H-bonding network and the far Infrared spectrum of liquid water\(^1\)

MANU SHARMA, Department of Chemistry, Washington Road, Princeton University, Princeton, NJ 08544, RAFFAELE RESTA, INFM DEMOCRITOS National Simulation Center, via Beirut 2, I-34014 Trieste, Italy, ROBERTO CAR, Department of Chemistry, Washington Road, Princeton University, Princeton, NJ 08544

We have performed Car-Parrinello molecular dynamics simulation based on maximally localized Wannier functions on a computational sample of liquid water containing 64 molecules in a cubic supercell. Using the Wannier function centers along the molecular dynamics trajectory, we have calculated the Infrared spectrum of liquid water and analyzed in detail the far Infrared region of the spectrum. We have devised several correlation functions that allow us to “cleanly” isolate the features of the spectrum in the far Infrared region. We observe that the \(~200 \text{ cm}^{-1}\) peak in the Infrared spectrum arises due to dynamical charge transfer between a water molecule and its nearest neighbors. Furthermore, we provide evidence that this peak is strongly anisotropic in nature and is Infrared active only when the local H-bonding environment in liquid water changes asymmetrically.

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