Vibrational frequencies of $(H_2O)_n$ and $(D_2O)_n$ clusters for n = 2 and 8: possible relevance to inelastic neutron scattering of ice

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VIBRATIONAL FREQUENCIES OF $(H_2O)_n$ AND $(D_2O)_n$ CLUSTERS FOR $n = 2$ AND 8: POSSIBLE RELEVANCE TO INELASTIC NEUTRON SCATTERING OF ICE

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Hartree-Fock plus MP2 corrections are reported for the vibrational frequencies in $(H_2O)_2$ and $(D_2O)_2$ and in the cubic octamers $(H_2O)_8$ and $(D_2O)_8$. The motivation was the inelastic incoherent neutron scattering of ice as studied experimentally by Li *et al.* (J.-C. Li, D. Londono, D.K. Ross, J.L. Finney, S.M. Bennington and A.D. Taylor (1992). *J. Phys. Cond. Matter*, **4**, 2109). Some contact is made between our results and these experiments, and also with earlier infrared and Raman studies of Bertie and coworkers.

1. INTRODUCTION

In work about a quarter of century ago, Stillinger and David [1] had already carried out a geometry search to locate the global energy minimum for $(H_2O)_8$. They noted that (i) the general importance of hydrogen bonding in clusters had 'clearly emerged' and (ii) the relevance of water-molecule clusters to condensed-phase phenomena was 'also obvious since the peculiar properties of solid and liquid water owe their explanations to the energetic and geometric characteristics of hydrogen bonds'.

Two other studies have also influenced us in reopening the question of hydrogen bonding in $(H_2O)_8$ and $(D_2O)_8$. One is the Monte Carlo study of $(H_2O)_8$ by Tsai and Jordan [2], in which they focussed on the cubic structures D_{2d} and S_4: see also the very recent discussion of the stability of the cubic water octamer by Belair and

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Francisco [3]. The second study that has provided motivation for the present investigation, which focusses on vibrational modes of both H_2O and D_2O clusters, with particular emphasis on the octamer, is that of Li *et al.* [4], in which experimental results using inelastic incoherent neutron scattering were reported for various phases of ice. These workers [4] also bring their findings into direct contact with both infrared [5,6] and Raman experiments [7] of ice Ih (H_2O). Our motivation in including here studies of $(D_2O)_n$ clusters (with $n = 2$ and 8) is afforded by the Raman scattering by the stretching modes of both H_2O and D_2O in the phases ice II and IX [8].

With this as background and motivation, the outline of the present electronic structure study of H_2O and D_2O clusters is as follows. Firstly, to gain orientation as to vibrational modes, we report briefly in Section 2 the normal mode frequencies associated with the dimers $(H_2O)_2$ and $(D_2O)_2$. Then in Section 3, where our major vibrational studies are reported, the cubic octamers $(H_2O)_8$ and $(D_2O)_8$ are both investigated. The two structures already referred to above, namely D_{2d} and S_4, provide the focus. In all the electronic structure calculations reported here, the Hartree-Fock (HF) method is used as a starting point. This is then supplemented by addition of low-order Møller–Plesset (MP) corrections, which take at least some account of electron correlation neglected in the HF theory. Section 4 constitutes a summary, with some proposals for further study which may prove fruitful.

2. DIMERS OF H_2O AND D_2O: ESPECIALLY VIBRATIONAL MODES

The much-studied water dimer is briefly considered here, the main point being our desire to compare normal mode vibrational frequencies in $(H_2O)_2$ with those in $(D_2O)_2$. Figure 1(a) shows the bond lengths obtained for the optimized geometry of oxygens and the hydrogen isotopes using the HF method with basis set 6-31G** [9]. When second-order Møller-Plesset (MP2) perturbation theory is added, there are modest changes in bond lengths as can be seen from Fig. 1(b). Table I then demonstrates that all the vibrational frequencies are real for the geometrical structures in Fig. 1(a) and (b). One immediate merit of having $(D_2O)_2$ for comparison is that obvious modes dominated by oxygen can be picked out and are labelled (O) in the table. Evidently, frequencies dominantly arising from the motion of hydrogen isotopes are grossly affected by isotopic mass, with frequencies roughly proportional to $1/\sqrt{2}$ in scaling from the H_2O isotopic dimer to $(D_2O)_2$.

(a)
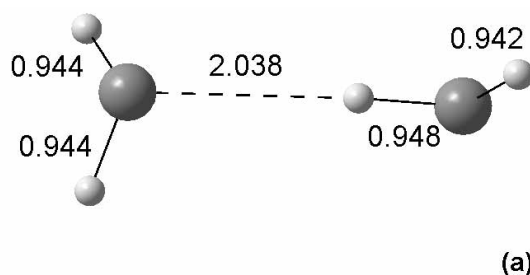
FIGURE 1 (a) Calculated equilibrium geometry of the $(H_2O)_2$ dimer at HF/6-31G** level, with bond lengths indicated in Angstroms; the hydrogen bond is denoted by a dashed line. (b) The equilibrium geometry of the $(H_2O)_2$ dimer at MP2/6-31G** level, with bond lengths in Angstroms indicated as before.

0.960

0.963   1.966

0.963   0.967
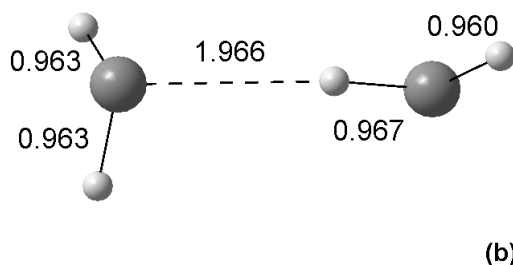
(b)

FIGURE 1   Continued.

TABLE I   Calculated normal mode frequencies for the dimers $(H_2O)_2$ and $(D_2O)_2$ at HF/6-31G** and MP2/6-31G** levels. Modes which primarily involve motion of oxygens are denoted by (O)

Water dimer vibrational frequencies (cm^{-1})		
	HF	*MP2*
$(H_2O)_2$	117.88	84.31
	138.35	140.97
	141.06	161.07
	177.25 (O)	204.22 (O)
	377.21	428.41
	612.24	659.95
	1768.12	1680.23
	1797.26	1713.82
	4098.97	3818.23
	4142.22	3876.32
	4238.06	3998.50
	4255.63	4006.88
$(D_2O)_2$	84.09	59.92
	102.74	106.60
	103.64	117.43
	164.56 (O)	189.45 (O)
	279.30	314.03
	441.06	474.28
	1294.20	1229.10
	1313.48	1252.02
	2958.90	2758.22
	2985.57	2794.19
	3103.24	2924.06
	3120.40	2935.19

3. STRUCTURE AND VIBRATIONAL STUDIES OF CUBIC OCTAMER $(H_2O)_8$ AND $(D_2O)_8$

With this admittedly elementary example, we turn to the major focus of this article, namely the (very numerous) vibrational frequencies of the two cubic octamers considered. Figure 2 shows the detailed structure for symmetry D_{2d}. The upper panel gives the HF bond lengths, while MP2 results are shown in the lower panel. Relatively modest changes in the bond lengths on adding some account of electron correlation are found. Figure 3 gives similar results for the cubic octamer with symmetry S_4, leading

FIGURE 2   (a) Equilibrium geometry of the $(H_2O)_8$ cubic octamer of D_{2d} symmetry as calculated at HF/6-31G** level; representative bond lengths (in Angstroms) are indicated. (b) Equilibrium geometry of the same cluster, at MP2/6-31G** level.

to similar conclusions. In going from HF to MP2 level, the energy of the D_{2d} structure drops from -608.31005 to -609.92108 a.u., while the energy of the S_4 structure goes from -608.30986 to -609.92097 a.u. The D_{2d} and S_4 structures are thus essentially degenerate at these levels of calculation, with D_{2d} lying only ~ 3 meV below S_4 at MP2 level.

We turn now to discuss the vibrational frequencies associated with the two structures. We note here that Tsai and Jordan [2] already recorded that all HF frequencies are real for the two cubic octamers with symmetries D_{2d} and S_4 but they recorded no numerical results. Out main interest here, as already mentioned, is to compare $(H_2O)_8$ and $(D_2O)_8$
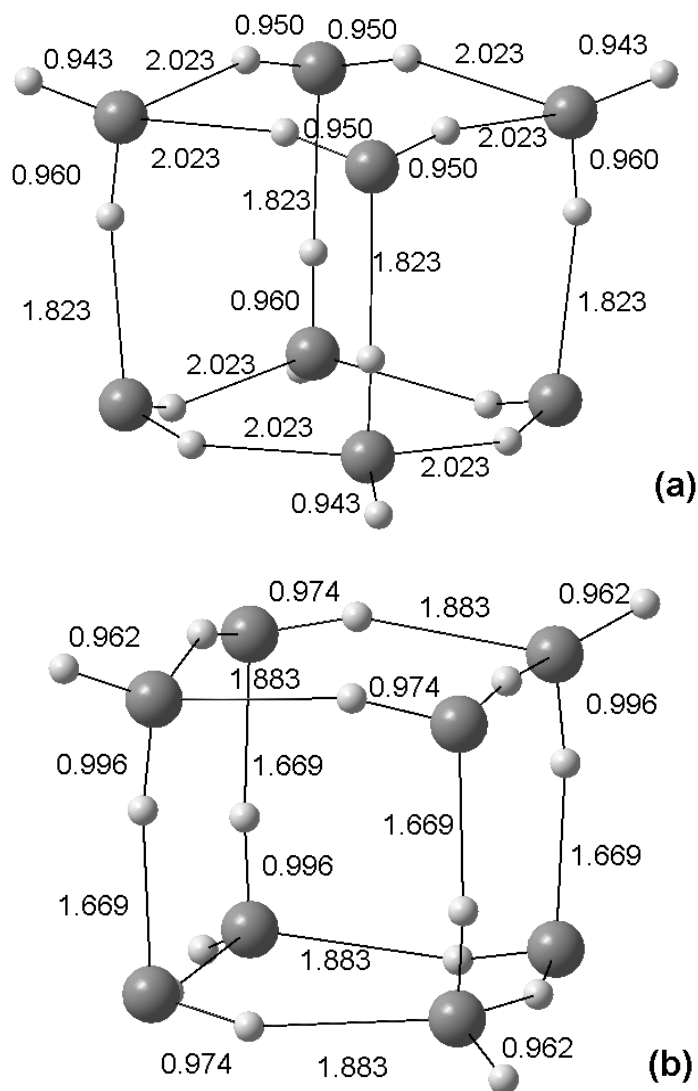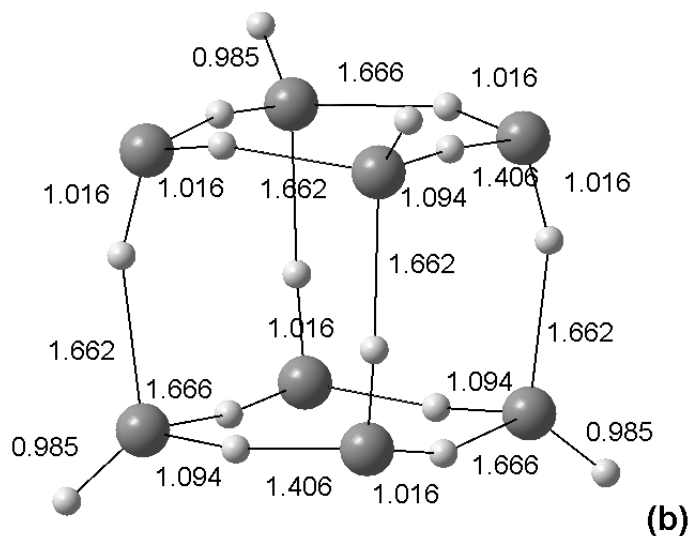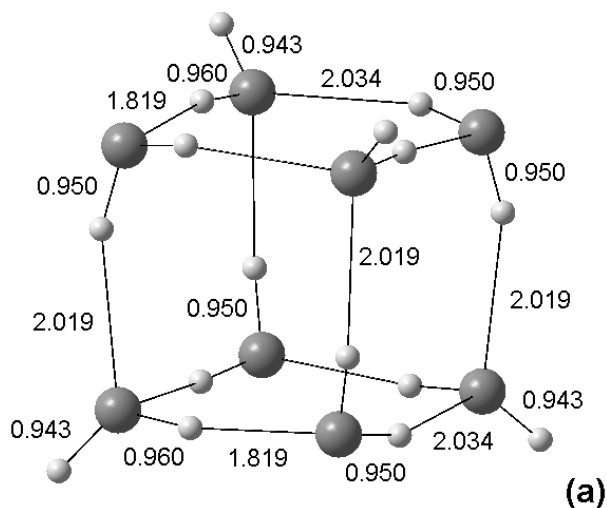
FIGURE 3 (a) Equilibrium geometry of the $(H_2O)_8$ cubic octamer of S_4 symmetry as calculated at HF/6-31G** level, with representative bond lengths indicated (in Angstroms). (b) The same cluster, at MP2/6-31G** level.

vibrational modes. Vibrational frequencies for the $(H_2O)_8$ cubic octamer in both D_{2d} and S_4 symmetries are given in Table II at the HF/6-31G** level. Comparison with the inelastic neutron scattering results given in Table I of Li *et al.* [4] gives frequencies in the range ~ 3780–$4350\,cm^{-1}$ and especially the high-frequency end appears to be reflected in the results of the present theoretical study, the normal modes with the highest frequencies lying at $\sim 4220\,cm^{-1}$. Related results for $(D_2O)_8$ with the same basis set are recorded in Table III. If we reduce the above $(H_2O)_8$ highest frequency, assuming the mode is dominated by the hydrogen isotopic mass M, by $M^{-1/2}$, i.e., by $1/\sqrt{2}$, we find $\sim 3000\,cm^{-1}$, which is reasonably close to the highest frequency for $(D_2O)_8$ in Table III.

TABLE II   Calculated vibrational mode frequencies in cm^{-1} for $(H_2O)_8$ cubic octamers, of both D_{2d} and S_4 symmetries, at HF/6-31G** level

	$(H_2O)_8$ vibrational frequencies (cm^{-1})		
D_{2d}	69.80	70.10	71.07
	72.51	72.51	102.95
	158.40	162.30	168.38
	168.38	178.51	192.51
	192.80	192.80	237.08
	242.66	247.54	247.54
	248.83	261.73	300.88
	300.88	398.35	405.63
	405.63	451.24	465.59
	498.88	500.68	500.68
	565.52	635.58	635.58
	636.01	699.38	699.38
	736.55	832.23	884.17
	965.15	965.15	1027.54
	1793.69	1798.77	1798.77
	1811.60	1811.60	1815.34
	1844.27	1853.57	3839.31
	3854.45	3854.45	3888.69
	4052.18	4052.18	4061.94
	4062.57	4121.65	4121.67
	4148.00	4148.00	4215.77
	4215.90	4215.90	4216.38
S_4	65.97	67.77	67.77
	68.92	73.81	98.20
	156.62	159.60	159.60
	165.43	178.42	191.49
	191.49	192.59	245.08
	246.58	256.49	257.57
	257.57	279.07	279.07
	297.85	396.69	410.04
	434.51	434.51	460.48
	524.90	524.90	535.43
	570.59	614.66	634.35
	634.35	717.81	717.81
	737.60	852.35	894.77
	894.77	979.58	1007.46
	1793.73	1793.73	1796.72
	1808.09	1831.56	1833.92
	1833.92	1849.76	3837.49
	3852.76	3869.45	3869.45
	4045.15	4048.37	4048.37
	4055.52	4115.02	4129.98
	4129.98	4141.45	4216.48
	4216.48	4216.58	4217.04

4. SUMMARY AND FUTURE DIRECTIONS

While the major results of the present investigation are contained in Table II, where the frequencies of the hydrogen isotopes in $(H_2O)_8$ and $(D_2O)_8$ can be compared, we want to make some brief observations first with regard to the neutron scattering results of Li *et al.* [4] recorded, in particular, in their Table I. They recorded these from the inelastic incoherent neutron scattering of ice Ih (H_2O) vibration spectra in a frequency range 3784–4347 cm^{-1}. This is compared with the infrared measurements of Ockman [6]

TABLE III   Calculated vibrational mode frequencies in cm^{-1} for $(D_2O)_8$ cubic octamers of D_{2d} and S_4 symmetries at HF/6-31G** level

	$(D_2O)_8$ vibrational frequencies (cm^{-1})		
D_{2d}	66.42	66.98	67.56
	69.56	69.56	99.42
	148.34	152.77	152.77
	153.26	169.39	171.97
	180.85	180.85	181.08
	182.34	226.83	226.83
	228.53	236.76	236.76
	249.45	287.82	295.14
	295.14	320.81	343.77
	359.55	359.55	363.32
	409.12	452.19	460.88
	460.88	512.80	512.80
	538.63	599.28	650.42
	694.15	694.15	737.15
	1309.00	1313.94	1313.94
	1321.05	1321.05	1324.61
	1345.28	1351.73	2785.07
	2796.19	2796.19	2820.00
	2921.93	2921.93	2929.04
	2929.12	3022.73	3023.03
	3041.00	3041.00	3075.71
	3075.71	3075.78	3076.45
S_4	62.91	64.69	64.60
	65.57	70.71	94.95
	147.12	147.61	147.61
	151.43	169.13	177.71
	178.36	178.36	183.66
	207.23	207.23	220.39
	235.86	240.69	247.35
	247.35	286.38	299.25
	317.39	317.39	329.45
	382.20	382.20	383.77
	414.00	442.64	454.32
	454.32	525.37	525.37
	544.29	623.81	644.54
	644.54	704.63	724.33
	1309.22	1309.22	1313.24
	1317.18	1337.58	1337.58
	1339.01	1346.34	2783.71
	2795.10	2806.86	2806.86
	2916.88	2919.39	2919.39
	2923.95	3018.20	3027.92
	3027.92	3036.35	3076.18
	3076.19	3076.19	3076.87

in the range 3955–4150 cm^{-1}. We assume that such frequencies would be reduced, of course, very approximately, by a factor roughly $M^{-1/2}$, where M is the isotopic mass, i.e., by $1/\sqrt{2}$ from H_2O to D_2O clusters. Such approximate reduction is evident in Table III of Bertie and Francis [8] from their measurements by Raman scattering of the stretching vibrations of both ices II and IX at atmospheric pressure. We have also in our present calculations isolated Raman and infrared active modes, but as we cannot expect, at best, more than semi-quantitative contact between octamer clusters and phases of ice, we shall not press the detail further at this stage of our theoretical studies.

As to larger clusters, suggestions have been made as to a solid–liquid like transition with increasing cluster size [2]. We conclude with two comments of possible longer-term relevance. Firstly, water clusters are of considerable interest because of the potential such an area has for giving insight into condensed phases. Thus, for liquid water, they afford a route to gain further insight into the nature of hydrogen bonding and hence to yield a deeper understanding of the liquid starting from properties at the molecular scale. Work on much larger water clusters than those considered here is therefore of continuing interest, and for such clusters the recent work of Rousseau *et al.* [10] shows clearly that density functional theory has great computational advantages. Of course, for small clusters, work such as that of Schenter [1] on the water dimer using path integral Monte Carlo techniques is of major importance. Secondly, future applications relating to nanotechnology seem promising. Thus Maite *et al.* [12] have considered by density functional theory the effect on the field emission current of absorbing one to five water molecules on carbon nanotube tips. Their conclusion is that water molecules are attracted to metallic nanotube tips under field-emission conditions and form complexes that are stable well above room temperature. Further work, both theoretical and experimental, may well prove fruitful in this area.

Acknowledgements

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