IMPROVED POTENTIAL ENERGY CURVE AND MOLECULAR CONSTANTS FOR THE $A\,^3\Pi_{1u}$ STATE OF I_2

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Some years ago we reported an analysis of a high resolution absorption spectrum for the $A\,^3\Pi_{1u} - X\,^1\Sigma_g^+$ system of I_2 consisting of approximately 9700 lines from 79 bands spanning the vibrational range $v' = 0 - 35$ and $v'' = 3 - 17$.[a] Results were presented in the forms both of empirical Dunham-type expansions and of near-dissociation expansion (NDE) expressions for the band constants of the A–state. Because of the use of NDE's, the resulting expressions were expected to be fairly reliable for extrapolation to dissociation ($v_{\mathcal{D}} = 55.57(\pm 0.01)$). Shortly thereafter, Yukiya *et al.*[b] reported additional high resolution absorption data spanning the range $v'(A) = 16 - 45$, and showed that the Appadoo *et al.*[a] NDE expression for B_v did not, in fact, extrapolate reliably. However, they analyzed their results only in terms of a set of band constants for levels $v'(A) = 16 - 45$. The present paper describes a comprehensive analysis of both data sets (which together span 99.2% of the potential well) which critically compares the utility of Dunham expansions *vs.* NDE expressions *vs.* direct-potential-fit techniques, and yields an optimum description of this system.

[a] D.R.T. Appadoo, R.J. Le Roy, P.F. Bernath, S. Gerstenkorn, P. Luc, J. Vergès J. Sinzelle, J. Chevillard and Y. D'Aignaux, *J. Chem. Phys.* **104**, 903–913 (1996).

[b] T. Yukiya, N. Nishimiya and M. Suzuki, *J. Mol. Spectrosc.* **182**, 271–279 (1997).