

HIGH-ACCURACY POTENTIALS FOR VAN DER WAALS SYSTEMS

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Recent experimental studies of vdWs systems including those by Moazzen-Ahmadi and McKellar,^{1,2} as well as microwave studies by Minei and Novick^{3,4} have observed previously unknown stable polar isomers for systems such as (NNO)₂ and (OCS)₂. The multi-welled floppy nature of the PESs and the small barriers between minima place stringent requirements on the PES for a successful theoretical description of these states. An automated method of generating accurate PESs for vdW systems has been developed and is demonstrated here.^{5,6} A limited number of ab initio data at the explicitly correlated CCSD(T)-F12b level are interpolated into analytic PESs with negligible fitting error. High-accuracy PESs were developed for a number of systems including (NNO)₂, (OCS)₂, (CO)₂, CO₂:CS₂ and (NH₃)₂.

Using the PESs, the rovibrational Schrödinger equation is solved with a symmetry-adapted Lanczos algorithm and an uncoupled product basis set. All inter-monomer coordinates are included in the calculations. Calculated transition frequencies are in very close agreement with experiment.

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