FIT FOR $Li_2(A\,^1\Sigma_u^+)$ USING A MODIFIED LONG-RANGE FORM THAT INCORPORATES THE TRANSITION FROM HUND'S CASE (a) to HUND'S CASE (c) COUPLING

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In recent work, Coxon and Melville[a] reported a comprehensive analysis of almost all available data for the $A\,^1\Sigma_u^+$ state of Li_2 observed in the *A–X* system and *E,F–A* systems, and determined analytic potential energy and Born-Oppenheimer breakdown functions which reproduced the experimental data within the estimated experimental uncertainties. The only shortcomings of that analysis were the neglect of photoassociation (PAS) data for levels very close to dissociation, and a limitation of the potential energy function used which would have made inclusion of those data problematic. In particular, at large internuclear distances, spin-orbit interactions mix the potentials for the $A\,^1\Sigma_u^+$ and $b\,^3\Pi_{0_u^+}$ states, so that the overall interaction cannot be properly described by the type of simple inverse-power term incorporated in the potential function form used by Coxon and Melville.[a] As a result, their A-state potential function dissociates to the Hund's case (a) limit, which lies between the two true spin-orbit Li(2p) levels. We introduce and apply an extension of a recently introduced "Morse/Long-Range" (MLR) potential function form[b] to re-investigate the $A\,^1\Sigma_u^+$ state of Li_2 as a single-channel problem. The modification takes account of spin-orbit coupling between the 0_u^+ components of the A and b states (perceptible beyond 50 Å), and the associated distance-dependent change in the character of the long-range multipole interaction.[c] A DPF fit using this new form fully accounts for all of the available data for this system, including the PAS measurements which had been omitted from the earlier analysis, and yields an analytic potential function which incorporates the effect of spin-orbit mixing near the Li(2s) + Li(2p) asymptote.

[a] J.A. Coxon and T.C. Melville, *J. Mol. Spectrosc.* **235**, 235 (2006).
[b] (a) R.J. Le Roy, Y. Huang and C. Jary, J. Chem. Phys. **125**, 164310 (2006); (b) R.J. Le Roy and R.D.E. Henderson, *Mol. Phys.* (2007, in press).
[c] M. Aubert-Frécon, G. Hadinger, S. Magnier and S. Rousseau, *J. Mol. Spectrosc.* **188**, 182 (1998).