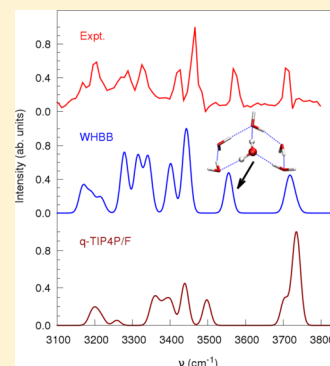


# Ab Initio Quantum Approaches to the IR Spectroscopy of Water and Hydrates

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**ABSTRACT:** This Perspective highlights progress in ab initio quantum approaches to IR spectroscopy of water and hydrates. Here, “ab initio” refers to many-body potentials and dipole moment surfaces for flexible water and hydrates. Specifically, these are mathematical representations of two-body and three-body interactions based on permutationally invariant fitting of tens of thousands of ab initio electronic energies, a spectroscopically accurate one-body monomer potential, and four- and higher-body interactions described by the long-range interactions incorporated into, for example, the TTM3-F family of potentials. There are currently two such potentials of this type, denoted WHBB and MB-pol, which are being used in expanding applications. Here, the focus is on infrared spectroscopy, using the WHBB potential and dipole moment surface, with an embedded, local monomer quantum method to obtain vibrational energies and dipole transition moments. Comparisons are also made with the popular q-TIP4P/F potential. Brief mention is made of an application to small HCl–H<sub>2</sub>O clusters.



The intense and widespread interest in the physical and chemical properties of water is both obvious from reading the literature and understandable from the central role that water plays in sustaining, if not originating, life. It is also clear that in many respects, water is a “quantum substance”. The simple fact that heavy water (D<sub>2</sub>O water) is toxic to life is almost certainly a manifestation of the quantum nature of H<sub>2</sub>O water.

Considering water as encompassing clusters, starting with the dimer to bulk ice and liquid phases, the IR spectroscopy of water is a huge topic and a major challenge for theoretical/computational spectroscopy.

The quantum nature of water is manifested, perhaps less dramatically, in the infrared (and neutron scattering) spectrum. Considering water as encompassing clusters, starting with the dimer to bulk ice and liquid phases, the IR spectroscopy of water is a huge topic and a major challenge for theoretical/computational spectroscopy. The spectral regions of the intramolecular bend at around 1600 cm<sup>−1</sup> up to the signature H-bond OH -stretch region at around 3400 cm<sup>−1</sup> have received the most attention. The low-frequency intermolecular region is also of interest; however, it is not as accessible experimentally as the high-frequency intramolecular region.

The simplest approach to simulate these spectra makes use of model potentials, for example, two-body Lennard-Jones plus Coulomb point-charge interactions (which give the dipole

moment) plus a simple monomer potential. These model potentials and dipole moments are used in a classical simulation, from which the dipole correlation function is calculated. The IR spectrum is directly obtained from the dipole correlation function via the usual Fourier transformation, perhaps with a harmonic quantum partition function “correction”. Examples of such potentials that are in wide use are SPC/Fw<sup>1,2</sup> and TIP4P/F.<sup>3</sup> These are both extensions of widely used antecedent point-charge models for rigid monomers that have appended separable expressions for the monomer bend and OH stretch potentials. Further refinements of these models to consider quantum effects were done recently. These potentials are denoted q-SPC/Fw<sup>4</sup> and q-TIP4P/F.<sup>5</sup> The former one was developed by Paesani et al.,<sup>4</sup> based mainly on liquid property results obtained using centroid molecular dynamics (CMD).<sup>6,7</sup> This potential was also used in calculations of the IR spectrum and self-diffusion constant of water<sup>8</sup> using the linearized IVR theory of Miller.<sup>9</sup> q-TIP4P/F was developed by Habershon et al.<sup>5</sup> based on ring polymer molecular dynamics (RPMD) simulations.<sup>10,11</sup> The dipole moment in each case is still obtained using the expression for fixed point-charges on each monomer and therefore are clearly of limited accuracy. These potentials do not describe dynamic polarization of the monomers and therefore are very efficient to evaluate. They also do not describe three- or higher-body effects. An example of a more sophisticated, flexible potential and dipole moment that does describe polarization is the TTM3-F potential.<sup>12</sup> In TTM3-F, the unperturbed monomer potential is described by a spectroscopically accurate one,<sup>13</sup> but

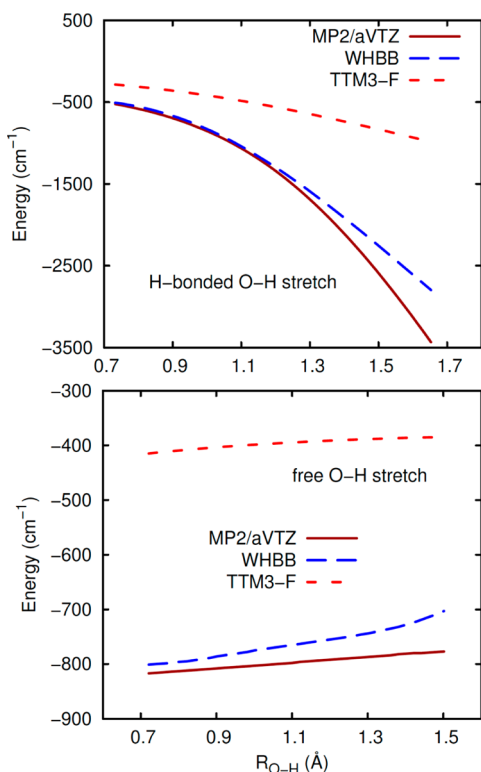
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the monomer dipole moment is modified to apply to the IR intensity of liquid water. Three- and higher-body interactions in TTM3-F are limited to long-range polarization/induction interactions. This potential and dipole moment have been used in CMD<sup>14</sup> and RPMD<sup>11</sup> calculations of the IR spectrum of liquid water.

From direct ab initio calculations on water clusters, with a special focus on the isomers of the hexamer<sup>15–17</sup> and now for clusters in the low 20s,<sup>17–19</sup> three-body interactions have been shown to account for roughly 18% of the electronic binding energy, while two-body interactions account for roughly 80% and four- and higher body interactions account for the remaining few percent. Clearly then, the three-body interaction is significant. In the context of IR spectroscopy, an examination of the three-body interaction as a function of the OH stretch coordinate is particularly relevant. This is shown in Figure 1 for



**Figure 1.** Variation of the three-body energy with the two OH stretches for the water trimer at the global minimum, from the indicated sources. The OO distance is 2.8 Å.

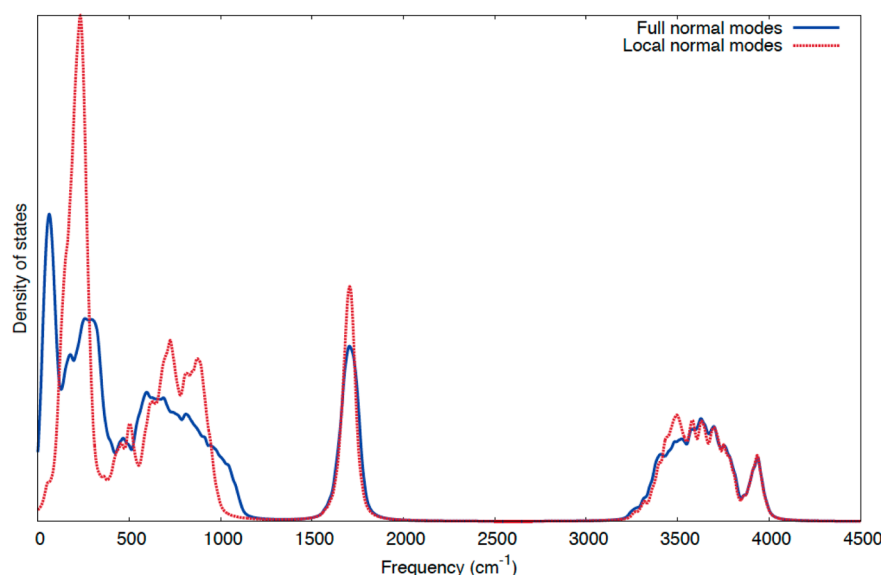
the water trimer at the equilibrium planar ring configuration (up–down–up). (This figure is similar to one shown earlier by Wang et al.<sup>17</sup> who examined ab initio two- and three-body interactions for many trimer configurations in connection with developing fits to ab initio two- and three-body interactions.) As seen, the three-body energy directly obtained from MP2/aug-cc-pVTZ calculations is much larger than the induction contribution described in TTM3-F, especially for the H-bonded OH stretch, where its variation with OH bond length is large. The fits labeled WHBB are from a precise mathematical fit to tens of thousands of three-body interactions, which will be briefly described below. As seen from this plot, the three-body interaction is large and also varies substantially with the OH bond length, especially the H-bonded OH stretch. Thus, this interaction is quite significant for vibrational energies in

addition to its major role in the binding energy. With this motivation, it is hopefully clear that a simple representation of the three-body interaction, from say induction only, is not adequate. Representing this interaction is not trivial, and we are not aware of a realistic model of the three-body interaction that could be accurately parametrized by, say, fitting a small number of parameters to a data set of three-body energies that span the relevant interaction region, including of course the OH stretches and bends. (For rigid monomers, such a representation of the three-body interaction has been reported based on fitting several hundred electronic energies.<sup>20</sup> Also, a very precise fit to thousands of high-level electronic, rigid monomer, three-body energies has recently been reported.<sup>21</sup> This is certainly the most accurate representation of rigid monomer three-body interactions currently available.) The alternative to a model is a high-dimensional mathematical fit to such data for flexible monomers. This is the approach that we have taken, as we describe next. The curves labeled WHBB in Figure 1 refer to such a fit.

To conclude this subsection, we note the important study of many-body interactions on harmonic frequencies on water clusters, up to the hexamer. These show the large role played by three-body interactions.<sup>22</sup>

**Ab Initio Potential Energy and Dipole Moment Surfaces.** The first effort that we are aware of to develop an ab initio water potential was the rigid monomer cc-Pol potential.<sup>16</sup> The most recent version of this potential uses very accurate ab initio electronic energies to represent two- and three-body interactions.<sup>21</sup> Obviously, this rigid monomer potential cannot be used for the calculation of the infrared spectra and/or general vibrational dynamics of intramolecular bends and stretches. The first potential developed for flexible monomers, based fully on ab initio electronic energies for two- and three-body interactions, is the so-called WHBB potential.<sup>17</sup> The monomer potential is represented by a spectroscopically accurate potential.<sup>13</sup> The two-body component of this potential is a permutationally invariant fit to roughly 30 000 CCSD(T)/aug-cc-pVTZ energies. The three-body potential is a permutationally invariant fit in 36 Morse variables (see below) to roughly 40 000 MP2/aug-cc-pVTZ energies. (The choice of MP2 for the calculation of this large number of three-body energies was made based on both the relative efficiency of that method and also the fact that three-body energies are roughly 1/5th the magnitude of the two-body ones.) These fits use a basis of permutationally invariant polynomials in so-called Morse variables of all of the internuclear distances,  $y_{ij} = \exp(-r_{ij}/\lambda)$ , as described in detail in ref 23. A subsequent ab initio, flexible, potential, “MB-pol”, is from the Paesani group.<sup>24,25</sup> It is similar in approach to WHBB (an earlier version used the two-body potential, denoted HBB2<sup>26</sup> contained in WHBB); however, it uses even more accurate CCSD(T) electronic energies and incorporates long-range electrostatic and induced interactions via switching functions similar to the procedure used in WHBB. It also uses permutationally invariant polynomials to represent the three-body energy. Currently, the only flexible ab initio dipole moment surface based on fitting ab initio data is part of the WHBB suite; it consists of invariant fits to monomer plus two-body MP2/aug-cc-pVTZ dipole moments. It has been tested against direct ab initio calculations up to the 20-mer.<sup>17</sup> It is the most accurate dipole moment surface available for water.

Before closing this subsection, it is perhaps useful to stress that these mathematical, many-body representations of the flexible water interactions occupy a unique niche in the large



**Figure 2.** Comparison of full and local normal mode harmonic density of states for the H<sub>2</sub>O 192-mer cluster with an Ice Ih configuration.

field of water potentials. There hopefully will be some future interaction between these representations and the more conventional and efficient ones. One major hurdle that we see to be overcome is an efficient and accurate representation of the three-body interaction over the entire range of interactions but especially in the region of OO distances of around 2.6–3.6 Å where exchange/repulsion interactions are large.

**Quantum Local Monomer Calculations of IR Spectra.** The quantum treatment of the IR spectrum is well-known in the context of gas-phase molecular spectroscopy. It is instructive though to remind the reader of the expression for the IR absorption intensity (in the usual weak-field and semiclassical treatment of the radiation field). It is

$$I(\omega, T) = \frac{\sum e^{-E_i\beta} \omega_{i \rightarrow f} R_{i \rightarrow f}}{\sum e^{-E_i\beta}} \quad R_{i \rightarrow f} = \sum_{\alpha} |\langle f | \mu_{\alpha} | i \rangle|^2$$

$$\omega_{i \rightarrow f} = \frac{(E_f - E_i)}{hc} \quad (1)$$

where  $|i\rangle$  and  $|f\rangle$  represent initial and final molecular eigenstates of the nuclear Hamiltonian,  $E_f$  and  $E_i$  are the corresponding energies,  $\mu_{\alpha}$  are the components of the dipole moment, and  $\beta$  is  $1/k_B T$ . (A similar expression applies for the Raman spectrum with the dipole moment replaced by the frequency-dependent polarizability tensor.) The rigorous application of the above equation to obtain the detailed (ro)vibrational IR spectrum is currently limited to tetraatomic and some special-case pentaatomic molecules. In most semiclassical or semiquantum theories, for example, CMD, RPMD, and IVR, the above expression, cast into a more compact form in terms of the usual Boltzmann trace over the Fourier transform of the exact quantum dipole correlation function, is used with further approximations to get the spectrum. This procedure is not applied here because we actually use eq 1 in the Local Monomer theory that we describe below.

For larger molecules, a vibrational spectrum is obtained by considering the zero-angular-momentum case and perhaps also by making further approximations to either the Hamiltonian or the treatment of the coupled vibrational dynamics. Such treatments in near or full dimensionality are feasible for the water dimer and trimer; see, for example, refs 25–27 and

references therein. However, for larger clusters, for example, the widely studied water hexamer, there are 48 vibrational degrees of freedom, and the exact application of a quantum approach, as in eq 1, is well beyond current computational resources. Another challenging issue for water clusters is the many isomeric forms of even a moderate-sized cluster. To describe this in an exact approach would require an exact treatment of the large-amplitude (perhaps tunneling) motion that connects all of these minima. However, progress can still be made because most experimental IR spectra of water are not at the level of resolution where fine structures, for example, tunneling splittings, are resolved. (These can and have been resolved in microwave spectroscopy of small water clusters.<sup>28</sup>)

With the given level of resolution in experimental IR spectra in mind, we developed an approximate embedded “Local Monomer” (LMon) method, specifically for water,<sup>27,29–34</sup> that aims to achieve a corresponding level of accuracy and resolution. This is a divide-and-conquer method that focuses on each monomer of a cluster (of arbitrary size) and solves the Schrödinger equation for monomer  $m$

$$[\hat{T}_m + U_m(Q_m) - E_i^{(m)}] \phi_i^{(m)}(Q_m) = 0 \quad (2)$$

where  $Q_m$  are the local normal modes of monomer  $m$  (see below),  $\hat{T}_m$  is the exact kinetic energy operator, and  $U_m$  is the potential experienced by monomer  $m$  in the presence of all other monomers, held fixed at the reference configuration, for example, a minimum. (Note,  $U_m$  is the full potential in these modes. For the isolated monomer, it is the exact H<sub>2</sub>O monomer potential.) In this sense, each monomer potential is an embedded one. The local normal modes are obtained from diagonalization of the  $9 \times 9$  mass-scaled Hessian matrix of monomer  $m$ . To see how this arises formally, we write the full Hessian matrix for  $N$  monomers as<sup>27,30</sup>

$$\mathbf{H} = \begin{bmatrix} \mathbf{H}_{11} & \mathbf{H}_{12} & \cdots & \mathbf{H}_{1N} \\ \mathbf{H}_{21} & \mathbf{H}_{22} & \cdots & \mathbf{H}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{H}_{N1} & \mathbf{H}_{N2} & \cdots & \mathbf{H}_{NN} \end{bmatrix}$$

where the mass-scaled coordinates are arranged in terms of the monomers so that each diagonal block is just the mass-scaled Hessian for each monomer. Thus,  $\mathbf{H}$  can be written as  $\mathbf{H} = \mathbf{H}_{\text{MM}} + \mathbf{H}_{\text{MM}'}$ , where  $\mathbf{H}_{\text{MM}}$  is the block-diagonal matrix of monomer Hessians and  $\mathbf{H}_{\text{MM}'}$  is the remainder. Then, if  $\mathbf{H}_{\text{MM}}$  is diagonalized by the matrix  $\mathbf{L}_{\text{M}}$ , we have

$$\mathbf{L}_{\text{M}}^t \mathbf{H}_{\text{MM}} \mathbf{L}_{\text{M}} = \mathbf{\Lambda}_{\text{M}} + \mathbf{L}_{\text{M}}^t \mathbf{H}_{\text{MM}'} \mathbf{L}_{\text{M}}$$

where  $\mathbf{\Lambda}_{\text{M}}$  is the matrix of eigenvalues of  $\mathbf{H}_{\text{MM}}$  and  $\mathbf{L}_{\text{M}}^t \mathbf{H}_{\text{MM}'} \mathbf{L}_{\text{M}}$  is the coupling matrix, which if neglected gives the local monomer approximation to the full normal modes analysis. (Note the coupling matrix or approximations to it can and have been used to incorporate monomer–monomer coupling.<sup>30</sup>)

It is worth commenting on the local monomer partitioning of the full Hessian matrix versus localization of full normal modes to obtain “local normal modes”. The localization of normal modes has been described by several procedures, all of which start with knowledge of the full normal modes.<sup>35</sup> Recent applications of this procedure,<sup>36</sup> together with the  $n$ -mode representation of the potential,<sup>37,38</sup> show the effectiveness of this approach. However, a major distinction is that a full normal-mode analysis is required for this localization procedure, whereas in the LMon approach, only a local analysis is needed, and this is quite efficient.

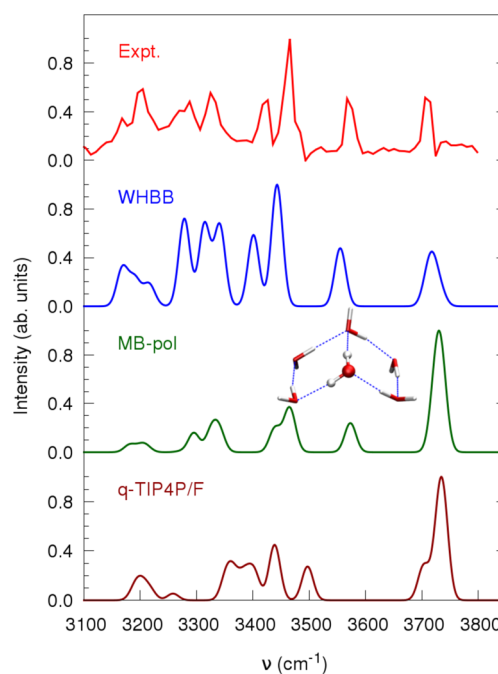
For a cluster of  $N$  water monomers, there are  $9N$  local modes and harmonic frequencies, which are obtained from the diagonalization of  $N$   $9 \times 9$  Hessians, compared to diagonalizing a  $9N \times 9N$  Hessian in the usual standard normal-mode analysis. (The contrast in computational effort is clear if, say, a high-level ab initio normal-mode analysis for even a moderate-sized cluster is considered.) To assess the accuracy of the local harmonic analysis, we show in Figure 2 a comparison of the harmonic vibrational density of states from a local monomer and full harmonic vibrational analysis of a 192-mer model of Ice Ih<sup>39</sup> using the WHBB potential. As seen, there is excellent agreement above  $1500 \text{ cm}^{-1}$ ; this was anticipated because this region is the intramolecular bend on the OH stretch region. These modes are the three high-frequency modes of each monomer. Agreement is good between  $500$  and  $1000 \text{ cm}^{-1}$ ; an examination of the normal modes<sup>39</sup> reveals that these modes are librational modes, and these are captured by the frustrated rotational local normal modes. Below roughly  $400 \text{ cm}^{-1}$ , the accuracy of the local mode model deteriorates and misses the peak at roughly  $60 \text{ cm}^{-1}$ . The region of discrepancy is characterized by low-frequency acoustic ( $\sim 60 \text{ cm}^{-1}$ ) and optical ( $200$ – $300 \text{ cm}^{-1}$ ) lattice modes, which are collective monomer translational modes. (A detailed analysis of these modes is given in ref 39.) Thus, these modes are not expected to be well-described by the local monomer modes. Therefore, for the IR (and Raman) spectral bands corresponding to the intramolecular modes, the local monomer approach is well justified, and even for the next lower band of intermolecular modes, it should provide good accuracy.

In the LMon application to water clusters, a set of modes, up to a maximum of 9, can be coupled, and the solutions to eq 2 can be obtained rigorously, accounting for anharmonicity. Clearly, the modes selected depend on the particular application of interest. The calculations that we have done couple a minimum of three intramolecular modes. For all calculations, we use the code MULTIMODE<sup>37,38</sup> to set up and solve the Schrodinger eq 2 and obtain the IR spectrum using eq 1. We reported a number of studies using this approach, with the WHBB suite of potential and dipole moment surfaces,

ranging from initial tests for the water dimer and trimer<sup>29</sup> to water clusters ranging from the tetramer to the 22-mer,<sup>27</sup> with a focus on the centrally important water hexamer<sup>31,32</sup> and models of ice, Ice Ih, and amorphous ice, using 192 monomers.<sup>32–34</sup>

These calculations used the minimum three-mode version of LMon, which we denote by LMon-3 (with the exception of the vibrational relaxation study<sup>34</sup> where six modes were used). These three-mode calculations are quite efficient per monomer, requiring set up and diagonalization of matrices of the order of 100. Also, it should be stressed that that LMon-3 captures the anharmonicity and coupling of the intramolecular vibrational modes.

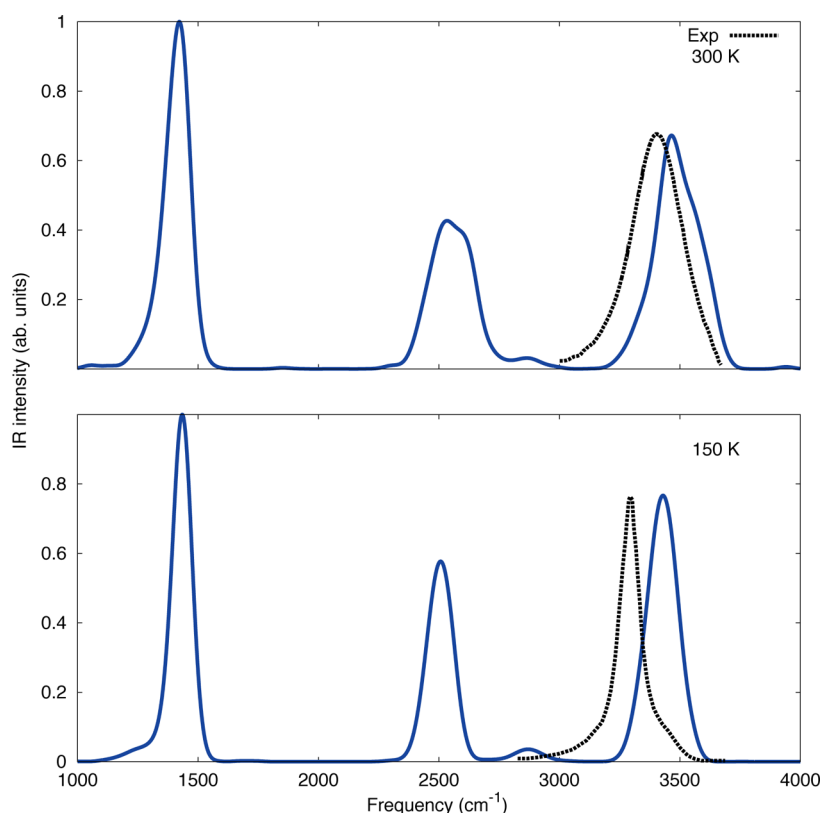
*Some Applications Using WHBB and Other Potentials.* An interesting application of LMon-3 is the IR spectrum of the book isomer of the water hexamer. The comparison, using the WHBB potential and dipole moment, with the experimental Ar-tagged spectrum<sup>40</sup> was reported recently by us.<sup>31</sup> Very good agreement was obtained, and a major point of that comparison was the importance of the bend overtone in establishing the identity of this cluster as the “book”. We have recalculated this spectrum using the MB-pol and q-TIP4P/F potentials and the q-TIP4P/F dipole. The calculated spectra were all Gaussian-broadened, as previously, to produce bandwidths comparable to the experimental spectrum. The results are shown in Figure 3.



**Figure 3.** IR spectrum of the book isomer of the water hexamer from the indicated sources. See the text for details.

As seen previously, WHBB is in good agreement with experiment, both in terms of the band positions and intensities. The experimental band at approximately  $3750 \text{ cm}^{-1}$  corresponds to the free OH stretch, and all potentials predict this position well. (Virtually every flexible water potential that treats the OH stretches as anharmonic oscillators will get the position of this band about right.) The band intensity in the spectral region between roughly  $3150$  and  $3250 \text{ cm}^{-1}$  is due to the bend overtone of the six monomers. This feature is described well by all of the potentials. The experimental band at approximately  $3600 \text{ cm}^{-1}$  is also described well by WHBB and MB-pol but not by q-TIP4P/F. This is an interesting band that we assign to the





**Figure 4.** IR spectra of dilute HOD in D<sub>2</sub>O obtained with LMon-3 calculations using the q-TIP4P/F potential and dipole moment (solid) and experiment (dashed).

one monomer, which in the figure is placed just above the MB-pol peak and is shown as the one ball and stick monomer. This unique monomer has two donor H atoms and thus no free OH stretch. The corresponding peak in the q-TIP4P/F spectrum is at around 3500 cm<sup>-1</sup>, which is roughly 100 cm<sup>-1</sup> below the peak in WHBB and experiment. Overall, there is good agreement in peak positions between WHBB and MB-pol, with however a systematic, small, upshift of MB-pol peak positions, relative to WHBB.

The intensities of the bands using the WHBB dipole moment are also in good agreement with experiment, in contrast to the results using the fixed partial charge dipole contained in the q-TIP4P/F. This failure of the q-TIP4P/F model to give accurate intensities was noted earlier by the developers of q-TIP4P/F<sup>5</sup> and is also noted in recent joint work on the IR spectrum of water<sup>41</sup> that is discussed briefly next. The main point of this illustration is to remind us that it is necessary to have both accurate potential and dipole moment surfaces to obtain an accurate IR spectrum.

The next example is from a recent calculation of the IR spectrum of dilute HOD in D<sub>2</sub>O at 150 and 300 K, using the q-TIP4P/F potential and dipole moment. This potential and dipole moment were used in recent joint work examining the consistency among LMon, CMD, and thermostated RPMD<sup>42</sup> calculations of the IR spectrum of water/ice.<sup>41</sup> (The q-TIP4P/F potential and dipole were used in these calculations in the interest of computational efficiency.) LMon calculations were done for the first time at nonzero temperatures. In brief, “snapshots” of the HOD were obtained from a thermal ensemble, and the LMon spectrum was obtained from the sum of LMon spectra over the ensemble. Thus, the spectrum is given by

$$I(\omega) \approx \sum_{t=0}^T \sum_{m=1}^N \sum_f \omega_{0 \rightarrow f_m}(t) R_{0 \rightarrow f_m}(t) \delta[\omega - \omega_{0 \rightarrow f_m}(t)]$$

$$R_{0 \rightarrow f_m}(t) = \sum_{\alpha} |\langle f_m | \mu_{\alpha, m} | 0_m \rangle|^2(t)$$

In this expression,  $T$  is the total simulation time, roughly 100 ps, and  $N$  is the number of monomers, one single HOD monomer for this case contained in a box (96 monomers in total) simulating the experimental density. The resulting spectra are shown in Figure 4 in the region of the HOD bend and OD and OH stretches. Note the small peak at around 2850 cm<sup>-1</sup>; this is the overtone of the HOD bend. As seen, the bands broaden at 300 K relative to 150 K. Also, the bend shows a slight down-shift, whereas the two stretches show up-shifts at 300 K relative to 150 K. These results are in qualitative agreement with experiment. The intensities of these bands are almost certainly incorrect based on the results above for the book hexamer. In particular, the bend intensity is too large. Also, the peak positions of the OH stretch are up-shifted from experiment by roughly 130 and 55 cm<sup>-1</sup> at 150 and 300 K, respectively.

This extension of the LMon-3 method to nonzero temperature is very encouraging given the simplicity of the method. In the joint work mentioned above, another important extension was considered, and that was to add the three highest-frequency *intermolecular* modes to the calculation. (These were the intermolecular modes with the largest IR intensity.) This was done in a straightforward but approximate way by adding one mode at a time, and thus, three LMon-4 calculations were done. These calculations opened up almost the entire spectral range of ice and water. They also showed the well-known (but weak)

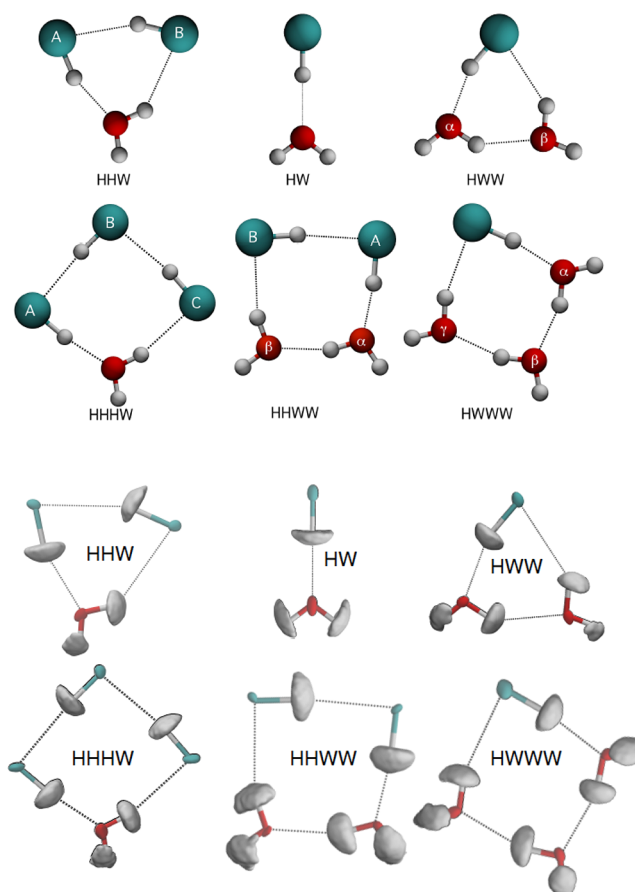
band for H<sub>2</sub>O at around 2300 cm<sup>-1</sup>, which was assigned to a combination band of the bend plus an intermolecular librational fundamental. We have applied a similar approach to obtain the IR spectrum of water at 298 K using the WHBB potential and dipole moment, and the preliminary results are very encouraging.

*Hydrates Illustrated by (HCl)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub>.* As a final example, consider how the many-body ab initio approach can be extended to consider hydration. We use as an example, our recent work on (HCl)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub> clusters, denoted in abbreviated notation by H<sub>n</sub>W<sub>m</sub>. The many-body representation of the potential up to three-body interactions is given by<sup>43</sup>

$$\begin{aligned}
 V(H_n, W_m) = & \sum_{i=1}^n V_H(i) + \sum_{i=1}^m V_W(i) \\
 & + \sum_{i < j}^n V_{HH}(i, j) + \sum_{i < j}^m V_{WW}(i, j) + \sum_{j=1}^n \sum_{i=1}^m V_{WH}(i, j) \\
 & + \sum_{i < j < k}^n V_{HHH}(i, j, k) + \sum_{i < j < k}^m V_{WWW}(i, j, k) \\
 & + \sum_{i < j}^n \sum_{k=1}^m V_{HHW}(i, j, k) + \sum_{i=1}^n \sum_{j < k}^m V_{HWW}(i, j, k)
 \end{aligned}$$

where the notation should be obvious. The water interactions are given by the WHBB potential, and this illustrates the transferability of the WHBB PES. The HCl one- and two-body potentials are spectroscopic and semiempirical potentials, and we developed a new ab initio three-body potential. Two of us also developed full-dimensional ab initio HW two- and three-body interactions.<sup>43,44</sup> This potential was used in vibrational studies of the clusters, HW, HHW, HWW, HHHW, HHWW, and HWWW, which all form rings. These all have important elements of delocalization of the respective ground-state wave function, which was obtained using rigorous diffusion Monte Carlo (DMC) calculations. The planar reference structures of these clusters are shown in Figure 5 along with isosurface representations of the DMC wave functions. LMon calculations of vibrational fundamentals of both HCl and H<sub>2</sub>O were reported for these clusters, and agreement with experiment was very good. In particular, for the HHWW cluster, the HCl fundamental is calculated at 2693 cm<sup>-1</sup>, in good agreement with the experimental value of 2670 cm<sup>-1</sup>.

To summarize, the LMon approach together with ab initio potentials has permitted the efficient and accurate characterization of water clusters to the bulk. There are several further extensions of the LMon method that come to mind. One is to simply add more intermolecular modes and to explicitly consider hot bands as well. Hot bands are of no consequence for LMon-3 calculations as the three intramolecular modes have negligible thermal populations even at 1000 K. However, they are of significance for low-frequency intermolecular modes even at 300 K. Another direction to take is a mixed quantum classical approach. This is already well-established for an OH stretch model of the vibrational dynamics. This model has a substantial history with many applications,<sup>45–48</sup> and its effective elaboration has been developed and extensively utilized by Skinner and co-workers.<sup>47,48</sup> The LMon “snapshot” approach clearly has no time history and thus no time coherence. The mixed classical/quantum approach can be directly applied to the LMon theory, and this is certainly worth investigating.



**Figure 5.** Planar structures of the indicated HCl–H<sub>2</sub>O (HW) clusters (upper panel) and isosurface representations of DMC zero-point wave functions, which have maximum amplitudes at the planar structures (lower panel).

We anticipate that quantum methods, the present local monomer one, centroid and ring polymer molecular dynamics, initial value representation semiclassical, mixed quantum classical methods, and other yet-to-be-developed ones, will play an expanding role in simulations of aqueous-phase physical chemistry.

Looking ahead generally, we anticipate that quantum methods, the present local monomer one, centroid and RPMD, initial value representation semiclassical, mixed quantum classical methods, and other yet-to-be-developed ones, will play an expanding role in simulations of aqueous-phase physical chemistry. These methods, when used with accurate potentials and dipole moment surfaces, certainly have the capability to be reliably predictive and insightful. The development of such potentials and dipole moments, based on many-body representations, is also a reality. Therefore, in the vernacular, “Are we there yet” in doing ab initio quantum treatments of condensed-phase dynamics? I think the answer is

“yes” for many aspects of these dynamics, including local short-time dynamics, such as vibrational relaxation, and probably “no” for long-time dynamics involving collective motions. Another very challenging issue for *ab initio* potentials, we think, is getting the potential *differences* of the many phases or even the many minima in a give phase of water accurately. These differences are clearly very small, and this is potentially where small many-body interactions beyond three- and four-body ones may be significant. Further, the dynamical barriers and pathways between these phases and among the many local minima within a phase will be a major challenge for theory.

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The authors declare no competing financial interest.

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## REFERENCES

- (1) Amira, S.; Spangberg, D.; Hermansson, K. Derivation and Evaluation of a Flexible SPC Model for Liquid Water. *Chem. Phys.* **2004**, *303*, 327–334.
- (2) Wu, Y. J.; Tepper, H. L.; Voth, G. A. Flexible Simple Point-Charge Water Model with Improved Liquid-State Properties. *J. Chem. Phys.* **2006**, *124*, 024503.
- (3) Lawrence, C. P.; Skinner, J. L. Flexible TIP4P Model for Molecular Dynamics Simulation of Liquid Water. *Chem. Phys. Lett.* **2003**, *327*, 842–847.
- (4) Paesani, F.; Zhang, W.; Case, D. A.; Cheatham, T. E.; Voth, G. A. An Accurate and Simple Quantum Model for Liquid Water. *J. Chem. Phys.* **2006**, *125*, 184507.
- (5) Habershon, S.; Markland, T. E.; Manolopoulos, D. E. Competing Quantum Effects in The Dynamics of a Flexible Water Model. *J. Chem. Phys.* **2009**, *131*, 024501.
- (6) Cao, J.; Voth, G. A. The Formulation of Quantum Statistical Mechanics Based on The Feynman Path Centroid Density. II. Dynamical Properties. *J. Chem. Phys.* **1994**, *100*, 5106–5117.
- (7) Jang, S.; Voth, G. A. A Derivation of Centroid Molecular Dynamics and Other Approximate Time Evolution Methods for Path Integral Centroid Variables. *J. Chem. Phys.* **1999**, *111*, 2371–2384.
- (8) Liu, J.; Miller, W. H.; Paesani, F.; Zhang, W.; Case, D. A. Quantum Dynamical Effects in Liquid Water: A Semiclassical Study on the Diffusion and the Infrared Absorption Spectrum. *J. Chem. Phys.* **2009**, *131*, 164509.
- (9) Miller, W. H. Quantum Dynamics of Complex Molecular Systems. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 6660–6664.
- (10) Habershon, S.; Manolopoulos, D. E.; Markland, T. E.; Miller, T. F. Ring-Polymer Molecular Dynamics: Quantum Effects in Chemical Dynamics from Classical Trajectories in an Extended Phase Space. *Annu. Rev. Phys. Chem.* **2013**, *64*, 387–413.
- (11) Habershon, S.; Fanourgakis, G. S.; Manolopoulos, D. E. Comparison of Path Integral Molecular Dynamics Methods for the Infrared Absorption Spectrum of Liquid Water. *J. Chem. Phys.* **2008**, *129*, 075401.
- (12) Fanourgakis, G. S.; Xantheas, S. S. Development of Transferable Interaction Potentials for Water. V. Extension of the Flexible, Polarizable, Thole-Type Model Potential (TTM3-F, v. 3.0) to Describe the Vibrational Spectra of Water Clusters and Liquid Water. *J. Chem. Phys.* **2008**, *128*, 074506.
- (13) Partridge, H.; Schwenke, D. S. The Determination of an Accurate Isotope Dependent Potential Energy Surface for Water from Extensive *Ab Initio* Calculations and Experimental Data. *J. Chem. Phys.* **1997**, *106*, 4618–4639.
- (14) Paesani, F.; Xantheas, S. S.; Voth, G. A. Infrared Spectroscopy and Hydrogen-Bond Dynamics of Liquid Water from Centroid Molecular Dynamics with an *Ab Initio*-Based Force Field. *J. Phys. Chem. B* **2009**, *113*, 13118–13130.
- (15) Xantheas, S. S. *Ab-Initio* Studies of Cyclic Water Clusters (H<sub>2</sub>O)<sub>N</sub>, N=1–6 0.2. Analysis of Many-Body Interactions. *J. Chem. Phys.* **1994**, *100*, 7523–7534.
- (16) Szalewicz, K.; Leforestier, C.; van der Avoird, A. Towards the Complete Understanding of Water by a First-Principles Computational Approach. *Chem. Phys. Lett.* **2009**, *482*, 1–14.
- (17) Wang, Y.; Huang, X.; Shepler, B. C.; Braams, B. J.; Bowman, J. M. Flexible, *Ab Initio* Potential, and Dipole Moment Surfaces for Water. I. Tests and Applications for Clusters up to the 22-mer. *J. Chem. Phys.* **2011**, *134*, 094509.
- (18) Cui, J.; Liu, H. B.; Jordan, K. D. Theoretical Characterization of the (H<sub>2</sub>O)<sub>21</sub> cluster: Application of an *n*-Body Decomposition Procedure. *J. Phys. Chem. B* **2006**, *110*, 18872–18878.
- (19) Góra, U.; Podeszwa, R.; Cencek, W.; Szalewicz, K. Interaction Energies of Large Clusters from Many-Body Expansion. *J. Chem. Phys.* **2011**, *135*, 224102, and references therein..
- (20) Tainter, C. J.; Pieniazek, P. A.; Lin, Y. S.; Skinner, J. L. Robust Three-Body Water Simulation Model. *J. Chem. Phys.* **2011**, *134*, 184501.
- (21) Góra, U.; Cencek, W.; Podeszwa, R.; van der Avoird, A.; Szalewicz, K. Predictions For Water Clusters from a First-Principles Two- and Three-Body Force Field. *J. Chem. Phys.* **2014**, *140*, 194101.
- (22) Howard, J. C.; Tschumper, G. S. N-Body:Many-Body QM:QM Vibrational Frequencies: Application to Small Hydrogen-Bonded Clusters. *J. Chem. Phys.* **2013**, *139*, 184113.
- (23) Braams, B. J.; Bowman, J. M. Permutationally Invariant Potential Energy Surfaces in High Dimensionality. *Int. Rev. Phys. Chem.* **2009**, *28*, 577–606.
- (24) Medders, G. R.; Babin, V.; Paesani, F. A Critical Assessment of Two-Body and Three-Body Interactions in Water. *J. Chem. Theory Comput.* **2013**, *9*, 1103–1114.
- (25) Babin, J. V.; Leforestier, C.; Paesani, F. Development of a “First Principles” Water Potential with Flexible Monomers: Dimer Potential Energy Surface, VRT Spectrum, and Second Virial Coefficient. *J. Chem. Theory Comput.* **2013**, *9*, 5395–5403.
- (26) Shank, A.; Wang, Y.; Kaledin, A.; Braams, B. J.; Bowman, J. M. Accurate *Ab Initio* and “Hybrid” Potential Energy Surfaces, Intramolecular Vibrational Energies, and Classical IR Spectrum of the Water Dimer. *J. Chem. Phys.* **2009**, *130*, 144314.
- (27) Wang, Y.; Bowman, J. M. *Ab Initio* Potential and Dipole Moment Surfaces for Water. II. Local-Monomer Calculations of The Infrared Spectra of Water Clusters. *J. Chem. Phys.* **2011**, *134*, 154510.

- (28) Keutsch, F. N.; Saykally, R. J. Water Clusters: Untangling The Mysteries of the Liquid, One Molecule at a Time. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 10533–10540.
- (29) Wang, Y.; Bowman, J. M. Anharmonic Quantum Vibrational Analysis of Water Clusters. *Chem. Phys. Lett.* **2010**, *491*, 1–10.
- (30) Wang, Y.; Bowman, J. M. Coupled-Monomers in Molecular Assemblies: Theory and Application to the Water Tetramer, Pentamer, and Ring Hexamer. *J. Chem. Phys.* **2012**, *136*, 144113.
- (31) Wang, Y.; Bowman, J. M. IR Spectra of the Water Hexamer: Theory, with Inclusion of the Monomer Bend Overtone, and Experiment are in Agreement. *J. Phys. Chem. Lett.* **2013**, *4*, 1104–1108.
- (32) Liu, H.; Wang, Y.; Bowman, J. M. Local-Monomer Calculations of the Intramolecular IR Spectra of the Cage and Prism Isomers of HOD(D<sub>2</sub>O)<sub>5</sub> and HOD and D<sub>2</sub>O Ice Ih. *J. Phys. Chem. B* **2014**, *118*, 14124–14131.
- (33) Liu, H.; Wang, Y.; Bowman, J. M. Quantum Calculations of Intramolecular IR Spectra of Ice Models Using Ab Initio Potential and Dipole Moment Surfaces. *J. Phys. Chem. Lett.* **2012**, *3*, 3671–3676.
- (34) Liu, H.; Wang, Y.; Bowman, J. M. Ab Initio Deconstruction of the Vibrational Relaxation Pathways of Dilute HOD in Ice Ih. *J. Am. Chem. Soc.* **2014**, *136*, 5888–5891.
- (35) Jacob, C. R.; Reiher, M. Localizing Normal Modes in Large Molecules. *J. Chem. Phys.* **2009**, *130*, 084106.
- (36) Cheng, X.; Steele, R. P. Efficient Anharmonic Vibrational Spectroscopy for Large Molecules Using Local-Mode Coordinates. *J. Chem. Phys.* **2014**, *141*, 104105.
- (37) Carter, S.; Culik, S. J.; Bowman, J. M. Vibrational Self-Consistent Field Method for Many-Mode Systems: A New Approach and Application to the Vibrations of CO Adsorbed on Cu(100). *J. Chem. Phys.* **1997**, *107*, 10458.
- (38) Bowman, J. M.; Carter, S.; Huang, X. MULTIMODE: A Code to calculate Rovibrational Energies of Polyatomic Molecules. *Int. Rev. Phys. Chem.* **2003**, *22*, 533–549.
- (39) Liu, H.; Wang, Y.; Bowman, J. M. Vibrational Analysis of an Ice Ih Model from 0 to 4000 cm<sup>-1</sup> using the Ab Initio WHBB Potential Energy Surface. *J. Phys. Chem. B* **2013**, *117*, 10046–10052.
- (40) Diken, E. G.; Robertson, W. H.; Johnson, M. A. The Vibrational Spectrum of the Neutral (H<sub>2</sub>O)<sub>6</sub> Precursor To The “Magic” (H<sub>2</sub>O)<sub>6</sub><sup>-</sup> Cluster Anion by Argon-Mediated, Population-Modulated Electron Attachment Spectroscopy. *J. Phys. Chem. A* **2003**, *108*, 64–68.
- (41) Rossi, M.; Liu, H.; Paesani, F.; Bowman, J. M.; Ceriotti, M. On the Consistency of Approximate Quantum Dynamics Simulation Methods for Vibrational Spectra in the Condensed Phase. *J. Chem. Phys.* **2014**, *141*, 181101.
- (42) Rossi, M.; Ceriotti, M.; Manolopoulos, D. E. How to Remove the Spurious Resonances from Ring Polymer Molecular Dynamics. *J. Chem. Phys.* **2014**, *140*, 234116.
- (43) Mancini, J. S.; Bowman, J. M. Effects of Zero-Point Delocalization on the Vibrational Frequencies of Mixed HCl and Water Clusters. *J. Phys. Chem. Lett.* **2014**, *5*, 2247–2253.
- (44) Samanta, A. K.; Czako, G.; Wang, Y.; Mancini, J. S.; Bowman, J. M.; Reisler, H. Experimental and Theoretical Investigations of Energy Transfer and Hydrogen-Bond Breaking in Small Water and HCl Clusters. *Acc. Chem. Res.* **2014**, *47*, 2700–2709.
- (45) Buch, V. Molecular Structure and OH-Stretch Spectra of Liquid Water Surface. *J. Phys. Chem. B* **2005**, *109*, 17771–17774, and references therein.
- (46) Torii, H. Time-Domain Calculations of the Polarized Raman Spectra, the Transient Infrared Absorption Anisotropy, and the Extent of Delocalization of the OH Stretching Mode Of Liquid Water. *J. Phys. Chem. A* **2006**, *110*, 9469–9477.
- (47) Shi, L.; Skinner, J. L. Proton Disorder in Ice Ih and Inhomogeneous Broadening in Two-Dimensional Infrared Spectroscopy. *J. Phys. Chem. B* **2013**, *117*, 15536–15544.
- (48) Gruenbaum, S. M.; Tainter, C. J.; Shi, L.; Ni, Y.; Skinner, J. L. Robustness of Frequency, Transition Dipole, and Coupling Maps for Water Vibrational Spectroscopy. *J. Chem. Theory Comput.* **2013**, *9*, 3109–3117.