Prediction of Accurate Anharmonic Experimental Vibrational Frequencies for Water Clusters, $(H_2O)_n$, $n = 2-5$

Meghan E. Dunn, Timothy M. Evans, Karl N. Kirschner,* and George C. Shields*

Department of Chemistry, Hamilton College, 198 College Hill Road, Clinton, New York 13323

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Accurate anharmonic experimental vibrational frequencies for water clusters consisting of 2−5 water molecules have been predicted on the basis of comparing different methods with MP2/aug-cc-pVTZ calculated and experimental anharmonic frequencies. The combination of using HF/6-31G* scaled frequencies for intramolecular modes and anharmonic frequencies for intermolecular modes gives excellent agreement with experiment for the water dimer and trimer and are as good as the expensive anharmonic MP2 calculations. The water trimer, the cyclic C_i and S_4 tetramers, and the cyclic pentamer all have unique peaks in the infrared spectrum between 500 and 800 cm^{-1} and between 3400 and 3700 cm^{-1}. Under the right experimental conditions these different clusters can be uniquely identified using high-resolution IR spectroscopy.

Introduction

Standard quantum chemistry codes have traditionally used the harmonic oscillator approximation to calculate vibrational frequencies, which leads to an overestimation of each vibrational mode with respect to experiment. Frequencies are calculated to verify a molecule's position on a potential energy hypersurface, to obtain thermodynamic information, and to obtain experimentally relevant vibrational data. The last two points require careful consideration of the approximations made in the calculations. It is known that harmonic frequencies are extremely sensitive to geometric structure,[1] and exact harmonic frequencies for diatomic molecules computed using accurate potential energy surfaces exceed experimental frequencies by about 3%.[2] Application of scaling factors to the Hartree−Fock (HF) frequencies makes a stunning improvement to their accuracy.[3] Several research groups have developed scaling factors for frequencies, thermal contributions, and zero-point vibrational energy that are dependent on the level of theory used (i.e., HF, DFT, MP2) and on the basis set used in the calculation.[4−8] Recently, different scaling factors have been developed for the correlation consistent basis sets of Dunning,[9−14] based on the idea that the frequencies below 1000 cm^{-1} are more anharmonic in nature.[15] A detailed study comparing eight different levels of theory using a database consisting of 1066 experimental anharmonic vibrational frequencies for 122 molecules reveals that the scaled HF frequencies are more accurate than scaled second-order Møller−Plesset (MP2) frequencies using the 6-31G* basis set.[7] The uncertainties in scaling factors for ab initio vibrational frequencies have been determined by Irikura et al.,[16] in a comprehensive study that makes use of the Computational Comparison and Benchmark Database (CCCBDB)[17] available on-line and maintained by the National Institute of Standards and Technology (NIST). The NIST researchers have used this database, which includes 4824 distinct vibrational frequencies obtained from experimental vibrational data for 386 molecules, to evaluate the uncertainties in the scaling factors obtained for HF, DFT, MP2, and QCISD calculations. They find that the HF scaling factors have less uncertainty than the MP2 scaling factors, and that in general the uncertainty in scaling factors is no better than 0.02.[16] Thus the finding that HF scaled frequencies are more accurate than MP2 scaled frequencies[7] is a manifestation of less inherent error in the scale factors that have been derived from experimental data for these methods.[16] More detail on important issues relevant to computational chemists investigating the spectroscopy of nuclear motion can be found in a recent text.[2]

Nonbonded species present a particular challenge for producing experimentally accurate frequencies because of the anharmonic nature of the lowest vibrational modes. The frequencies for hydrogen bonded complexes display the interesting characteristic that the lowest energy vibrations arise from intermolecular motions of the contingent molecules whereas the higher energy vibrations arise from the intramolecular motion of individual molecules within the complex. The lower energy intermolecular modes are more anharmonic in nature than the intramolecular modes, and much work has been devoted to pursuing accurate calculations for frequencies of water clusters and other hydrogen bonded systems.[18−47] These calculations, combined with water cluster experiments[48−60] and ion−water cluster experiments,[48,61−64] have given us a good baseline for consideration of accurate anharmonic frequency calculations for water clusters. The water dimer, the simplest model for water clusters and an atmospherically important species,[30,35,65−70] has been the subject of anharmonic calculations that have been compared against the best available experimental values.[22,24,28,31,34,40,44,53,71−73] The experimentally determined water dimer frequencies are sensitive to matrix effects, and there is no single gas-phase experiment that gives a complete list of gas-phase frequencies. We have assembled what we believe to be the most relevant values to compare against gas-phase spectroscopic results.[72] In our previous work on the water dimer we have shown that HF/6-31G* frequencies scaled by 0.8929 have a 24 cm^{-1} root-mean-square deviation (RMSD) from experiment, whereas combining scaled frequencies for the intramolecular modes with anharmonic frequencies for the intermolecular modes improves the RMSD to 20 cm^{-1}.[72] We now extend this work to include water clusters containing three to five water molecules, with a goal of providing experimentalists reliable values to aid in their search for these clusters in the gas phase. We make use of Barone's recently implemented second-order perturbation approach to obtain anharmonic fre-

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TABLE 1: HF Scaled Harmonic, Mixed, and Anharmonic Frequencies (Scaled for $\nu > 1000$ cm^{-1} and Anharmonic for $\nu < 1000$ cm^{-1}), and MP2(full) Scaled Harmonic and Anharmonic Frequencies Compared to Experimental Frequencies for $(H_2O)_2$[a]

	HF/6-31G*			MP2(full)/aug-cc-pVDZ			MP2(full)/aug-cc-pVTZ			MP2(full)/aug-cc-pVQZ			intensity		
vibrational mode[b]	scaled global	anh	mixed	scaled global	scaled split	anh	scaled global	scaled split	anh	scaled global	scaled split	anh	IR	R	exp
ν_3(a)	3731	3997	3731	3771	3771	3750	3778	3778	3770	3804	3804	3776	m	w	3745[c,d]
ν_3(d)	3716	3992	3716	3752	3752	3723	3760	3760	3758	3785	3785	3769	m	m	3735[c,d]
ν_1(a)	3630	3909	3630	3648	3648	3616	3667	3667	3668	3689	3689	3671	w	m	3660[e]
ν_1(d)	3597	3893	3597	3558	3558	3554	3575	3575	3602	3590	3590	3597	m	s	3601[c]
ν_2(d)	1655	1798	1655	1579	1579	1593	1578	1578	1599	1590	1590	1600	m	w	1616[f]
ν_2(a)	1629	1775	1629	1561	1561	1581	1554	1554	1585	1572	1572	1590	m	w	1599[f]
out-of-plane bend	553	521	521	618	708	509	627	698	549	610	679	517	m	w	523[f]
in-plane bend	342	308	308	346	396	315	357	398	316	346	385	308	m	w	311[f]
intermol stretch	163	135	135	178	203	150	181	201	157	180	201	144	m	w	143[g]
twist	127	82	82	146	167	109	146	163	150	149	166	108	s	w	108[h]
wag	121	84	84	143	164	116	143	160	147	143	159	113	m	w	103[h]
torsion	103	80	80	124	142	61	124	138	91	122	136	65	m	w	88[h]
std deviation	24.0	169	20.5	42.5	71.4	23.0	45.3	68.3	22.9	43.6	64.8	16.5			

[a] Relative peak strength for infrared intensity and Raman activity estimated as weak (w), medium (m) or strong (s). Standard deviations relative to experiment. [b] Mode motion: ν_1 for symmetric stretching; ν_2 for bending; ν_3 for asymmetric stretching. The use of (a) signifies hydrogen bond acceptor water, and the (d) signifies the hydrogen bond donor water. [c] Reference 102. [d] Reference 51. [e] Reference 102, extrapolated from matrix. [f] Reference 40, neon matrix, 5K. [g] Reference 104. [h] Reference 103.

quencies.[74] Small water clusters are of intrinsic atmospheric interest because they are predicted to be present in the atmosphere under humid conditions at appreciable concentrations.[70,75]

Methods

Frequencies based on solving Schrödinger's equation for the harmonic oscillator model generally overestimate the experimental frequencies as a consequence of the anharmonicity of bond stretching. As a result frequencies obtained from the harmonic approximation are scaled to bring the calculated frequencies into better agreement with experiment. Scaling factors are determined empirically, and a large body of work attests to the importance of proper scaling of the harmonic frequencies.[1−8] Recent work has verified the historical view that scaled HF frequencies are more accurate relative to experimental values than scaled MP2 frequencies[15] and shown that the inherent uncertainty in the MP2 scale factors is greater than the inherent uncertainty in the HF scale factors.[16] Although MP2 is more accurate than HF for closed-shell molecules, the uncertainty averaged over a large number of molecules is greater for MP2 because MP2 is much worse in the atypical cases such as NO and PO.[3,76] Perturbation theory is an extrapolated procedure and can give spurious results when a molecule's electronic structure is peculiar.[76] More detail can be found in a recent paper.[77]

Anharmonic frequency calculations represent a different approach, and much effort has been expended investigating anharmonic modes using variational and perturbative vibrational methods.[28,73,78−93] An effective way to treat medium-sized molecules uses second-order perturbation theory (PT2), which has been shown to give good results.[37−39,94−96] The PT2 approach, though less expensive than a more rigorous converged variational calculation, is still computationally expensive. The PT2 expressions are exact for a one-dimensional Morse oscillator, but not correct for the quartic potential of polyatomic molecules.[74] Application of the Morse oscillator model to the quartic potential can effectively include higher order terms, so that PT2 predictions can be quite accurate.[95,96] Analytical second derivatives are used to compute third and semidiagonal fourth derivatives using a finite difference approach, and the results are used for the PT2 treatment.[74]

We have used the lowest energy trimer, tetramers, and pentamer structures believed to be minima on the MP2 potential energy hypersurfaces as starting structures for all of the calculations reported in this paper.[72] All structures were optimized at the HF/6-31G* level with tight geometry convergence criteria (opt=tight) in Gaussian03, version C.02.[97] Harmonic and anharmonic calculations were carried out for all 17 water clusters, and the harmonic calculations were scaled by 0.8929.[4,5] This same scaling is used in the G3 method,[98] allowing for accurate calculations of neutral and ionic clusters containing waters.[70,72,75,99−101] Additionally, the water dimer was geometry optimized at the MP2(full)/aug-cc-pVDZ, MP2(full)/aug-cc-pVTZ and MP2(full)/aug-cc-pVQZ levels, and harmonic and anharmonic frequency calculations were performed on these structures. The high and low energy MP2 harmonic frequencies were scaled by 0.9604 and 1.0999 for the aug-cc-pVDZ basis set, by 0.9557 and 1.0634 for the aug-cc-pVTZ basis set, and by 0.9601 and 1.0698 for the aug-cc-pVQZ basis set.[15]

Results

Table 1 contains the scaled harmonic and anharmonic frequencies for the water dimer determined using the 6-31G* basis set for the HF method and the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets for the MP2 method. Table 1 contains two sets of scaled frequencies for the MP2(full) results. In the first set the harmonic frequencies were scaled by the high-frequency scale factor of 0.9604, 0.9557, and 0.9601 for the double, triple, and quadruple basis set.[15] In the second set the intramolecular frequencies (above 1000 cm^{-1}) were scaled by the high-frequency scale factors, whereas the intermolecular frequencies (below 1000 cm^{-1}) were scaled by a low-frequency scale factor of 1.0999, 1.0634, and 1.0698 for the double, triple, and quadruple basis sets.[15] Instead of presenting the results obtained using a split set of scaling factors, for the HF/6-31G* calculations we report a mixed set of frequencies where the intramolecular frequencies were scaled by 0.8929 and the intermolecular frequencies are those determined by the anharmonic calculations. Table 1 also contains experimental frequencies and the overall standard deviations for each method relative to the experimental values. The middle range of experimental frequencies were obtained from an Ar or Ne matrix experiment and thus are expected not to agree as well to the calculated

TABLE 2: Scaled Harmonic, Mixed, and Anharmonic Frequencies As Approximated by HF and MP2 Theory for the (uda) Cyclic Water Trimer[a]

	HF/6-31G*			MP2/aug-cc-pVTZ					
mode[b]	scaled	mixed	anh	scaled	split scaled	anh	IR	R	exp[c]
ν_3(a)	3707	3707	3979	3733	3733	3732	m	s	
ν_3(d)	3706	3706	3977	3732	3732	3730	m	s	3717, 3726
ν_3(u)	3703	3703	3973	3729	3729	3726	m	s	
ν_1^{nc}(ua)	3562	3562	3857	3488	3488	3500	s	m	3530, 3533
ν_1^{nc}(du)	3558	3558	3853	3480	3480	3489	s	m	
ν_1^{c}(uad)	3519	3519	3825	3419	3419	3442	w	s	3518[d]
ν_2^{c}(ad)	1665	1665	1812	1593	1593	1593	w	w	
ν_2(u)	1653	1653	1809	1569	1569	1595	m	w	1608[d]
ν_2^{nc}(ad)	1644	1644	1791	1567	1567	1595	m	w	
ω^{c}(bonded H uad)	814	749	749	825	918	684	w	w	
ω^{nc}(bonded H du)	598	567	567	638	710	569	s	w	569[d]
ω^{nc}(bonded H ad)	514	436	436	550	612	443	m	w	
ρ^{c}(da), τ(u)	407	366	366	426	475	369	m	w	
ρ(du), ω(a)	314	284	284	343	382	307	w	w	
ρ^{nc}(ua)	296	247	247	332	369	273	w	w	
ω^{c}(free H du), ρ(a)	221	184	184	229	255	168	w	w	
ring compression	196	183	183	209	233	187	w	w	
ω^{nc}(free H du)	167	116	116	192	213	145	m	w	
heavy atom distortion	164	149	149	180	200	153	w	w	
heavy atom distortion	159	147	147	174	194	142	w	w	
ω(free H)	148	71	71	165	183	102	m	w	
std dev	52	41	186	53	86	0			

[a] Modes are assigned from visualization of the HF/6-31G* frequencies. The relative intensity for infrared absorption (IR) and Raman activity (R) are characterized as weak (w), medium (m) or strong (s) and are displayed to the right. See Figure 1 for water molecule assignment. Standard deviations relative to anharmonic MP2/Aug-cc-pVTZ values. [b] Mode motion: c for concerted; nc for nonconcerted; ω for wag; ρ for rock; τ for twist. [c] Experimental data from refs 52 and 54. [d] Experimental data from ref 60, in a neon matrix.

results because of matrix effects. Table 2 displays the HF/6-31G* and MP2/aug-cc-pVTZ scaled harmonic, anharmonic, and mixed (scaled above 1000 cm^{-1} and anharmonic below 1000 cm^{-1}) frequencies for the most abundant water trimer.[72] Table 3 reports the mixed frequencies for the cyclic water tetramer with S_4 symmetry, which is the most abundant configurational isomer at 298 K on the tetramer free energy surface.[72] The experimental data reported in this table were obtained from a neon matrix experiment and therefore are expected to be in some disagreement with calculated results because of matrix effects. Table 4 reports the mixed frequencies for the cyclic water pentamer, which is the most abundant isomer from 5 to 300 K.[72] Table 5 presents the most intense IR absorptions for the lowest energy water clusters, which can be used by experimentalists searching for water clusters in the intramolecular and intermolecular frequency ranges.

Figure 1 displays the most stable structures of the water trimer, water tetramer, and water pentamer at 298 K.[72] The labeling of the waters in the figures will be used to uniquely identify the vibrational modes described in the tables. For the trimer the "u", "d", and "a" labels refer to the unique, donor, and acceptor water molecules in this cluster. The unique water possesses the dangling hydrogen that is aimed in the opposite direction of the dangling hydrogens in the other two waters; the donor water (d) is distinguished because it is donating a hydrogen bond to the unique water, whereas the acceptor water (a) is accepting a hydrogen bond from the unique water. In Table 2 the acceptor ν_3(a) mode refers to the anharmonic asymmetric stretching vibration of the acceptor water (a) within the trimer. This mode is predicted to occur at 3707 cm^{-1} according to the scaled HF/6-31G* results for the trimer depicted in Figure 1. The ν_1^{nc}(ua) nomenclature means that the fourth trimer mode consists of motion of two waters within the trimer, the unique water and the acceptor water, which are both undergoing a symmetric O−H stretch. The superscript nc refers to the two water motions as nonconcerted, because the two stretches on

TABLE 3: Scaled Harmonic (ν > 1000 cm^{-1}) and Anharmonic (ν < 1000 cm^{-1}) Frequencies for the S_4 Symmetric Water Tetramer, Approximated by HF/6-31G* Theory[a]

mode[b]	mixed	IR	R	exp[c]
ν_3^{c}(udud)	3701	0	s	
ν_3^{nc}(dd)	3700	m	m	3714, 3717
ν_3^{nc}(uu)	3700	m	m	
ν_3^{nc}(uu/dd)	3699	m	w	
ν_1^{nc}(dudu)	3521	w	m	
ν_1^{nc}(uu)	3496	s	w	3405, 3416
ν_1^{nc}(dd)	3496	s	w	
ν_1^{c}(udud)	3442	0	s	
ν_2^{c}(udud)	1672	0	w	
ν_2^{nc}(uu/dd)	1657	m	w	
ν_2^{nc}(ud/ud)	1657	m	w	
ν_2^{nc}(d*u*/d*u*)	1657	m	w	
ω^{c}(bonded H udud)	806	0	w	
ω^{nc}(bonded H uu)	673	s	w	669
ω^{nc}(bonded H dd)	673	s	w	
ω^{nc}(uu/dd)	670	s	w	
ρ^{nc}(dd)	370	w	w	
ρ^{nc}(uu)	370	w	w	
ρ^{nc}(uu/dd)	357	w	w	
τ^{c}(uu/dd)	290	0	w	
ω^{c}(free H udud)	248	0	w	
heavy atom ring distortion	210	w	w	
ω^{nc}(free H uu), ρ^{nc}(dd)	195	m	w	
ω^{nc}(free H dd), ρ^{nc}(uu)	195	m	w	
ω^{nc}(free H d*u*/d*u*)	195	w	w	
ω^{nc}(free H ud/ud)	195	w	w	
ring compression	179	0	w	
ω^{nc}(free H uu/dd)	152	w	w	
heavy atom ring distortion	66	w	w	
τ(ring)	46	0	w	

[a] Relative peak strength for infrared intensity and Raman activity estimated by weak (w), medium (m) and strong (s) are displayed in the far right columns. [b] Mode motion: c for concerted movement; nc for nonconcerted movement; ω for wag; ρ for rock; τ for twist; / used to separate concerted motions from nonconcerted motions. [c] References 52, 54 and 60.

TABLE 4: Frequencies for the Cyclic Water Pentamer, Using Scaled Harmonic Values for $\nu > 1000$ cm^{-1} and Anharmonic Values for $\nu < 1000$ cm^{-1}, Approximated by HF/6-31G* Theory[a]

mode[b]	mixed	IR	R
ν_3(u1)	3704	w	m
ν_3(u2)	3702	w	m
ν_3(u3)	3701	w	m
ν_3(d2)	3699	m	m
ν_3(d1)	3698	m	m
ν_1^{nc}(u1d1)	3513	w	m
ν_1^{nc}(u2u3/d1)	3509	w	m
ν_1^{nc}(u1d2/u3d1)	3479	s	w
ν_1^{nc}(u2d1/u3d2)	3476	s	w
ν_1^{c}(ring H)	3431	w	s
ν_2^{c}(ring)	1680	w	w
ν_2^{nc}(u1d2/u2d1u3)	1671	m	w
ν_2^{nc}(u1u2/u3d2)	1666	m	w
ν_2^{nc}(u1d1/d2u2)	1657	w	w
ν_2^{nc}(d1d2/u3)	1656	m	w
ω^{c}(bonded H ring)	814	w	w
ω^{nc}(bonded H u2d1/d2)	727	m	w
ω^{nc}(bonded H u1d2/u2u3d1)	688	m	w
ω^{nc}(d1d2/u3)	675	m	w
ω^{nc}(bonded H u1/u2d1)	605	w	w
ρ^{c}(u1u2)	371	w	w
ρ(u3), τ^{c}(d1d2)	375	w	w
ρ^{nc}(d1d2)	359	w	w
ρ^{nc}(u1d1u3d2/u2)	332	w	w
ρ^{nc}(u1u3/u2d1d2)	306	w	w
ω^{c}(Free H u2d1u3d2)	219	w	w
Heavy atom distortion (d1d2u1)	240	w	w
Heavy atom distortion (u1u2d1d2)	239	w	w
ω^{nc}(free H d1d2), ρ(u3)	178	m	w
Heavy atom ring distortion	190	m	w
Heavy atom ring distortion	190	w	w
ω^{nc}(u1u2/u3)	136	m	w
ω^{c}(free H d1d2), τ^{c}(u1u2u3)	128	w	w
ω^{c}(free H u1u2u3), τ^{c}(d1d2)	130	w	w
ω^{nc}(free H u1d1/u2d2)	30	w	w
Asymmetric compression	45	w	w
Asymmetric compression	41	w	w
Heavy atom distortion (d1u3d2)	36	w	w
Heavy atom distortion (u1u2d1)	19	w	w

[a] The relative intensities for infrared absorption and Raman activity characterized as weak (w), medium (m) or strong (s) are displayed in the far right. [b] Mode motion: c for concerted movement; nc for nonconcerted movement; ω for wag; ρ for rock; τ for twist; / used to separate concerted motions from nonconcerted motions.

each water are out-of-phase. This nomenclature for the vibrational modes is also used in Tables 2−4.

Discussion

The water dimer has six intramolecular modes above 1000 cm^{-1} and six intermolecular modes below 1000 cm^{-1}. The intermolecular modes are the most anharmonic.[72] The experimental anharmonic frequencies for the water dimer have been compiled using the most reliable experimental data, as selected

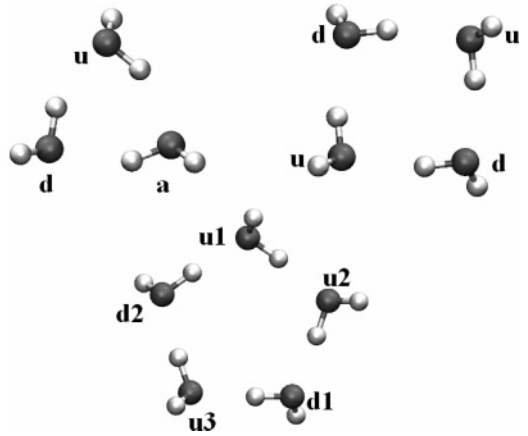

Figure 1. uda trimer (top left), S_4 tetramer (top right), and the cyclic pentamer (bottom) geometries and constituent monomer nomenclature.

by the Buck, Huisken, Saykally, and Perchard groups.[40,51,52,102−104] As noted by these authors, interpretation of the high-resolution data is difficult, and continual effort is being made to ensure an accurate assignment of each peak.[104] Matrix experiments are easier to interpret, but the matrix perturbs the intermolecular frequencies from their gas-phase values by as much as 20%.[40] This makes comparison between theory and experiment difficult. Table 1 contains what we believe to be the currently accepted experimental anharmonic frequency values for the water dimer. As illustrated in Table 1, HF/6-31G* harmonic frequencies scaled by 0.8929, have a standard deviation of 24 cm^{-1} relative to experiment. Combining the scaled harmonic values for the intramolecular modes (frequencies above 1000 cm^{-1}) with the anharmonic values for the intermolecular modes (frequencies below 1000 cm^{-1}), results in a standard deviation of 20.5 cm^{-1} for the mixed frequencies. MP2(full) anharmonic calculations using the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets have standard deviations of 23, 23, and 16.5 cm^{-1}. Previous anharmonic calculations at the MP2 level, without full electron correlation, using the aug-cc-pVTZ and D95++(2d,2p) basis sets have standard deviations relative to this data set of 15 and 17 cm^{-1}.[40,44,72] Applying a single scaling factor[15] for the MP2/aug-cc-pVTZ harmonic frequencies (rmsd = 39.3 cm^{-1}), or two scaling factors[15] in the split-scaled method (rmsd = 60 cm^{-1}) result in less accurate values than the anharmonic MP2/aug-cc-pVTZ results (rmsd = 14.7 cm^{-1}) (see Supporting Information). By comparing the MP2(full) and MP2 aug-cc-pVTZ results, one can see that including all electrons in the correlation increases the anharmonic frequencies by roughly 20 cm^{-1}, whereas the standard deviation increases from 15 to 23 cm^{-1}. Increasing the MP2(full) basis set to quadruple-ζ lowers most of the anharmonic modes, improving the results relative to this set of experimental numbers. Though the anharmonic MP2 calculations are the most accurate, they are extremely expensive. Comparison of the various methods indicates that the least expensive way to calculate accurate anharmonic frequencies for

TABLE 5: Strong Infrared Absorptions for the Low Energy Clusters $(H_2O)_n$, $n = 2-5$, along with the C_i Tetramer[a]

modes and shifts	dimer	trimer	S_4 tetramer	C_i tetramer	pentamer
upper ν_1	3630	3562	3496	3505	3479
lower ν_1	3597	3558	3496	3500	3476
red shift from dimer					
upper ν_1 to upper ν_1	0	68	134	125	151
lower ν_1 to lower ν_1	0	39	101	97	121
ω^{nc}(bonded H)	521	567	673, 670	708, 677	727, 688, 675
blue shift from dimer	0	46	152	187, 156	206, 167, 154
blue shiftfrom preceding cluster	0	46	106	141, 110	54, 15, 2

[a] The ν_1 frequencies and ω from 500 to 750 cm^{-1} are from the "mixed" HF/6-31G* frequencies.

the water dimer is the mixed HF/6-31G* scaled harmonic/anharmonic method, where the intramolecular harmonic frequencies are scaled by 0.8929 and combined with the intermolecular anharmonic frequencies calculated at this same level of theory. This method yields a standard deviation of 20.5 cm^{-1}, is very quick, and therefore we have used it to make accurate estimates for the frequencies of other cyclic water clusters.

The water trimer results are presented in Table 2. As seen by comparing the HF/6-31G* and MP2/aug-cc-pVTZ results for the low energy trimer, the combination of using a single scaling factor for all of the frequencies, or using the scaled frequencies for the intramolecular modes (above 1000 cm^{-1}) and anharmonic frequencies for the intermolecular modes (below 1000 cm^{-1}) (i.e., mixed method), compare quite well to the MP2 anharmonic frequencies. The standard deviation of the scaled HF/6-31G* frequencies versus the MP2 anharmonic frequencies is 52 cm^{-1}, whereas the standard deviation of the mixed method is 41 cm^{-1}. The standard deviation of the scaled MP2 frequencies versus the MP2 anharmonic frequencies is 53 cm^{-1}. On the basis of the MP2 results for the water dimer, the MP2 anharmonic frequencies are expected to have a standard deviation of about 20 cm^{-1} in comparison to experimental gas-phase results. The mixed method that combines the scaled and anharmonic HF frequencies agrees well with the MP2 anharmonic results. Two sets of experimental frequencies for the O−H stretching have been reported for the water trimer in the gas phase, at 3726/3717 and 3533/3530 cm^{-1}.[52,54,60] The higher energy mode (∼3726 cm^{-1}) is a free O−H stretch, which matches up with the ν_3 asymmetric mode in Table 2. According to the HF/6-31G* scaled frequencies, this mode occurs at 3707, 3706, and 3703 cm^{-1} for the acceptor water (a), the donor water (d), and the unique water (u) in the cyclic trimer. These same modes are predicted to have frequencies of 3732, 3730, and 3726 cm^{-1} by the anharmonic MP2/aug-cc-pVTZ method. The experimentally observed peak likely contains all three asymmetric modes arising from each contingent water in the trimer.

It appears that the experimental mode around 3530 cm^{-1} corresponds to an O−H stretching motion in the trimer. The scaled HF method predicts that a nonconcerted (ua) symmetric O−H stretch vibration, ν_1^{nc}(ua), is at 3562 cm^{-1}, a nonconcerted (du) vibration, ν_1^{nc}(du), is at 3558 cm^{-1}, and the ν_1^{c}(uad) ring O−H stretch is at 3519 cm^{-1}. The same three vibrations are predicted to be at 3500, 3489, and 3442 cm^{-1} by the anharmonic MP2 calculations. As the predicted IR intensity is strong for the ν_1^{nc}(ua) and ν_1^{nc}(du) vibrations, and weak for the ν_1^{c}(uad) ring OH stretch, we believe that one of the nonconcerted vibrations was detected by the experimentalists. Thus, the scaled HF predictions are 29 to 25 cm^{-1} higher than the observed 3533 cm^{-1} mode,[52] whereas the anharmonic MP2 predictions are 37−44 cm^{-1} lower than the 3533 cm^{-1} experimental result.[52] There are several other experimentally reported vibrational frequencies in the far-infrared spectral region in the Ne matrix experiments. The most notable frequency is at 569 cm^{-1},[60] a relatively intense peak, which matches well with our computed 567 cm^{-1} (HF anharmonic) and 569 cm^{-1} (MP2 anharmonic). This mode can be described as a wagging of a bonded hydrogen on the contingent (d) and (u) waters within the trimer.

Table 3 contains the predicted frequencies for the cyclic water tetramer, which possesses S_4 symmetry. Figure 1 labels the water tetramer molecules by the orientation of the free hydrogens, as up (u) and down (d). Two experimental gas-phase frequencies have been detected for the cyclic water tetramer, one at 3714/3717 cm^{-1} originally described as a free O−H stretch and another at 3405/3416 cm^{-1} described as a ring vibration.[52,54] A second set of experimental frequencies, obtained from a neon matrix, have been reported at 3719, 3717, and 3382 cm^{-1}.[60] The scaled HF frequencies predict the asymmetric O−H stretch (ν_3) at 3701, 3700, 3700, and 3699 cm^{-1} for the cyclic S_4 water tetramer, values that are within 18 cm^{-1} of the experimental values. The symmetric O−H stretch (ν_1) is predicted to occur at 3521, 3496, 3496 and 3442 cm^{-1}. The ν_1^{c}(udud) mode (3442 cm^{-1}) is not IR active as the dipole of the tetramer does not change during the concerted vibration, and the ν_1^{nc}(dudu) mode (3521 cm^{-1}) has weak IR intensity, leaving the two strong ν_1^{nc}-(uu) and ν_1^{nc}(dd) vibrations at 3496 cm^{-1} as the most likely experimentally observed modes.[52,54] These modes correspond to the nonconcerted O−H stretch of two waters, a symmetric stretch involving the two waters with dangling hydrogens below the plane (dd) or the two waters with the dangling hydrogens above the plane (uu). In addition to this, an intense peak is seen at 669 cm^{-1} in a neon matrix, which was described as a shear libration motion. Theoretically, this peak is predicted at 673 cm^{-1} with a strong intensity and can be described as a degenerate nonconcerted wagging motion of the bonded hydrogen of the (uu) and (dd) water molecules.

In Figure 1, molecules comprising the water pentamer are labeled according to the free hydrogen's orientation (u and d represent up and down, respectively) and the order around the ring (u1, u2, d1, etc.) The predicted frequencies for the cyclic water pentamer in Table 4 reveal that the ν_3 (asymmetric OH stretch) occurs with medium intensity at 3698 and 3699 cm^{-1}, each involving only a single water in the pentamer. These values are 16 and 15 cm^{-1} lower than the experimentally observed value of 3714 cm^{-1}.[52] The experimental value for the ring vibration, ν_1, is 3360 cm^{-1},[52,54] which we believe corresponds to the nonconcerted O−H stretching with strong IR intensities predicted at 3476 and 3479 cm^{-1}, more than 100 cm^{-1} higher than the experimental value. These two modes involve complex motion of four out of the five waters, where two waters are stretching concertedly but are out-of-phase with the concerted motion of two other waters.

Comparing the values in the Tables 1-4, we see two regions of the spectrum where each water cluster can be uniquely identified. The two regions of the IR spectrum between 3400 and 3700 cm^{-1}, and between 500 and 750 cm^{-1} have unique vibrational modes for the dimer, trimer, cyclic S_4 tetramer, and cyclic pentamer. The values and relative shifts are summarized in Table 5. The water dimer has an experimentally observed out-of-plane bend at 523 cm^{-1}. The HF/6-31G* predicted anharmonic value is 521 cm^{-1} for the dimer, which is in very good agreement. The trimer has a predicted anharmonic rocking mode, ω^{nc}(bonded H du), at 567 cm^{-1}, a blue shift of 46 cm^{-1} relative to the water dimer. The cyclic S_4 tetramer has two strong IR intensity twisting motions predicted at 670 and 673 cm^{-1}, a blue shift of about 106 cm^{-1} relative to the trimer. The cyclic pentamer has three medium IR intensity peaks predicted at 675, 688, and 727 cm^{-1}. The 675 cm^{-1} wagging mode is barely shifted relative to the tetramer frequencies, whereas the 688 and 727 cm^{-1} wagging motions are significantly shifted by about 15 and 54 cm^{-1}, respectively. The only other predicted vibration in the 500−750 cm^{-1} IR region is a weak-intensity wagging mode for the cyclic pentamer at 605 cm^{-1}.

At the low temperatures of most spectroscopy experiments, the structures mentioned above are the predominant structures.[72] One of the cyclic tetramer structures does have C_i symmetry with an electronic energy one kcal/mol higher than the S_4 cyclic cluster, and at 298 K the free energy difference between the two structures is 0.26 kcal·mol^{-1}. At room temperature a

Boltzmann distribution calculation reveals that the S_4 isomer makes up 52% of the population and the C_i isomer makes up 33% of the population for the five possible tetramers.[72] The C_i tetramer has two strong predicted vibrations at 708 and 677 cm^{-1}, placing it between the two vibrations of the S_4 structure and the two highest frequencies of the pentamer, so that it could be uniquely identified in a spectroscopic experiment.

In contrast to the blue shift in the 500−750 cm^{-1} region of the spectrum, a red shift occurs in the 3400−3700 region of the spectrum. As shown in Table 5 the red shift relative to the dimer ranges from 68 to 151 cm^{-1} for the upper ν_1 vibrational mode, and from 39 to 121 cm^{-1} for the lower ν_1 vibrational mode. The combination of observing a red shift at high wavenumber and a blue shift at low wavenumber should be a powerful way to identify unique modes. By combination of the observed frequencies in the two different IR regions with the water pressure dependence of each peak, the cyclic trimer, tetramers, and pentamer can be detected.

Conclusions

The combination of using HF/6-31G* scaled frequencies for intramolecular modes and anharmonic frequencies for intermolecular modes gives excellent agreement with experiment for the water dimer, and the resulting frequencies are as good as the expensive anharmonic MP2 calculations. Scaling the harmonic MP2 frequencies is not recommended for accurate calculation of water cluster frequencies, as scaled HF/6-31G* frequencies are better than any type of scaling for MP2 frequencies when compared to experimental values. The MP2/aug-cc-pVTZ anharmonic frequencies compare best against experiment, and this level of theory and basis was used as a benchmark for the water trimer. The combination of using HF/6-31G* scaled frequencies for intramolecular modes and HF/6-31G* anharmonic frequencies for intermolecular modes is the fastest and most accurate method for obtaining accurate frequencies for the water trimer. The water trimer, the cyclic C_i and S_4 tetramer, and the cyclic pentamer all have unique peaks in the infrared spectrum between 500 and 800 cm^{-1} and between 3400 and 3700 cm^{-1}. The low frequency vibrations are blue shifted as the water cluster size increases, whereas the high frequency vibrations are red shifted with increase in water cluster size. Thus, under the right experimental conditions these different clusters can be uniquely identified using high-resolution IR spectroscopy.

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Supporting Information Available: Harmonic, scaled, split scaled and anharmonic frequencies, optimized geometries for the dimer, trimer, tetramer, and pentamer. This material is available free of charge via the Internet at http://pubs.acs.org.

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