

A NUMERICALLY EXACT FULL-DIMENSIONAL CALCULATION OF RO-VIBRATIONAL LEVELS OF WATER DIMER

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We have developed a new method for computing numerically exact rovibrational levels of a Van der Waals dimer with flexible monomers and applied it to water dimer, a 12-dimensional cluster. The method uses basis functions that are products of an inter-monomer function and an intra-monomer function. The inter-monomer function is a product of Wigner functions, used to study dimers within the rigid monomer approximation. The intra-monomer functions are monomer vibrational wavefunctions. When the coupling between inter- and intra-monomer coordinates is weak, this new basis is very efficient and only a few monomer vibrational wavefunctions are necessary. The product structure of the basis makes it efficient to use the Lanczos algorithm to calculate eigenvalues and eigenfunctions of the Hamiltonian matrix. In particular, potential matrix-vector products are evaluated, without storing the potential on a full-dimensional grid, by adapting the F-matrix idea previously used to compute rovibrational levels of 5-atom and 6-atom molecules with a contracted basis and an iterative eigensolver.^a We have obtained numerically exact and converged inter-monomer energy levels and compare these with results obtained using the 6D + 6D adiabatic approach on the CCpol-8sf *ab initio* potential energy surface.^b We have also obtained the water bend levels and their shifts. We compare with results of the previous adiabatic calculation and experiment.

^aX.-G. Wang and T. Carrington Jr. J. Chem. Phys. **119**, 101 (2003) and **129**, 234102 (2008).

^bC. Leforestier, K. Szalewicz, and A. van der Avoird, J. Chem. Phys. **137**, 014305 (2012).