

523. Accession number:WOS:000306142600018

Title:Spectra of water dimer from a new ab initio potential with flexible monomers

Authors:Leforestier, C. (1); Szalewicz, K. (2); van der Avoird, A. (3)

Author affiliation: (1) Univ Montpellier 2, CNRS, Inst Charles Gerhardt, CTMM,UMR 5253,CC 1501, F-34095 Montpellier 05, France; (2) Univ Delaware, Dept Phys & Astron, Newark, DE 19716 USA; (3) Radboud Univ Nijmegen, Inst Mol & Mat, NL-6525 AJ Nijmegen, Netherlands

Source title:JOURNAL OF CHEMICAL PHYSICS

Abbreviated source title:J CHEM PHYS

Volume:137

Issue:1

Issue date:JUL 7 2012

Pages:014305

Language:English

ISSN:0021-9606

Document type:Article

Publisher:AMER INST PHYSICS, CIRCULATION & FULFILLMENT DIV, 2 HUNTINGTON QUADRANGLE, STE 1 N O 1, MELVILLE, NY 11747-4501 USA

Abstract:We report the definition and testing of a new ab initio 12-dimensional potential for the water dimer with flexible monomers. Using our recent accurate CCpol-8s rigid water pair potential [W. Cencek, K. Szalewicz, C. Leforestier, R. van Harrevelt, and A. van der Avoird, Phys. Chem. Chem. Phys. 10, 4716 (2008)] as a reference for the undistorted monomers' geometries, a distortion correction has been added, which was taken from a former flexible-monomer ab initio potential. This correction allows us to retrieve the correct binding energy $D_e = 21.0 \text{ kJmol}^{-1}$, and leads to an equilibrium geometry in close agreement with the one obtained from benchmark calculations. The kinetic energy operator describing the flexible-monomer water dimer has been expressed in terms of Radau coordinates for each monomer and a recent general cluster polyspherical formulation describing their relative motions. Within this formulation, an adiabatic scheme has been invoked in order to decouple fast (intramolecular) modes and slow (intermolecular) ones. Different levels of approximation were tested, which differ in the way in which the residual potential coupling between the intramolecular modes located on different monomers and the dependence of the monomer rotational constants on the dimer geometry are handled. Accurate calculations of the vibration-rotation-tunneling levels of $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$ were performed, which show the best agreement with experiments achieved so far for any water potential. Intramolecular excitations of the two monomers were calculated within two limiting cases, to account for the lack of non-adiabatic coupling between intramolecular modes due to the intermolecular motion. In the first model, the excitation was assumed to stay either on the donor or the acceptor molecule, and to hop between the two moieties upon donor-acceptor interchange. In the second model, the excitation remains on the same molecule whatever is the dimer geometry. Marginal frequency differences, less than 2 cm^{-1} , were obtained for all modes, and the resulting infrared shifts are in good agreement with experiments. (C) 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4722338>]

Number of references:71

Main heading:Physics

DOI:10.1063/1.4722338