DPF ANALYSES YIELD FULLY ANALYTIC POTENTIALS FOR THE $B\,^1\Pi_u$ "BARRIER" STATES OF $\mathrm{Rb_2}$ and $\mathrm{Li_2}$ AND AN IMPROVED GROUND-STATE WELL DEPTH FOR $\mathrm{Rb_2}$

KAI SLAUGHTER, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada*; NIKESH S. DATTANI, *Graduate School of Science, Department of Chemistry, Kyoto University, Kyoto, Japan*; CLAUDE S. AMIOT, *Laboratoire Aimé Cotton, CNRS, Orsay, France*; AMANDA J. ROSS, *UMR 5306, ILM University Lyon 1 and CNRS, Villeurbanne, France*; ROBERT J. LE ROY[a], *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada*.

Determining full model potential energy functions for molecular states that have a 'natural' rotationless barrier which protrudes above the potential asymptote, such as the $B\,^1\Pi_u$ states of alkali dimers, is a challenging problem. The present work extends our previous Direct-Potential-Fit (DPF) analysis of data for the $B\,^1\Pi_u$ state of $\mathrm{Li_2}$[b] by introducing a more sophisticated model for the long-range tail of the fully analytic 'Double Exponential Long-Range' (DELR) potential function form[a] that takes account of the interstate coupling that occurs near the asymptotes of $nS + nP$ alkali dimers.[c] This type of analysis is then applied to data for the $B\,^1\Pi_u$ state of $\mathrm{Rb_2}$, and a concurrent extension of the DPF analysis of Seto and Le Roy[d] yields an improved fully analytic potential energy function for its ground $X\,^1\Sigma_g^+$ state. The effect of taking account of the long-range inter-state coupling on the shapes of the outer walls of the $B\,^1\Pi_u$ state potential functions for these two species will also be examined.

---

[a] leroy@uwaterloo.ca

[b] Y. Huang and R.J. Le Roy, *J. Chem. Phys.*, **119**, 7398 (2003)

[c] M. Aubert-Frécon and G. Hadinger and S. Magnier and S. Rousseau, *J. Mol. Spectosc.*, **288**, 182 (1998).

[d] J.Y. Seto and R.J. Le Roy, *J. Chem. Phys.*, **113**, 3067 (2000).