AN EXTENSION OF THE ‘MLR’ POTENTIAL FUNCTION FORM WHICH ALLOWS FOR AN ACCURATE DPF TREATMENT OF Li₂(1³Σ⁺), WHICH COUPLES TO TWO OTHER STATES NEAR THEIR ASYMPTOTES

NIKESH S. DATTANI and ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada; AMANDA J. ROSS, Université de Lyon F-69622, Lyon, France; Université Lyon 1, Villeurbanne; CNRS, UMR5579, LASIM; COLAN LINTON, Physics Department, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada.

The only potential energy functions for the 1³Σ⁺ state of Li₂ published to date were conventional RKR curves based on experimental data for the vibrational levels v = 1 – 7, and they do not yield realistic predictions for the very weakly bound levels v = 62 – 89 for 7,7Li₂ and v = 59–79 for 6,6Li₂, which were subsequently observed using photoassociation spectroscopy (PAS). A recent analysis of data for the 1³Σ⁺ – a 3Σ⁺ and 2³Π – a 3Σ⁺ systems of Li₂ was unable to incorporate these PAS data, and this was due to the lack of a potential function form with the ability to accurately describe the behaviour of the potential for a molecule which becomes coupled to two other distinct states near the dissociation asymptote. The current work presents and tests an extension of the ‘Morse/Long-Range’ (MLR) potential function form which does provide an accurate description of the 1³Σ⁺ – state potential at all internuclear distances, including the long-range region where the three-state coupling occurs. The extension is based on expressions reported by Aubert-Fréon and co-workers, which show that the long-range tail of this potential is one of the eigenvalues of a 3x3 Hamiltonian matrix. Accordingly, this extension requires the diagonalization of this matrix at each internuclear distance r. Although this can be done analytically, we show that the diagonalization is in fact computed more efficiently numerically, and leads to a more accurate potential energy function.

---