DIRECT POTENTIAL FIT ANALYSIS OF EMISSION INTO X $^1\Sigma_g^+$ STATE Rb_2: NOTHING ELSE WILL DO!

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High resolution A–X emission data involving ground state levels up to $v'' = 111$ (spanning 99.5% of the potential well) have been acquired for three isotopomers of Rb_2 in the ground electronic state. While a good fit ($\bar{\sigma}_f = 1.18$) to the 12144 transition frequencies (with uncertainties $\pm 0.001\ \mathrm{cm}^{-1}$) is obtained from an unconstrained combined-isotopomer Dunham-type analysis, it requires a large number (66) of expansion parameters, and the resulting unconstrained centrifugal distortion constants (CDC's) will be unreliable for extrapolations to higher–J. Moreover, Dunham or near-dissociation expansion fits using constrained theoretical CDC's up to O_v fail to properly represent the data, as even higher-order CDC's are required. In contrast, a direct fit of these data to a "Modified Lennard-Jones" analytical potential[a] defined by only 15 fitted parameters yields essentially the same standard error as the unconstrained Dunham fit, and should yield reliable predictions for essentially all J's. This potential form incorporates the proper R^{-6} asymptotic behaviour and is constrained to have the theoretically predicted C_6 dispersion coefficient.[a] Although the data set involves the three isotopomers (85,85), (85,87) and (87,87), none of these analyses were able to determine any Born-Oppenheimer Breakdown effects.

[a] P.G. Hajigeorgiou and R.J. Le Roy, Paper WE04 at the *49'th Ohio State University International Symposium on Molecular Spectroscopy*, 1994