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Accession number:20123415361317
Title:Understanding the origins of dipolar couplings and correlated motion in the vibrational spectrum of water
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Source title:Journal of Physical Chemistry Letters
Abbreviated source title:J. Phys. Chem. Lett.
Volume:3
Issue:16
Issue date:August 16, 2012
Publication year:2012
Pages:2135-2140
Language:English
E-ISSN:19487185
Document type:Journal article (JA)
Publisher:American Chemical Society, 2540 Olentangy River Road, P.O. Box 3337, Columbus, OH 43210-3337, United States
Abstract:The combination of vibrational spectroscopy and molecular dynamics simulations provides a powerful tool to obtain insights into the molecular details of water structure and dynamics in the bulk and in aqueous solutions. Applying newly developed approaches to analyze correlations of charge currents, molecular dipole fluctuations, and vibrational motion in real and k-space, we compare results from nonpolarizable water models, widely used in biomolecular modeling, to ab initio molecular dynamics. For the first time, we unfold the infrared response of bulk water into contributions from correlated fluctuations in the three-dimensional, anisotropic environment of an average water molecule, from the OH-stretching region down to the THz regime. Our findings show that the absence of electronic polarizability in the force field model not only results in differences in dipolar couplings and infrared absorption but also induces artifacts into the correlated vibrational motion between hydrogen-bonded water molecules, specifically at the intramolecular bending frequency. Consequently, vibrational motion is partially ill-described with implications for the accuracy of non-self-consistent, a posteriori methods to add polarizability. © 2012 American Chemical Society.
Number of references:28
Main heading:Molecular dynamics
Controlled terms:Couplings - Molecules - Polarization
Uncontrolled terms:Ab initio molecular dynamics - Bending frequency - Bio-molecular - Bulk water - Charge current - Correlated fluctuations - Correlated motions - Dipolar couplings - Electronic-polarizability - Force field models - Hydrogen-bonded water molecules - Infrared

response - K-space - Molecular dipole - Molecular dynamics simulations - Polarizabilities - Posteriori - Vibrational motions - Water models - Water molecule - Water structure
Classification code:602 Mechanical Drives and Transmissions - 711.1 Electromagnetic Waves in Different Media - 801.4 Physical Chemistry - 931.3 Atomic and Molecular Physics
DOI:10.1021/jz300748s
Database:Compendex
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