

Which quantum statistics–classical dynamics method is best for water?

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There are a variety of methods for including nuclear quantum effects in dynamics simulations by combining quantum Boltzmann statistics with classical dynamics. Among them are thermostatted ring-polymer molecular dynamics (TRPMD) [1], centroid molecular dynamics (CMD) [2], quasi-centroid molecular dynamics (QCMD) [3], and the linearised semi-classical initial value representation (LSC-IVR) [4]. Here we make a systematic comparison of these methods by calculating the infrared spectrum of water in the gas phase, and in the liquid and ice phases (using the q-TIP4P/F model potential [5]). Some of these results are taken from previous work, some of them are new (including the LSC-IVR calculations for ice, and extensions of all the spectra into the near-infrared region dominated by overtone and combination bands). Our results suggest that QCMD is the best method for reproducing fundamental transitions in the spectrum, and that LSC-IVR gives the best overall description of the spectrum (albeit with large errors in the bend fundamental band caused by zero-point-energy leakage). The TRPMD method gives damped spectra that line up with the QCMD spectra, and is by far the cheapest method [6].

References

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