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Food Chemistry 82 (2003) 23–28

Food Chemistry

www.elsevier.com/locate/foodchem

Ab initio calculations of polyhedra liquid water☆

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Received 31 October 2002; received in revised form 29 November 2002; accepted 10 December 2002

Abstract

Ab initio calculations have been performed using the 6-31G* basis set for different structures of water clusters $(H_2O)_n$, $n = 1$–10, 15. When increasing the number of water molecules, it appears that for $n > 5$, we observe a transition from planar to three-dimensional structures. All the different clusters present many stable geometries that are all very close in energy. To be sure that a minimum of the energy potential surface has been reached, vibrational frequencies for both $(H_2O)_n$ and $(D_2O)_n$ were calculated. When n increases, the O–O distance is always decreasing. From this study, we deduced that in the temperature range −10 to 100 °C, the most abundant clusters in liquid water at density 1 g/ml contain more than five water molecules.

Keywords: Clathrate; Cluster of water molecules; Vibrational spectra; Ab initio calculations

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1. Introduction

Although in the recent years, much information has been obtained on the nature of water clusters, the contribution of these clusters to the properties of liquid water may not have been developed to the fullest possible extent. The hydrophobic effect is a dominant force in biomolecular conformation and stability. For instance, in proteins nonpolar residues cannot participate in hydrogen-bonding interactions with bulk water (Lipscomp, Zhou, & Williams, 1996).

Despite the enormous amount of information now available, the mystery of the structure of water remains unsolved. In fact, different models have been proposed but they are either mutually or contradicting and complementary approaches. They are represented by using the continuum models (uniformist) and the mixture models (cluster approaches). In the first description model, each water molecule is depicted as being surrounded in the same way by other molecules in distorted positions. In that case, the hydrogen bonding (Jeffrey, 1997) is supposed to be complete and thus water molecules are considered as a three-dimensional network of hydrogen-bonds that interconnect the water molecules in a dynamical process. The molecules have a continuous distribution of bond angles, as well as the associated hydrogen-bond network considering distances and angles, and bond energies. However, it should be pointed out that the continuum models are incompatible with some thermodynamic particular properties such as the compressibility minimum and the density maximum (Horne, 1972). In the second description model, liquid water is considered to be a mixture of a small number of distinctly different species that are in equilibrium. Most mixture models assume that water molecules exist in few classes of structural species that are more or less well defined. Then, numerous works have been published and correspond to different theoretical approaches (Chaplin, 1999; Dougherty & Howard, 1998; Frank & Wen, 1957; Hagler, Scheraga, & Nemethy, 1972; Jorgensen, Chandrasekhar, Madura, Impey, & Klein, 1983; Maheshwary, Patel, Sathyamurthy, Kulkarni, & Gadre, 2001; Nemethy & Scheraga,

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☆ This work was partially presented at the 2nd International workshop on water in food, and was dedicated to the memory of Professors J. Kroon and G. Jeffrey.

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0308-8146/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0308-8146(02)00589-7

1962; Walrafen, Fisher, Hokmabadi, & Yang, 1986; Xantheas, 1993, 1994, 1995, etc.).

In order to understand more about the hydrophobic effects in biomolecules, we decided to focus our attention in a first step on water molecules and clathrate hydrates. These latter water clusters provide a good model for describing the water molecules which are organized around the hydrophilic and hydrophobic aminoacid side chains in globular proteins and particularly for explaining the behavior of water towards nonpolar side groups.

The classical vibrational spectroscopy of liquid water has been reviewed by Scherer (Scherer, 1980). In this review, the first figure gives the scarcity of Raman spectral data for H_2O in the solid, liquid and near gazeous states. Different points are then discussed such as the OH-stretching bands (shift from above 3600 cm^{-1} at high temperature and low density to below 3200 cm^{-1} in the spectra of ice at low temperature) and the HOH-bending modes.

Thus, we have calculated the structures, geometries, and vibrational spectra (see Table 1) of water molecules increasing the number of molecules.

2. Material and methods

2.1. Quantum mechanical procedures

Using the program Gaussian'94 and then the '98 version (Frisch et al., 1994), with Hartree–Fock calculations at a 6-31G* level, we have calculated the energy minimized structures for $(HOH)_1$, $(HOH)_2$, $(HOH)_3$, $(HOH)_4$, $(HOH)_5$, $(HOH)_6$, $(HOH)_7$, $(HOH)_8$, $(HOH)_9$, $(HOH)_{10}$ and $(HOH)_{15}$ as well as their deuterated analogs.

Standard quantum chemistry yields a stable molecule. It is well known that within Hartree–Fock approximation, the computed water structure has an HOH angle slightly too wide relative to experimental data, but the correct value is easily obtained by correlating the electron's motions.

2.2. Normal coordinates of water

One of the major problem in simulations of water is that (i) by using ab initio calculations one simulates the gaseous state or a semi-liquid state, (ii) by using empirical methods the results are very sensitive to the used potential. A rigorous calculation of the normal coordinates of liquid water requires a detailed knowledge of the structure and of the intra- and intermolecular force constants for numerous hydrogen-bonding states. However, the corresponding force field for the liquid water remained not appropriate for efficient simulations and very difficult to be precisely derived. The usual internal coordinates R_i of the water molecule may be defined as the two OH Δr_1 and Δr_2 stretching coordinates and the $\Delta\alpha$ valence angle bending coordinate. For empirical procedures, the force constants have been determined from fitting between harmonic and observed frequencies. It is well known (Scherer, 1980), that the totally symmetric OH stretch as has very little contribution from the bending coordinate. Similarly, the bending mode has little contribution to the stretching mode. However, these modes are very sensitive depending for instance upon environment and temperature.

3. Results and discussion

The classical vibrational spectroscopy of liquid water has been reviewed by Scherer (1980). Very precise calculations were done using a lot of quantum models (see in this series, the paper of Starzak and Mathlouthi, 2003). However, increasing the number of water molecules, $(H_2O)_i + H_2O \leftrightarrow (H_2O)_{i+1}$, even for few water molecules in the small water clusters, leads to clusters presenting many stable geometries that are all very close in energy. Thus, in these cases one has to face a difficult minimization problem. Moreover, it should be pointed out that the cluster study provides also very interesting geometrical arrangements of hydrogen bonded structures, leading to clathrate or to be precise in that case "clathrate-like" complexes. Similar behaviours obtained both from theoretical calculations (quantum mechanics and Monte-Carlo computations) and from experimental data obtained using far-infrared laser Vibration–Rotation Tunneling (VRT) spectroscopy were observed by Saykally and coworkers (Liu, Brown, Carter et al., 1996; Liu, Brown, Cruzan, & Saykally, 1996; Liu, Cruzan, & Saykally, 1996; Cruzan et al., 1996; Gregory, Clary, Liu, Brown, & Saykally et al., 1997). Nevertheless, because of statistical fluctuations, it is very unlikely that one could build up indefinitely the cluster size. As it was recently proved, the most stable conformations of the cluster appear to be like water tubes with a four or five water molecules basis (Krallafah, 2002; Maheshewary et al., 2001).

From the obtained optimized structures, it appears that, when the number of water molecules exceeds $n = 5$, there are a lot of different stable conformations. These conformations are very close in energy. The minimized structure of the pentamer is always the same (not focusing on the flip-flop of OH orientation) no matter what the starting structure is. Using such calculation, it seems to be impossible to obtain the tetrahedral conformation as a stable one in an isolated environment. Similar data were obtained from both experimental evidences and computational results (Liu, Brown, Cruzan et al., 1996).

However, when $n=6$ or more, it also becomes evident that the corresponding water clusters seem to prefer to adopt one or more three-dimensional optimised structures rather than a single cyclic structure. For instance, for $n=6$, one cyclic structure, one bipyramidal structure with a square base, one prism structure and one cage structure are found as optimised solutions (Fig. 1). For $n=7$–9, a lot of different spatial structures coexist. Moreover, it seems that for even numbers of water molecules very high symmetric conformations should be preferred. For the 10-mer water cluster, the most favorable computed structure corresponds to that drawn in Fig. 1.

When, the size of the cluster increases, it seems evident that hydrogen-bond cooperativity exists: the O–O distance is always decreasing. It also should be noted that, whereas bifurcated hydrogen bonds are often found in proteins or in biomolecules which possess

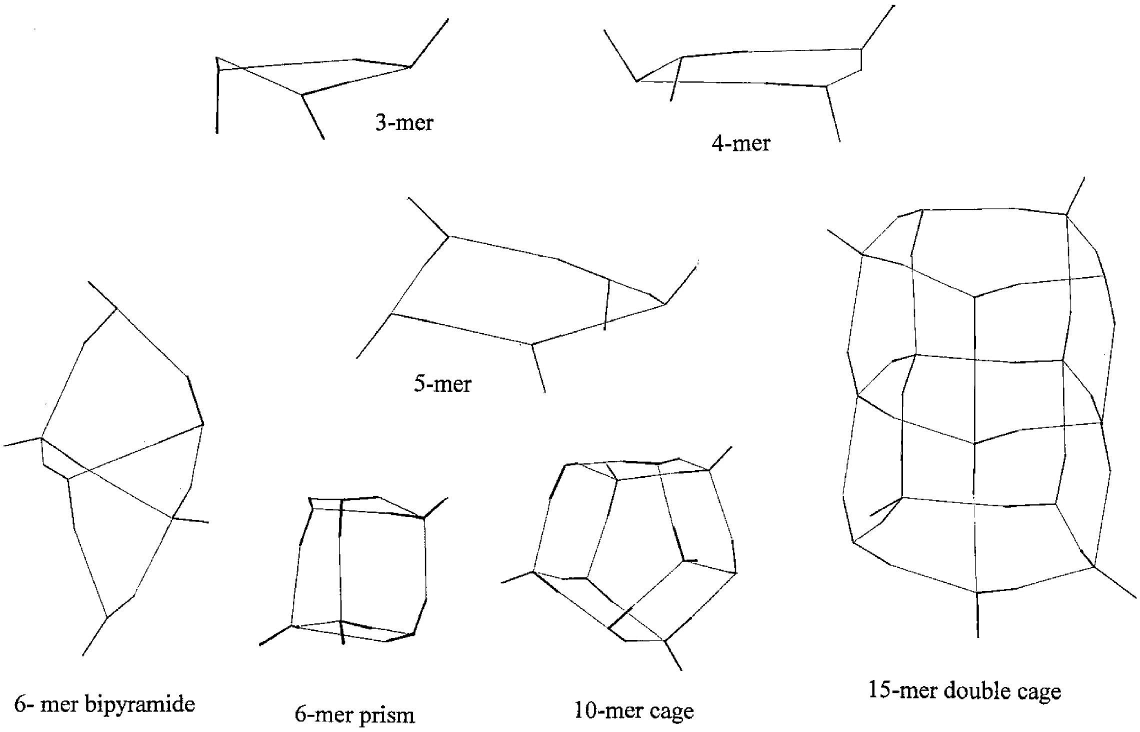

Fig. 1. Some of the low energy structures for $n=3$, 4, 5, 6, 10 and 15.

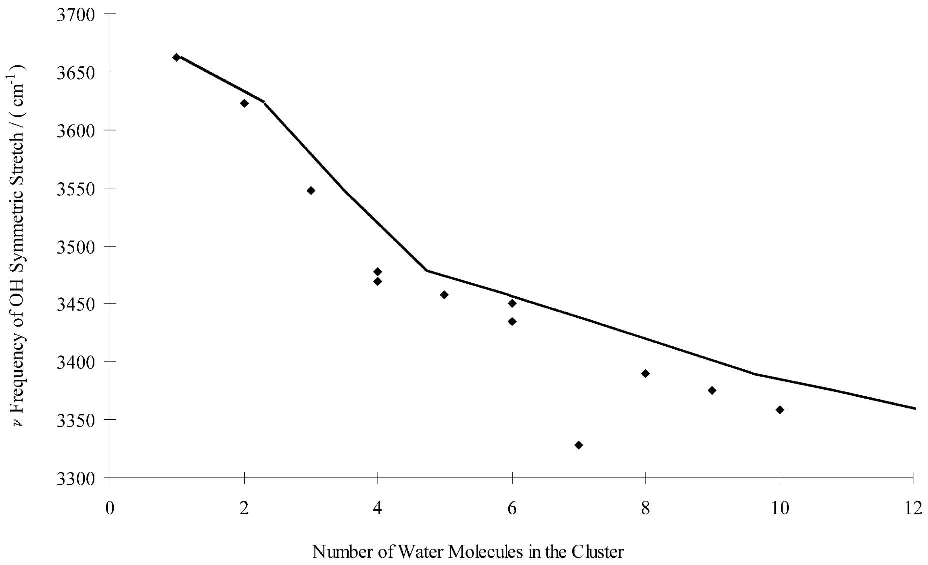

Fig. 2. Frequency of ν_s(OH) symmetric stretch (cm^{-1}) versus n number of water molecules in the cluster.

Table 1
Calculated and scaled frequencies ($f = 0.89$) for $n = 1–6$, and 10 water clusters

H_2O		2 H_2O		3 H_2O		4 H_2O		5H_2O		6H_2O		10H_2O	
Calcd	Scaled	Calcd	Scaled	Calcd	Scaled	Calcd	Scaled	Calcd	Scaled	Calcd	Scaled	Calcd	Scaled
1827	1626	123	109	165	147	31.4	28	19.3	17	41.1	36.5	53.8	47.9
4069	3621	144	128	178	157	70.7	63	39.8	35.4	51.5	45.8	57.4	51
4187	3726	150	133	184	164	156	139	55.1	49	68	60.5	60	53.4
		184	164	187	166	193	172	60.5	54	83	73.8	60.8	54.3
		379	337	219	194	202	179	147	131	111	98.7	63	56
		622	554	247	220	225	200	173	154	126	112	65.1	57.9
		1824	1623	331	294	232	205	176	156	172	153	67.3	59.6
		1855	1651	352	313	236	210	212	189	180	160	88.3	78.6
		4026	3583	455	405	243	216	219	195	184	164	90.8	80.9
		4065	3618	575	512	267	238	223	198	188	167	148	132
		4160	3702	670	596	343	305	251	223	200	178	150	133
		4179	3719	911	811	382	340	275	245	215	191	154	137
				1841	1639	455	405	277	246	227	202	159	141
				1851	1647	524	466	287	258	249	221	169	150
				1864	1659	626	557	371	330	273	243	169	150
				3941	3507	710	632	390	347	275	253	187	166
				3985	3547	791	704	415	369	324	288	194	173
				3989	3550	939	836	425	378	354	315	196	174
				4147	3690	1852	1648	505	449	392	349	221	197
				4150	3693	1860	1656	660	587	419	373	226	202
				4152	3695	1868	1662	756	673	469	417	239	213
						1877	1670	799	711	520	463	251	223
						3865	3440	820	730	301	534	269	239
						3919	3488	939	836	303	537	280	249
						3925	3493	1854	1650	641	570	285	253
						3948	3514	1855	1651	691	615	294	262
						4144	3688	1865	1660	702	625	297	264
						4144	3688	1871	1665	751	668	299	266
						4146	3690	1882	1675	897	798	308	274
						4146	3690	3842	3419	1006	895	386	343
								3892	3464	1839	1637	411	366
								3897	3467	1844	1640	422	375
								3930	3498	1853	1649	432	384
								3934	3501	1875	1668	470	419
								4142	3686	1886	1678	488	433
								4142	3686	1901	1692	496	441
								4144	3688	3697	3290	536	477
								4145	3698	3931	3498	555	494
								4148	3692	3945	3510	562	500
										3988	3549	578	514
										3995	3555	605	538
										4010	3569	623	554
										4034	3591	626	558
										4103	3652	659	587
										4132	3677	680	605
										4145	3689	714	638
										4149	3693	753	670
										4160	3702	765	681
												793	706
												874	779
												934	831
												939	836
												987	878
												1014	902
												1849	1646
												1851	1647
												1854	1650
												1857	1653

(continued on next page)

Table 1 (*continued*)

H_2O		2 H_2O		3 H_2O		4 H_2O		$5H_2O$		$6H_2O$		$10H_2O$	
Calcd	Scaled	Calcd	Scaled	Calcd	Scaled	Calcd	Scaled	Calcd	Scaled	Calcd	Scaled	Calcd	Scaled
												1865	1660
												1881	1674
												1884	1677
												1891	1684
												1904	1694
												1912	1702
												3732	3359
												3745	3334
												3782	3366
												3784	3368
												3903	3474
												3919	3488
												3968	3531
												3972	3535
												3981	3543
												3997	3557
												4038	3594
												4048	3603
												4059	3613
												4069	3621
												4087	3638
												4134	3680
												4135	3681
												4137	3682
												4137	3682
												4142	3686

numerous hydroxyl groups such as carbohydrates, this type of H-bond does not exist in these clathrate hydrates.

Of particular interest is the calculated HOH totally symmetric stretching vibrational mode (which is strongly active in the classical Raman effect) involving the symmetric displacement of the O–H bonds in all $(HOH)_n$ molecules which is found to monotically decrease in frequency when the number of water molecules in the cluster increases (Fig. 2). The used scaling factor (see Table 1) was determined by the results of vibrational analyses for the water monomer, dimer and relevant experimental data.

In the field of food research, it has long been recognized that water presents different properties than free and bulk water and is referred as bound water (Fennema, 1976). The major characteristics of this bound water are its unfreezability even at very low temperatures (Leung & Steinberg, 1979), low vapor pressure, and also include reduced molecular mobility (Labuza, 1977).

Water molecules may be associated with food components by different ways as described below. Nevertheless, the structures and properties of water in foods differ considerably from those of ordinary free water, so by studying the nature and forces of binding between water molecules and food components (depending upon their chemical structures), it is possible to study the effect of water on texture and other quality aspects of foods. Thus, association of water molecules with food components could be (i) like water of crystallization strongly chemically bound water, (ii) like water adsorbed on hydrophilic specific sites by very low hydrogen bonding, (iii) like water organized as structured water molecules, close to the surface of the considered macromolecules in clathrate types and (iv) like water molecules in solutions. In this latter case, one can find, in solution, a lot of different small solute molecules such as linear sugars or carbohydrates, salts which can depress the activity of water molecules.

4. Conclusion

Studying both the structures and their corresponding energies and the vibrational data, it seems evident that hydrogen-bond cooperativity exists in these clathrate hydrate models. We noted a correlation for the experimental frequency corresponding to the maximum Raman intensity versus temperature. Thus, we deduced that in the temperature range −10 to 100 °C, the most abundant clusters in liquid water at density 1 g/ml contain more than five water molecules. For $n = 10$ and $n = 15$, we can obtain specific hydrate models like cages that allow to entrap either ions or small molecules. Some conformations ($n = 15$) or those recently obtained by Maheshwary and coworkers have a tube shape, and an internal diameter similar to those observed in pore proteins. However, from these results, the view of liquid water has to be approached from a random, dynamical and three-dimensional network of hydrogen bonds.

Acknowledgements

M.D. is indebted to Pr. Krallafah A. for helpful discussions. W.L.P. thanks the University of Reims Champagne-Ardenne for a 3-month fellowship.

References

Chaplin, M. F. (1999). A proposal for the structuring of water. *Biophysical Chemistry*, *83*, 211–221.

Cruzan, J. D., Braly, L. B., Liu, K., Brown, M. G., Loeser, J. G., & Saykally, R. J. (1996). Quantifying hydrogen bond cooperativity in water: Vibration-Rotation Tunneling spectroscopy of the water tetramer. *Science*, *271*, 59–62.

Dougherty, R. C., & Howard, L. N. (1998). Equilibrium structural model of liquid water: evidence from heat capacity, spectra, density and other properties. *J. Chem. Phys.*, *109*, 6393–7379.

Fennema, O. (1976). Water and protein hydration. In J. A. Whitaker, & S. R. Tannebaum (Eds.), *Food Proteins.* Avi Publishing Co. Wesport, CT, USA.

Frank, H. S., & Wen, W. Y. (1957). Structural aspects of ion-solvent interaction in aqueous solutions: a suggested picture of water structure. *Disc. Faraday Soc.*, *24*, 133–140.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replodge, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzales, C., & Pople, J. A. (1994). *Gaussian94*. Pittsburgh, PA, USA: Gaussian Inc.

Gregory, J. K., Clary, D. C., Liu, K., Brown, M. G., & Saykally, R. J. (1997). The water dipole moment in water clusters. *Science*, *275*, 814–817.

Hagler, A. T., Scheraga, H. A., & Nemethy, G. (1972). Structure of liquid water. Statistical thermodynamic theory. *J. Phys. Chem.*, *76*, 3229–3243.

Horne, R. A. (1972). *Water and aqueous solutions: structure, thermodynamics and transport processes.* New York, USA: Wiley Interscience.

Jeffrey, G. A. (1997). *An introduction to hydrogen bonding*. New York, USA: Oxford University Press.

Jorgensen, W. L., Chandrasekhar, J., Madura, J. D., Impey, R. W., & Klein, M. L. (1983). Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.*, *79*, 926–935.

Krallafah, A. (2002). Personnal communication [to be published].

Labuza, T. P. (1977). The properties of water in relationship to water binding in foods: a review. *J. Food Proc. Pres.*, *1*, 167.

Lipscomb, L. A., Zhou, F. X., & Williams, L. D. (1996). Clathrate hydrates are poor models of biomolecule hydration. *Biopolymers*, *38*, 177–181.

Liu, K., Brown, M. G., Carter, C., Saykally, R. J., Gregory, J. K., & Clary, D. C. (1996). Characterization of a cage form of the water hexamer. *Nature*, *381*, 501–503.

Liu, K., Brown, M. G., Cruzan, J. D., & Saykally, R. J. (1996). Vibration–Rotation Tunneling spectra of the water pentamer: structure and dynamics. *Science*, *271*, 62–64.

Liu, K., Cruzan, J. D., & Saykally, R. J. (1996). Water clusters. *Science*, *271*, 929–933.

Leung, H. K., & Steinberg, M. P. (1979). Water binding of food constituents as determined NMR, freezing, sorption and dehydration. *Journal of Food Science*, *44*, 1212–1220.

Maheshwary, S., Patel, N., Sathyamurthy, N., Kulkarni, A. D., & Gadre, S. R. (2001). Structure and stability of water clusters $(H_2O)_n$, n = 8-20: an *ab initio* investigation. *J. Phys. Chem. A*, *105*, 10525–10537.

Nemethy, G., & Scheraga, H. A. (1962). Structure of water and hydrophobic bonding in proteins. I. A model for thermodynamic properties of liquid water. *J. Chem. Phys.*, *36*, 3382–3400.

Scherer, J. R. (1980). The vibrational spectroscopy of water. In R. J. H. Clark, & R. E. Hester (Eds.), *Advances in infrared and raman spectroscopy. Vol 5* (pp. 149–216). London Philadelphia, Rheine: Heyden.

Starzak, M., & Mathlouthi, M. (2003). Cluster composition of liquid water derived from laser-Raman spectra and molecular simulation data. *Food Chemistry*, this issue.

Walrafen, G. E., Fisher, M. R., Hokmabadi, M. S., & Yang, W. H. (1986). Temperature dependence of the low and high frequency Raman scattering from liquid water. *J. Chem. Phys.*, *85*, 6970–6982.

Xantheas, S. S. (1993). Ab initio studies of cyclic water clusters $(H_2O)_n$, n = 1-6. I. Optimal structures and vibrational spectra. *J. Chem. Phys.*, *99*, 8774–8792.

Xantheas, S. S. (1994). Ab initio studies of cyclic water clusters $(H_2O)_n$, n = 1-6. II. Analysis of many body interactions. *J. Chem. Phys.*, *100*, 7523–7534.

Xantheas, S. S. (1995). Ab initio studies of cyclic water clusters $(H_2O)_n$, n = 1-6. III. Comparison of density functional with MP2 results. *J. Chem. Phys.*, *102*, 4505–4517.