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 Novick3,4 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 Schrdinger 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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