

NEW EMPIRICAL POTENTIAL ENERGY FUNCTIONS FOR THE HEAVIER HOMONUCLEAR RARE GAS PAIRS:  
Ne<sub>2</sub>, Ar<sub>2</sub>, Kr<sub>2</sub>, and Xe<sub>2</sub>

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The many decades of work on determining accurate analytic pair potentials for rare gas dimers from experimental data focussed largely on the use of bulk non-ideal gas and collisional properties, with the use of spectroscopic data being somewhat of an afterthought, for testing the resulting functions. This was a natural result of experimental challenges, as the very weak binding of ground-state rare gas pairs made high resolution spectroscopy a relatively late arrival as a practical tool in this area. However, we believe that it is now time for a comprehensive reassessment. Following up on a preliminary report at this meeting five years ago,<sup>a</sup> this paper describes work to determine a new generation of empirical potential energy functions for the four heavier (i.e., not involving He) homonuclear rare gas pairs from direct fits to all available spectroscopic, pressure virial, and acoustic virial coefficient data, with the resulting functions being ‘tuned’ by comparisons with available thermal transport property data: viscosity, mass diffusion and thermal diffusion, and thermal conductivity data, and tested against the best available *ab initio* potentials. The resulting functions are everywhere smooth and differentiable to all orders, incorporate the correct (damped) theoretical inverse-power long-range behaviour, and have sensible short-range extrapolation behaviour.

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<sup>a</sup>R.J. Le Roy, C.J.W. Mackie, P. Chandrasekhar and K.M. Sentjens, “*Accurate New Potential Energy Functions From Spectroscopic and Virial Coefficient Data for the Ten Rare Gas Pairs formed from Ne, Ar, Kr and Xe*”, paper MF03 at the 66<sup>th</sup> Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 13-17 (2011).