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The ground state structure and properties of erythritol in gas phase and in different solvents: A DFT / SC-IPCM approach

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Quantum mechanical study of the ground state structure and properties of erythritol was carried out in gas phase and in different solvents at the hybrid B3LYP DFT level with complete geometry optimization and varying basis sets [6-311G (d,p) and 6-311++G (d,p)] in order to provide detailed information of the model molecule in solvents of low, medium and high dielectric constant. It was found that the molecule is stabilized by solvation in all cases, the order of stability being water > DMSO > carbontetrachloride. The dipole moment was increased. The charge density on O-atoms were increased almost as per above order indicating that there are two types of O-H groups in the molecule in agreement with the reported experimental findings. Carbon skeleton were planar in water and DMSO by 6-311++G (d,p) basis set gave non planar structure in CCl$_4$. The geometries in water and DMSO were in excellent agreement with the experiment. The calculated IR frequencies are well when compared with the experimental results. The HOMO-LUMO gap remained almost same on solvation.

Key words: B3LYP DFT, GAUSSIAN, erythritol, charge distribution, gas phase.

INTRODUCTION

The rapid development of both theory and software makes it possible to have detailed studies of the structure and properties of different molecules in gas phase and in solution. There is a growing interest in the study of important bio-molecules both theoretically (Ladik, 2004) and experimentally. Among the bio-molecules, carbohydrates are very important as they coordinate with various metal ions like Cu^{+2}, Mn^{+2}, Fe^{+2}, Zn^{+2} etc. in playing vital role in versatile metabolic activities. Why these metal ions do so is to be answered. Carbohydrate research is a challenging field and its progress is much slower experimentally.

Recently, single crystals of co-ordinated complexes of neutral erythritol ($C_4H_{10}O_4$) with various metal ions were synthesized and studied using FT-IR and single crystal X-ray diffraction analysis (Yang et al., 2004a and b). There are several theoretical (gas phase and water phase) and experimental reports (Jesus et al., 2005a and b; 2006; Ceccarelli et al., 1980; Shimada et al., 1959; Hao et al.,

2005) on the erithritol molecule. In reference to Jesus et al. (2005a), a detailed study of the molecule has been done in gas phase using DFT method using 6-311++G (d,p) basis set and in reference to Jesus et al. (2005b), enthalpy of sublimation of erythritol in solid state has been determined and some terms have been calculated in gas phase by DFT method using 6-311++G(d,p) basis set. In reference to Jesus et al. (2006), a beautiful study of the same molecule in water phase has been done using CPCM model. Ceccarelli et al. (1980) and Shimada et al. (1959) have reported the crystal structure of the erythritol molecule been and Hao et al. (2005) has reported the solubility of erythritol in different solvents and solvent mixture (water, methanol, ethanol, acetone). Structure and properties of erythritol in its ground state and first excited state in gas phase without the solvent effects have been reported theoretically using lower basis set (De et al., 2006). In the present work, we have undertaken the detailed systematic and comprehensive theoretical investigation on the structure and properties of the simplest representative of the carbohydrates, that is erythritol in its ground state both in gas phase and in different solvents of low, medium and high dielectric

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constant by the hybrid B3LYP DFT method (*Gaussian 03W Program*,(Gaussian, Inc., Wallingford, CT) 2004; Lee, 1988; Becke et al., 1993) using [6-311G (d,p) and 6-311++G (d,p)] basis set in order to have detailed information about the model molecule because the higher basis sets are more reliable in this respect. This theory (DFT) has recently become popular in quantum chemistry because present day approximate functionals provide a useful balance between accuracy and computational cost, allowing much larger systems to be treated than traditional *ab initio* methods, retaining much of their accuracy. This theory is the way of approaching any interacting problem, by mapping it exactly to a much easier-to-solve non-interacting problem using higher basis set. Three solvents [carbon tetrachloride (ε = 2.228), DMSO (ε = 46.7) and water (ε = 78.39)] were chosen as the case study.

COMPUTATIONAL DETAILS

Complete geometry optimizations for the ground state in the gas phase were carried out with B3LYP DFT method with 6-311G (d,p) and 6-311++G (d,p) basis sets using GAUSSIAN 03W program (*Gaussian 03W Program*,(Gaussian, Inc., Wallingford, CT) 2004; Lee, 1988; Becke et al., 1993). In case of solution the optimized energies were computed using the SCIPCM SCRF model and B3LYP DFT method with the same basis set. The iso-density PCM (IPCM) model defines the cavity as an iso-density surface of the molecule. This iso-density is determined by an iterative process in which an SCF cycle is performed and converged using the current iso-density cavity. The resultant wave function is then used to compute an updated iso-density surface, and the cycle is repeated until the cavity shape no longer changes upon completion of the SCF.

An iso-density surface is a very natural, intuitive shape for the cavity since it corresponds to the reactive shape of the molecule to as great a degree as is possible (Rather than being a simpler, pre-defined shape such as a sphere or a set of overlapping spheres).

However, a cavity defined as an iso-surface and the electron density are necessarily coupled. The Self-consistent iso-density Polarized Continuum Model (SCI-PCM) was designed to take this effect fully into account. It includes the effect of solvation in the solution of the SCF problem. This procedure solves the electron density which minimizes the energy, including the solvation energy-which itself depends on the cavity which depends on the electron density. In other words, the effects of solvation are folded into the iterative SCF computation rather than comprising an extra step afterwards. SCI-PCM thus accounts for the full coupling between the cavity and the electron density and includes coupling terms that IPCM neglects.

In the frequency calculation we specified, scf = tight, criteria and the basis set is 6-311G (d,p) only for all the solvents, because of computation time problem.

RESULTS AND DISCUSSION

Calculated equilibrium geometry of erythritol in its ground state both in gas phase and in different solvents are given in Table 1 along with the numbering scheme of the atoms of the molecule. Some important properties of the molecule are listed in Table 2. Mulliken atom electron density is recorded in Table 3. Atomic charge is not an observable quantum mechanical property. All methods for computing the atomic charges are necessarily arbitrary. Electron density among the atoms in a molecular system is being partitioned. Mulliken population analysis computes charges by dividing orbital overlap equally between the two atoms involved. Therefore the values are non-unique and depend on the basis set used. Still, it is widely used. Figures 1 to 8 show the three dimensional structure of erythritol molecule with atom numbering at the calculated equilibrium geometry in gas phase, water, DMSO and carbon tetrachloride respectively. The significance of the figures is that it shows the complete three dimensional structures which are not completely reflected from the selected geometrical parameters given in the table. From Table 1, it is seen that the geometrical parameters do not change significantly between the basis sets but the chemical properties (Table 2) change a lot. In the gas phase the torsion angle, C1-C4-C5-C6 of the molecule calculated by both basis sets shows non planarity of the carbon skeleton as expected. In water and DMSO this angle comes out to be 173.9 and -174.6 respectively only by 6-311++G (d,p) basis set calculation showing planarity of the carbon skeleton supporting the chemical expectations whereas the other results show non planarity. In carbon tetrachloride, the skeleton remains non planar as in the gas phase indicating that solvent polarity has marked influence on the structure of the molecule. This is further revealed in other results of torsion angles like O-C-C-O, C-C-C-O where the experimental results are well reproduced in water and DMSO but not in carbon tetrachloride. Regarding the C-O and C-C distances, they are in excellent agreement with the experimental results [7, 8, and 12] in all calculations and in all solvents. The same is true for the C-C-H, C-C-O and C-C-C angles.

From Table 2 it is clear that the molecule is stabilized in all solvents by all calculations because of the less nuclear repulsion in each case. The solvation energy is of the order water > DMSO > carbon tetrachloride as obvious from chemical expectation arising out of the dielectric constant of the solvents. The dipole moment is increased in all solvents indicating that the charge separation is higher in the solution as is expected for a polar molecule. This is supported by the data from Table 3 where it is seen that the charge density on O-atoms are much more increased than that in the gas phase. Among the four oxygen atoms in the molecule the O13 carries the highest negative charge in all calculations and in all solvents with the exception of water by 6-311G (d, p). This indicates that O13-H18 group may behave differently from the other three O-H groups of the molecule showing that the molecule can behave as a bidentate ligand. This is in excellent agreement with the experimental findings (Yang et al. 2004a and b).

From Table 3 it is also seen that all the carbon atoms are negatively charged both in gas phase and in solvated phase by 6-311++G (d, p) set as expected by electro-negativity

Table 1. Some selected geometrical parameters of erythritol molecule at the calculated ground state equilibrium geometry both in gas phase and in solution phase (distances in Å and angles in ˚).

Geometrical parameter	Gas phase		Solution phase					
			Water		DMSO		Carbon tetrachloride	
Bond length, bond angle and torsion angle	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)
C1-O14 §	1.4291	1.4291	1.4284	1.4276	1.4286	1.4271	1.4291	1.4292
C4-011 §	1.4274	1.4286	1.4310	1.4329	1.4310	1.4328	1.4288	1.4302
C5-O12 §	1.4215	1.4244	1.4267	1.4302	1.4265	1.4313	1.4238	1.4265
C6-O13 §	1.4343	1.4362	1.4338	1.4307	1.4336	1.4360	1.4339	1.4356
O14-H15	0.9696	0.9643	0.9650	0.9657	0.9648	0.9658	0.9613	0.9686
O11-H16	0.9679	0.9676	0.9707	0.9714	0.9704	0.9623	0.9686	0.9688
O12-H17	0.9648	0.9643	0.9631	0.9625	0.9634	0.9623	0.9643	0.9638
O13-H18	0.9607	0.9611	0.9623	0.9631	0.9622	0.9658	0.9613	0.9645
C1-C4	1.5215	1.5225	1.5216	1.5245	1.5216	1.5250	1.5216	1.5226
C4-C5	1.5485	1.5484	1.5454	1.5451	1.5455	1.5450	1.5473	1.5473
C5-C6	1.5223	1.5250	1.5257	1.5291	1.5252	1.5294	1.5233	1.5261
C1-H2	1.0902	1.0903	1.0903	1.0903	1.0904	1.0902	1.0902	1.0902
C4-H7	1.1015	1.1009	1.1012	1.1003	1.1012	1.1003	1.1014	1.1007
C5-H8	1.0970	1.0961	1.0959	1.0951	1.0960	1.0948	1.0966	1.0957
C6-H9	1.0954	1.0945	1.0953	1.0941	1.0952	1.0941	1.0953	1.0943
C1-C4-H7	108.2	107.8	107.9	107.8	107.9	108.0	108.0	107.6
C4-C5-H8	106.5	107.3	107.3	108.5	107.2	108.6	106.8	107.6
C5-C6-H10	108.8	109.0	108.9	109.1	109.1	109.1	108.9	109.1
C4-C1-O14 ¤	111.7	112.3	112.1	112.2	112.1	113.7	111.9	112.6
C1-C4-O11 ¤	106.7	106.6	106.6	105.7	106.7	105.6	106.9	106.6
C5-C6-O13 ¤	107.6	107.9	108.4	109.1	108.2	109.1	107.8	108.2
C1-C4-C5	111.7	112.5	112.6	113.5	112.5	113.8	112.0	112.8
C4-C5-C6	112.1	112.3	112.3	112.9	112.2	112.9	112.2	112.3
H15-O14-C1	106.1	107.3	106.3	106.6	108.9	109.0	106.4	107.4
H16-O11-C4	106.2	107.2	105.7	107.2	105.7	107.3	105.9	107.0
H3-C1-O14	111.2	110.9	111.1	110.5	111.0	112.2	111.2	110.9
C1-C4-C5-C6	160.7	161.15	166.7	173.9	-166.2	-174.6	-162.8	-163.9
O11-C4-C1-O14¶	71.9	71.6	67.7	61.2	68.8	59.5	71.4	70.2
C1-C4-C5-O12 #	-40.9	-42.8	-47.9	-56.7	-47.1	-57.4	-43.2	-45.4

§ experimental C – O distance: 1.425 – 1.433 Å; # experimental C1-C4-C5-O12 torsion angle: -59.9 to 58.4˚; ¶ experimental O11-C4-C1-O14 torsion angle: 62.9˚; ¤ experimental ∠OCC: 107.7, 109.7 and 112.2˚.

Table 2. Some important properties of erythritol molecule (energy in hartree, dipole moment in debye) in equilibrium ground state both in gas phase and solution phase.

Property	Gas Phase		Solution phase					
			Water		DMSO		Carbon tetrachloride	
	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)
Total energy	-459.4537	-459.4734	-459.4652	-459.4852	-459.4650	-459.4849	-459.4586	-459.4783
ΔE^a			-0.0115	-0.0118	-0.0113	-0.0115	-0.0050	-0.0049
Nuclear repulsion energy	431.5862	430.0950	430.2809	428.4894	430.4555	428.3326	431.1510	428.4384
Dipole moment	2.5437	2.5647	3.1988	3.5505	3.0125	3.6434	2.7739	2.8383
X	-2.4755	-2.49	-3.0990	-3.4525	-2.9293	-3.5517	-2.6946	-2.7630
Y	-0.3035	-0.19	-0.0550	0.4382	-0.3845	0.5012	-0.2511	0.0991

Table 2. Contd.

Z	0.4993	0.5585	0.7910	0.0703	0.5885	0.6392	0.6086	0.6420
H0M0	-0.2609	-0.2721	-0.2564	-0.2645	-0.2565	-0.2647	-0.2582	-0.2676
LUMO	0.0178	-0.0229	0.0508	0.0016	0.0503	0.0013	0.0334	0.0103

ΔE^a = Solvation energy = Total energy in solution phase - Total energy in gas phase; 1hartree= 627.5095 kcal (mole)$^{-1}$ = 27.2116 eV.

Table 3. The net mullikan charge on the atoms of erythitol molecule in the ground state both in gas phase and solution phase.

Atom	Gas Phase		Solution Phase					
			Water		DMSO		Carbon tetrachloride	
	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)	6-311 G(d,p)	6-311++ G(d,p)
C1	-0.1102	-0.5091	-0.0065	-0.4232	-0.0144	-0.4221	-0.1136	-0.4995
H2	0.1179	0.1990	0.1186	0.1908	0.1240	0.1884	0.1192	0.2010
H3	0.1182	0.1796	0.1147	0.1782	0.1192	0.1752	0.1183	0.1798
C4	0.0128	-0.0132	00107	-0.0641	0.0096	-0.0735	0.0130	-0.0159
C5	0.0033	-0.3730	-0.0011	-0.3679	0.0029	-0.3665	0.0015	-0.3614
C6	0.0116	-0.3107	0.0231	-0.728	0.0200	-0.2519	0.0159	-0.3091
H7	0.0949	0.1805	0.1039	0.1938	0.1078	0.1934	0.0983	0.1857
H8	0.1085	0.2543	0.1142	0.2462	0.1118	0.2414	0.1111	0.2546
H9	0.1148	0.1744	0.1162	0.1812	0.1149	0.1820	0.1163	0.1767
H10	0.1063	0.1828	0.1152	0.1891	0.1111	0.1893	0.1097	0.1851
O11	-0.4188	-0.2583	-0.4491	-0.3224	-0.4448	-0.3244	-0.4315	-0.2802
O12	-0.4112	-0.2314	-0.4456	-0.3120	-0.4412	-0.3102	-0.4250	-0.2560
O13	-0.4376	-0.3401	-0.4476	-0.4061	-0.4743	-0.4055	-0.4530	-0.3661
O14	-0.4243	-0.2542	-0.4518	-0.2962	-0.4536	-0.2963	-0.4368	-0.2759
H15	0.2495	0.2595	0.2679	0.2911	0.2731	0.2901	0.2585	0.2753
H16	0.2502	0.3027	0.2580	0.3223	0.2591	0.3235	0.2536	0.3101
H17	0.2557	0.2831	0.2823	0.3329	0.2726	0.3281	0.2641	0.2969
H18	0.2588	0.2739	0.3067	0.3393	0.3018	0.3386	0.2776	0.2989

Table 4. Theoretical [DFT–B3LYP; 6-311G (d,p)] and experimental hydroxyl stretching frequency (cm^{-1}) of erythitol

Bond	Theoretical str. freq. data (O-H)				Experimental [a] str. freq. data (O-H)
	Gas phase	Solution phase			
		Water	DMSO	Carbon tetrachloride	
O13-H18	3255	3244	3244	3250	
O12-H17	3209	3227	3227	3212	
O14-H15	3204	3203	3205	3208	3251
O11-H16	3164	3103	3107	3142	

[a] The value is taken from Yang et al. (2004a).

rule whereas 6-311G (d, p) set shows C1 to be negatively charged both in gas phase and in solution phase and C5 to be negatively charged in solution phase with the exception of DMSO where it is positively charged which is unusual according to the electro negativity rule. The H-atoms attached to O-atoms contain almost equivalent positive charges whereas those attached to C-atoms are less positively charged than the former both in gas phase and in solution phase and in all calculations as expected from the general electro negativity rule. The HOMO-LUMO gap (not shown in the Table 2) increases on solvation and remains almost equivalent in all solvents. Table 4 reports the calculated O-H frequencies using a scale factor 0.8439 generated in the present study. In
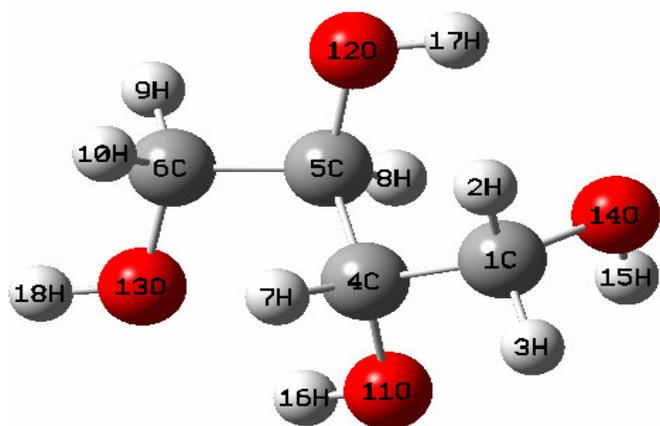
Figure 1. Three dimensional structure of erythritol calculated by DFT B3LYP / 6-311G (d,p) in gas phase.

Figure 2. Three dimensional structure of erythritol calculated by DFT B3LYP / 6-311G++ (d,p) in gas phase.

Figure 3. Three dimensional structure of erythritol calculated by DFT B3LYP / 6-311G (d,p) in water.
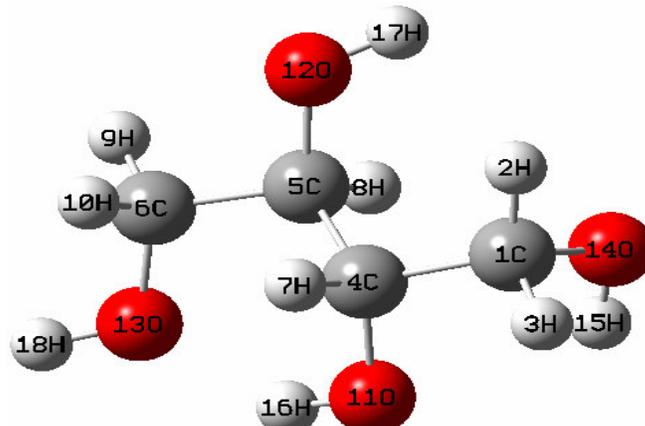
Figure 4. Three dimensional structure of erythritol calculated by DFT B3LYP / 6-311G++ (d,p) in water
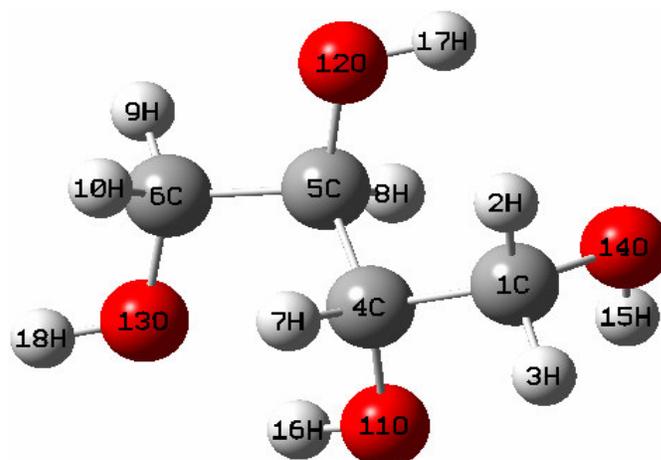
Figure 5. Three dimensional structure of erythritol calculated by DFT B3LYP / 6-311G (d,p) in DMSO.
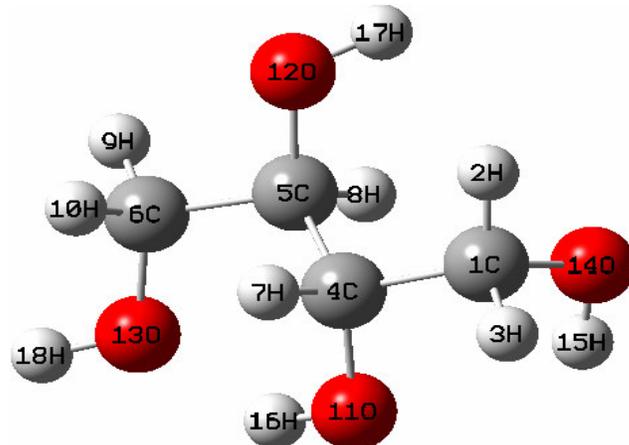
Figure 6. Three dimensional structure of erythritol calculated by DFT B3LYP / 6-311G++ (d,p) in DMSO.
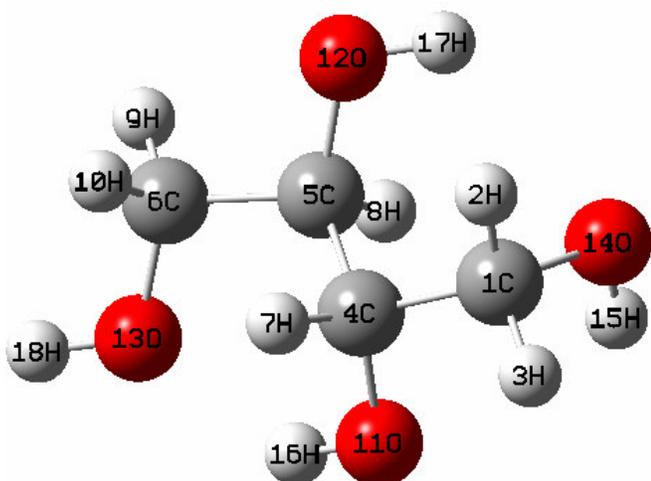
Figure 7. Three dimensional structure of erythritol calculated by DFT B3LYP / 6-311G (d,p) in carbon tetrachloride.
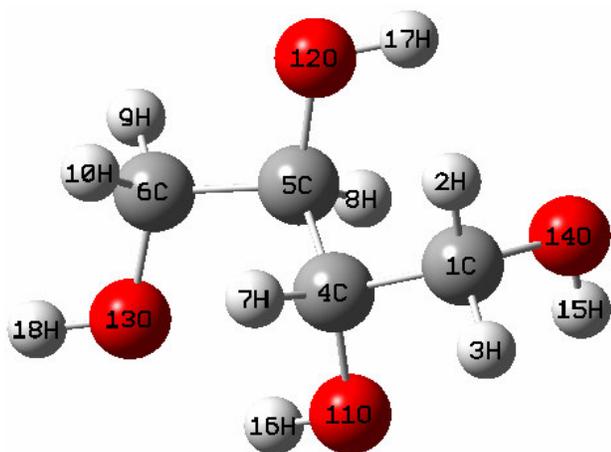
Figure 8. Three dimensional structure of erythritol calculated by DFT B3LYP / 6-311G++ (d,p) in carbon tetrachloride.

Yang et al. (2004a), the IR spectra were measured on a Nico-plan IR microscope attached on a Nicolet Magna-IR 750 FT-IR spectrometer. Four O-H vibrations have been computed to see whether there is any difference between them. The results show that there are two types of O-H frequencies. The results are well compared with the experimental findings (Yang et al., 2004a). The O13-H18 frequency is highest among the four O-H bonds both in gas and solution phase. The value is little decreased from the gas phase value in water and in DMSO, but remains

almost same in carbon tetrachloride as expected from the solvent polarity point of view.

Conclusion

From the present study it can be concluded that neutral erythritol can coordinate with various transition metal ions through O-H groups in the ground state both in gas and solution phase, the complexation being better in solvents of higher dielectric constants. The two types of O-H groups confirm that the molecule may behave as a bidentate ligand in excellent agreement with the experimental findings (Yang et al., 2004a and b). B3LYP DFT 6-311++G (d, p) results are more reliable in the present study.

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