

Theoretical study of the microhydration of 1-chloro and 2-chloro ethanol as a clue for their relative propensity toward dehalogenation

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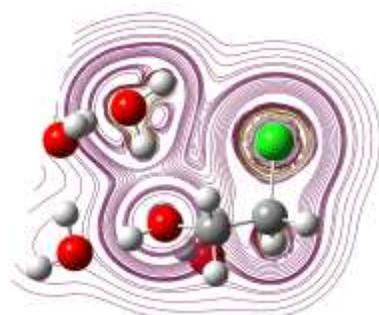
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ABSTRACT

This work reports a computational analysis of hydrogen bonded clusters of mono-, di-, tri- and tetra hydrates of the chlorohydrins CH_3CHClOH (1ClEtOH) and $\text{CH}_2\text{ClCH}_2\text{OH}$ (2ClEtOH). The goal of the study is to assess the role of the water solvent into the facilitation of the initial step for dehalogenation of these compounds, a process of interest in several contexts. Molecular orbital methods (MP2), density functional methods (B3LYP, M06 and ω B97X-D) and composite model chemistries (CBS-QB3, G4) were employed to investigate the structure, electronic distribution and hydrogen-bonded structure of 7 monohydrates, 6 dihydrates, 5 trihydrates and 5 tetrahydrates of both species. Standard reaction enthalpy and standard Gibbs free reaction energy ($\Delta_r G_{298}^0$) were computed for all aggregates with respect to n independent water molecules and with respect to the dimer, trimer and tetramer of water, respectively, in order to evaluate stability and hydrogen bonding network. The influence of the water chains on the length and vibrational frequencies, especially of the C-Cl and O-H bonds, was evaluated.

GRAPHICAL ABSTRACT



propensity toward dehalogenation.

2-Chloroethanol is a precursor of vinyl alcohol—a molecule of atmospheric and interstellar interest—by dehalogenation. Ice particles present in those environments contribute to this reaction. Patterns of microhydration, designed to mimic the interaction with ice clusters, were determined for 2-chloroethanol and the 1-chloroethanol isomers, to investigate the contribution of hydrogen bonding and electrostatic interactions into the elongation of the C-Cl bond and the

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1 | INTRODUCTION

Halogenated hydrocarbons are organic species of considerable interest in environmental sciences, for instance in atmospheric chemistry where the role of chlorofluorocarbons (CFCs) in the depletion of the ozone layer [1-3] is extremely important. On the other side, absorbable organic halogen (AOX) species produced in the course of chlorine or chlorine dioxide bleaching of pulp in the Kraft process [4,5], and some byproducts of water disinfection [6-8], contribute to surface water contamination. Other products used in the industry or agriculture further contribute to the presence of halogenated hydrocarbons in the environment.

One of the simplest halogenated halocarbon families is that of halohydrins (halogenated alcohols) and one of their important reactions is dehalogenation, i.e. HX elimination, which can occur by pyrolysis in gas phase [9-11], and by base catalysis [12-14] or oxidation [15] in solution. Enzymes that produce this dehalogenation process (known as dehalogenases [16] and dehaloperoxidases [17]) are also present in numerous organisms.

Leaving aside the pyrolysis, all other mechanisms occur in aqueous solutions. For that reason, we wanted to investigate what is the role of the molecules of the solvent on the initial species to be dehalogenated. In this work, we present a study of the geometrical structure and energetics of clusters of 1ClEtOH and 2ClEtOH with n water molecules ($n=1-4$). While 2ClEtOH has been studied several times and is well known, much less information exists in the literature about the 1ClEtOH isomer, which nonetheless may play some important role in the dehalogenation path of 2ClEtOH.

We show here how the water chains influence the charge distribution on the solutes and the equilibrium distance of the C-Cl bond-to be broken in the dehalogenation reaction. Studying the dependence of the stabilization energy with the number of water molecules, we show that a cluster of the solute with three water molecules is sufficient to single out the most important effects of the solvent.

2 | COMPUTATIONAL METHODS

Several computational methods have been used to study the clusters of 1ClEtOH and 2ClEtOH with n water molecules ($n=1-4$). The simple correlated molecular orbital (MO) method MP2 [18] was used to obtain optimum geometries, energies and frequencies. Composite methods, which rely on relatively simple calculations that are later stepwise corrected for extension of the basis set to the complete basis set (CBS) limit, for higher levels of correlation energy (MP4, CCSD(T)) and add empirical factors to correct for dissociation energies with respect to atoms, were also employed. In particular, in this paper we used the CBS-QB3 [19,20] and G4 [21] methods, which are all approximations, increasingly accurate, to CCSD(T)/CBS calculations, which are not feasible on molecules of this size. Finally, three density functional theory (DFT [22]) procedures were employed, namely B3LYP [23], M06 [24], and ω B97X-D [25] methods. B3LYP is the oldest

adiabatically connected (or hybrid) generalized-gradient method, which is able to afford reasonable geometries and bond energies accurate to about 4 kcal/mol between main-group atoms and about 1.3 kcal/mol for noncovalent interactions. M06 is a member of the Minnesota group of functionals developed by Truhlar's group. It includes the kinetic energy functional and reduces the error in main-group bond energies to 1.8 kcal/mol and the error in noncovalent interactions to 0.4 kcal/mol. Finally, ω B97X-D is a last generation functional developed by the group of Head Gordon, which additionally includes corrections for dispersion and long-range interactions. While mostly ω B97X-D and M06 behave similarly, the former performs better on the noncovalent interactions (like the hydrogen bonds explored in this paper).

It is a known fact that DFT methods do not have such a heavy dependence on the quality of the basis set as MO methods have. However, when low stabilization energy hydrogen-bonded clusters are studied, it is reasonable to have an appraisal of the situation employing different basis sets. In our case, we chose several Pople's basis sets [18], namely 6-31G(d), 6-31++G(d,p), 6-311++G(d,p), 6-311++G(2d,2p) and 6-311++G(3df,2pd) as examples of relatively low-cost (i.e. less complete) sets. Additionally, we used the correlation consistent basis sets of Dunning [18], cc-pVTZ, aug-cc-pVTZ, cc-pVQZ and aug-cc-pVQZ as examples of more complete (and costly) basis sets. In both cases, the rationale was to extend smoothly the valence, diffuse and correlation spaces of the sets to approach the CBS limit.

Several properties of the clusters were studied using the methods previously described. Optimum geometries of the clusters were obtained with all the methods. 1, 2, 3 and 4 water clusters were built incrementally, first looking for all the possible *n-1* isomers and then adding the *n-th* water molecule in all possible positions that kept the water in contact with the solute (i.e. all waters considered were in the first solvation shell). These structures are, of course, only snapshots of the dynamical behavior of next neighbor water molecules in a real solvated chloroethanol. Second derivatives of the energy with respect to the geometrical coordinates were calculated at all levels and the IR and Raman spectra of the clusters were approximated using harmonic frequencies. Differential spectra of the solvated species with respect to the unsolvated ones were calculated to assess the influence of the water molecules in the spectra. Thermochemical properties were evaluated at standard conditions using the harmonic-rigid rotor approximation and the usual formulas of statistical thermodynamics. The charge distribution was analyzed calculating the electrostatic potential and point charges derived from a Natural Bond Orbital (NBO) [26] analysis, on one side, and derived from the electrostatic potential (HLY method [27]) on the other. This allowed us to calculate the amount of charge transfer to the water portion in each of the clusters. Finally, the net of hydrogen bonds in the clusters were investigated calculating the laplacian of the electronic density on different planes which include the hydrogen bonds to be investigated.

All calculations were performed by using the Gaussian 09 set of computer codes [28].

While to the extent of our knowledge there is no experimental determination of the structure of 1ClEtOH, two experimental studies have determined the structure of 2ClEtOH. Azrak and Wilson [29] analyzed the microwave (MW) spectrum, while Almemmingen et al [30] performed a study using electron diffraction (ED) to determine the anti-gauche ratio as a function of temperature. Both studies are reasonably in agreement with respect to the C-C, C-O and O-H bond distances, as well as with respect to the dihedral angle between the ClCC and CCO planes, but differ on the result for the C-Cl distance. While Azrak and Wilson found 1.7886 ± 0.0038 Å for the latter, Almemmeingen et al reported a value of 1.801 ± 0.001 Å. Although the discrepancy is not very large, it is significant. One must assume that the ED data is more accurate, since the Cl is the heaviest atom in the molecule and the determination of the C-Cl distance should be the better determined structural parameter in this study. Durig et al [31] gave an explanation of the biased value in the microwave experiment.

From the theoretical point of view, we did not find in the literature high level calculations (i.e. CCSD(T) or better) of the geometry of 2ClEtOH. Former calculations used normally HF, B3LYP or MP2 with at most 6-311++G(d,p) or aug-cc-pDZ basis sets, which are superseded by the calculations in this paper. In all cases the gauche Gg' structure [31] is the most stable one (a decomposition analysis of the interactions was performed by Baranac-Stojanović et al [32] who determined the effect to be caused mainly by electrostatic attraction). The dihedral angle between the ClCC and CCO planes is well reproduced by all the calculations. DFT results for the CCl bond are nearer to the ED data than those of MP2, these being nearer to the MW experimental results than to those obtained by ED. Two aspects in which the calculation fail are the OH bond length, that theoretically is predicted much shorter than the experimental value, and the hydrogen bond Cl-H, which the calculations predict longer than the experimental one. In this specific case, however, MP2 performs better than DFT. Both theoretical drawbacks can easily be explained by the fact that our calculations do not include anharmonicity corrections.

1ClEtOH and 2ClEtOH geometries clearly exhibit the differences caused by the different location of the chlorine atom. The C-C distance is larger by about 0.008 Å and the C-O bond is larger by about 0.027 Å in 2ClEtOH with respect to 1ClEtOH. On the contrary, the C-Cl bond is about 0.038 Å shorter. The results of these modifications are that the distance between chlorine and the H atom in the hydroxyl group is 0.081 Å shorter in 2ClEtOH than in 1ClEtOH, implying a stronger interaction in the former than in the latter.

Also included in Fig. 1 are the laplacian of the density for both molecules calculated at the ω B97X-D/cc-pVTZ level. One can see that in neither of those diagrams is there a critical point between the H in OH and chlorine, discarding the presence of a hydrogen bond, thus confirming Baranac-Stojanović et al [32] analysis that the attraction is mainly electrostatic. The charge separation between the negative chlorine and the positive hydrogen (0.56 electrons according to the NBO analysis at the ω B97X-D/aug-cc-pVQZ level) also supports this view.

Finally, in Fig. 2 are included the IR spectra of both 1ClEtOH and 2ClEtOH calculated at the ω B97X-D/cc-pVTZ level. The most important data, for the purpose of this study, is the position of

the C-Cl and O-H stretchings, because they will be the most affected by the solvating water molecules. In Table 1 is shown a compendium of the position of the bands with the different chemical models, as well as the ratio of the intensities of the CCl stretching band to the OH stretching band.

Two characteristics of these bands can be noticed in Table 1. First, that there is an inverse shift of both bands. While the $\nu_{str}(C-Cl)$ frequency is smaller in 1ClEtOH than in 2ClEtOH, the $\nu_{str}(O-H)$ frequency is larger. Although the exact value varies a little with the method and the basis set, it is of about 40 cm^{-1} for the former and about 20 cm^{-1} for the latter. Also, the ratio of the intensities is larger than one for 1ClEtOH and smaller than one for 2ClEtOH, which may serve as a characteristic indicator to indicate the presence of one or the other isomer. This variation may be traced to the charge separation between the C-Cl and C-O atoms (and, therefore, the bond dipoles). The charge separation between the atoms in the O-H bond is approximately the same in 2ClEtOH (1.17 according to NBO) than in 1ClEtOH (1.16). It does not happen the same however in the atoms of the C-Cl bond. The charge separation in 1ClEtOH is actually about 70% larger than in 2ClEtOH (0.50 against 0.30 according to the NBO analysis). Consequently, the intensity of the C-Cl stretch in 1ClEtOH is larger than in 2ClEtOH and this is part of the explanation of the inversion of intensities observed in the spectra.

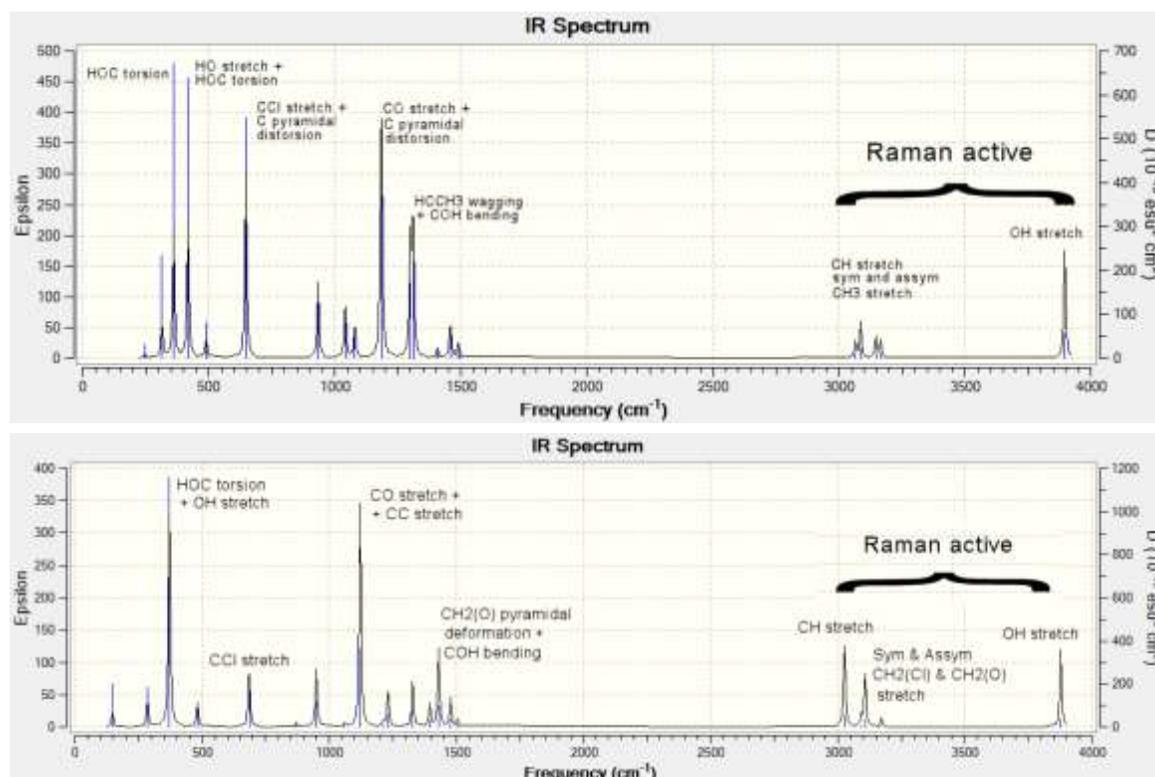


Figure 2. IR spectra of 1ClEtOH (upper panel) and 2ClEtOH (lower panel)

TABLE 1 Frequencies corresponding to the CCl and OH stretchings in 1ClEtOH and 2ClEtOH (in cm⁻¹). The ratio of the respective intensities is also shown.

		1ClEtOH			2ClEtOH		
		$\nu(\text{C-Cl})$	$\nu(\text{O-H})$	$I_{\text{Cl}}/I_{\text{OH}}$	$\nu(\text{C-Cl})$	$\nu(\text{O-H})$	$I_{\text{Cl}}/I_{\text{OH}}$
MP2	6-311++G(3df,2pd)	679	3861	1.19	713	3849	0.59
	cc-pVTZ	669	3837	1.27	705	3823	0.65
	aug-ccpVTZ	668	3815	1.28	702	3798	0.63
B3LYP	6-311++G(3df,2pd)	609	3824	1.11	652	3809	0.92
	cc-pVTZ	602	3804	2.04	647	3786	1.05
	aug-ccpVTZ	603	3799	1.79	645	3784	0.96
M06	6-311++G(3df,2pd)	635	3885	1.26	676	3862	0.66
	cc-pVTZ	627	3866	1.51	670	3845	0.79
	aug-ccpVTZ	627	3858	1.53	669	3835	0.77
ω B97X-D	6-311++G(3df,2pd)	650	3907	1.53	686	3890	0.77
	cc-pVTZ	644	3890	1.71	682	3870	0.88
	aug-cc-pVTZ	644	3885	1.67	681	3866	0.84
	cc-pVQZ	647	3897	1.61	684	3876	0.82
	aug-cc-pVQZ	648	3897	1.61	685	3877	0.75

3.2 | Structure of the clusters

Fig. 3 shows the structure of the clusters identified for 1ClEtOH and Fig. 4 shows the general structure of the water clusters of 2ClEtOH. Important geometrical parameters are shown in the figures at the ω B97X-D/cc-pVTZ level. Full geometries are given in the Supplementary Information section.

Four different monohydrated complexes were found for 1ClEtOH (1_1W_A, _B, _C and _D) while only two were found for 2ClEtOH (2_1W_A and _B). Letters were assigned in order of decreasing stability, with the A complex being the more stable one (see later on). The isomers 1_1W_A to 1_1W_C and 2_1W_A have interactions of the water molecule with both the chlorine atom and the OH residue, while 1_1W_D and 2_1W_B exhibit only an interaction of the water with the OH fragment. Moreover, while in 1_1W_A, 1_1W_B and 2_1W_A the OH group acts like a hydrogen donor, in 1_1W_C, 1_1W_D and 2_1W_B it acts as a hydrogen acceptor.

Isomers 1_1W_A and 1_1W_B are essentially equivalent. The only difference is whether the OH bond is *syn* or *anti* to the CH bond. The Cl-H hydrogen bond is clearly equivalent and the OH-O hydrogen bond is slightly tighter in 1_1W_A. 1_1W_C exhibits the peculiarity of an attractive interaction between the H in the CH group and the oxygen of water, besides the other two interactions with the Cl and the OH group. An important point to notice is that the more stable monohydrate is also the one that presents the larger elongation of the CCl bond with respect to the isolated 1ClEtOH. In the case of 2ClEtOH it happens something similar, 2_1W_A is more stable than 2_1W_B and exhibits a larger increase in the C-Cl bond length. Notice however that this increase is much shorter than in the 1ClEtOH corresponding complexes. Another important piece of data is the shortening of the Cl-H distance in 1_2W_B. The simple presence of a water bound to

the hydroxyl group is enough to move the chlorine nearer to the hydrogen. This correlation between stability and increasing in the CCl bond length is a hint that water may be helping the abstraction of HCl, most noticeably in the case of 1ClEtOH.

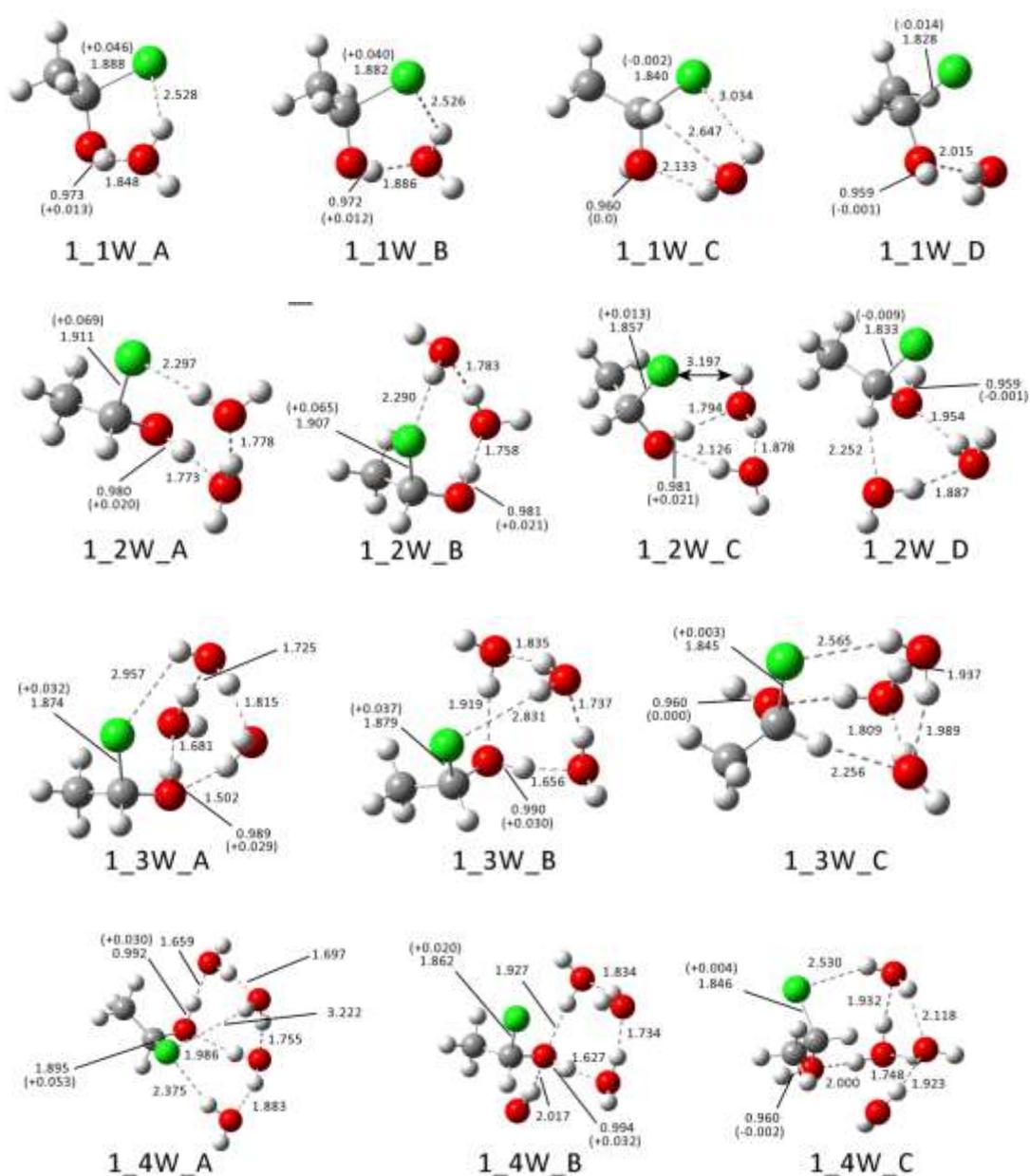


Figure 3. Optimized structures at the ω B97X-D/cc-pVTZ level of 1ClEtOH with 1, 2, 3 and 4 water molecules. Important interatomic distances are shown in Å. Values in parenthesis are the bond length increase or decrease with respect to isolated 1ClEtOH.

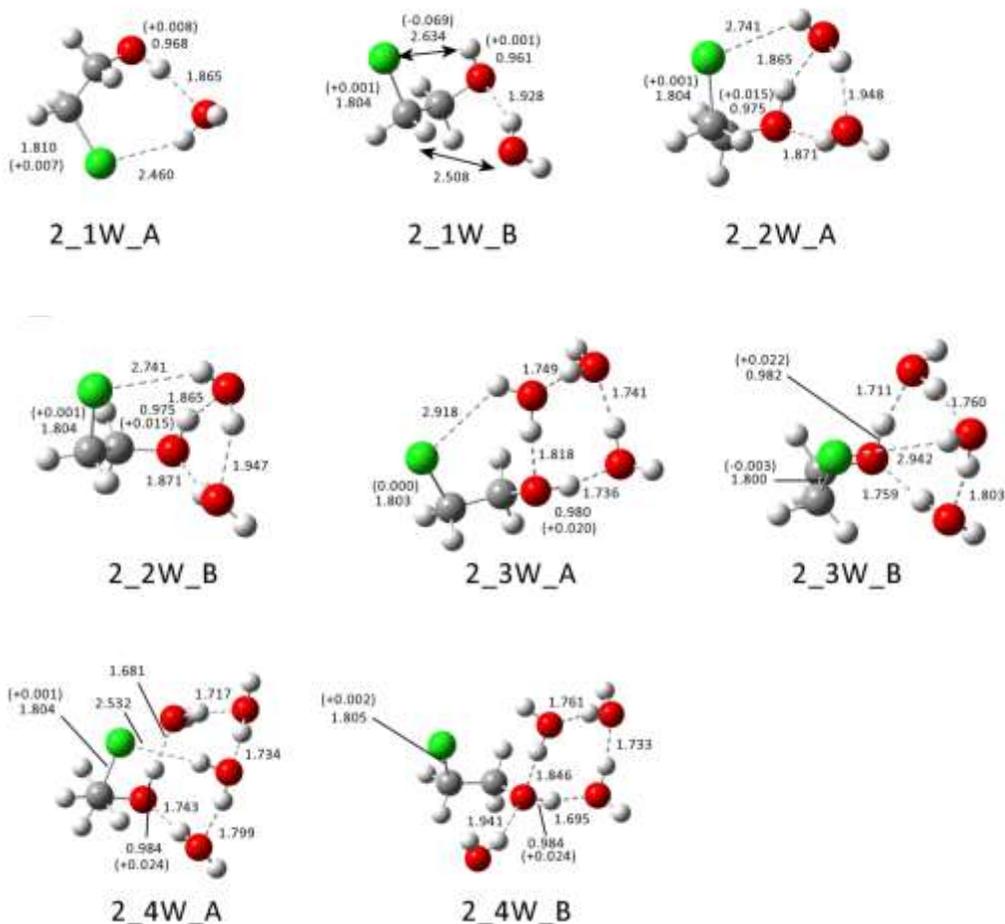


Figure 4. Optimized structures at the ω B97X-D/cc-pVTZ level of 2ClEtOH with 1, 2, and 3 water molecules. Important interatomic distances are shown in Å. Values in parenthesis are the bond length increase or decrease with respect to isolated 2ClEtOH.

Four complexes of 1ClEtOH with two water molecules were found. As seen in Fig. 3, the four complexes present some form of the water dimer bound in different ways to the solute. 1_2W_A and 1_2W_B present interactions of the water dimer with both chlorine and the hydroxyl group. A true Cl-H hydrogen bond is noticed in these cases and the OH group works as a hydrogen donor. 1_2W_C instead shows the solvation of the hydroxyl group with two water molecules, and the interaction with chlorine is weaker, more an electrostatic attraction than a true hydrogen bond. In this case, the hydroxyl group acts both as a hydrogen donor and acceptor. Finally, 1_2W_D exhibits a hydrogen acceptor OH and the second water molecule interacts with the acidic hydrogen in the CH bond. This is a true hydrogen bond, although weaker than those with the O-H-O structure. In the case of 2ClEtOH only two complexes were identified. 2_2W_A presents the

water dimer as a hydrogen bonded chain between the chlorine and the hydroxyl group, which in this case works as a hydrogen donor. 2_2W_B exhibits the water dimer solvating the hydroxyl group, both a hydrogen donor and a hydrogen acceptor in this case, but also an interaction with chlorine. In this case the hydrogen bond is weaker than in 2_2W_A but it is nonetheless a true hydrogen bond.

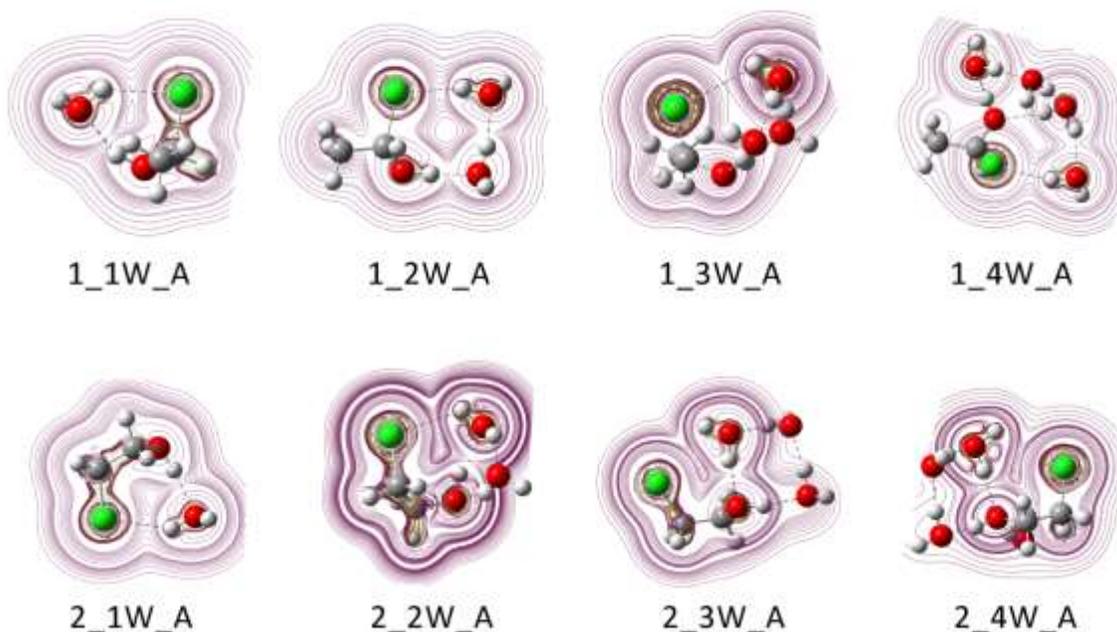


Figure 5. Isovalue level curves of the laplacian of the electronic density for the most stable complexes of 1ClEtOH and 2ClEtOH with 1 to 4 water molecules.

The complexes with three water molecules, three for 1ClEtOH and two for 2ClEtOH respectively, all involve bonds to both chlorine and the OH group. In the case of 1_3W_C also a CH-O hydrogen bond is visible. The hydrogen bonding between Cl and water is longer in all the 3W complexes than in the 2W complexes for the 1ClEtOH and, consequently, the C-Cl bond distance increase is smaller. The same effect, although smaller, is noticed for 2ClEtOH.

Finally, the larger cases studied were the complexes of 1ClEtOH and 2ClEtOH with four water molecules. Three such complexes were found for the former species and only two for the latter. Only 1_4W_A and 2_4W_A are fully interconnected clusters, both 1_4W_B and 2_4W_B exhibit an unconnected water as the third solvent molecule attached to the hydroxyl group, while 1_4W_C shows it completely unconnected to the solute.

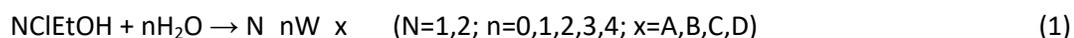
One remaining aspect to consider is the existence or not of hydrogen bonds with respect to chlorine. As we showed previously, that is not the case in the isolated molecules but it is yet to

be proved whether such a hydrogen bond exists in the complexes. To avoid irrelevant information, we will comment only on the 1_nW_A and 2_nW_A complexes, with n=1, 2, 3, 4, leaving aside the least stable B, C, and D complexes. The procedure followed was to identify the three atoms (Cl,H,O) supposedly involved in the hydrogen bond and to calculate the gradient of the electronic density in the plane defined by them. The presence or not of a hydrogen bond, as opposed to a simple electrostatic interaction, was assessed by the appearance or not of a critical point of the density between the Cl and H atoms [38]. The corresponding images are collected in Fig. 5

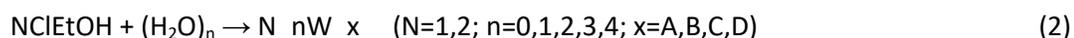
What the diagrams in Fig. 5 show is that chlorine is not always hydrogen bonded to the hydrogens in the water molecules. This can be seen, for instance in 2_3W_A and 2_4W_A where, even if an electrostatic attraction and some shared density are noticeable, chlorine is not bound to any of the two hydrogens, but somehow to a point in between. In other cases, like in 2_2W_A, there is a clear hydrogen bond to one of the hydrogen atoms, while there is no density shared with the second one. Finally, there are clear cases in which Cl is hydrogen bonded, like all the series 1_nW_A and 2_1W_A. Again one notices the preferential effect of the water solvent on 1ClEtOH with respect to 2ClEtOH.

3.3 | Energetics of the complexation

The $\Delta_r H_0^0$, $\Delta_r H_{298}^0$ and $\Delta_r G_{298}^0$ for the complexes were calculated in two ways. On the one hand, the properties were computed with respect to the solute and n isolated water molecules, like in (1)



In this case, the properties were divided by n (the number of water molecules) to obtain an estimate of the average contribution per monomer. Additionally, the properties were calculated with respect to water multimers. These monomer, dimer, trimer and tetramer of water were optimized starting from the structure of the water chains in N_nW_A. No attempt was made to find the most stable isomer of these water clusters, but just the one more similar to the structure present in the solvated complex. The equation would look as in (2).



The formal $n=0$ structure has also been included, which obviously corresponds to a zero energy in both equations. The optimum structures and energetics of the water molecule and water multimers are given in the Supplementary Information.

The numerical data for the complexation energies are given in Table 2, while a comparative analysis is shown in Fig. 6 (only for $\Delta_r H_{298}^0$). An important observation in Table 2 is that for most of the complexes, the free energy of reaction is positive, implying that the clusters would not form spontaneously in gas phase at 298.15K. Only in the case of 1_3W_A most of the methods (except B3LYP) predict spontaneous formation. This is not extraordinary. Even in the case of the isolated water clusters themselves, Shields et al [34] showed positive values of $\Delta_r G_{298}^0$ at 25°C while negative values were observed at smaller temperatures. We show this also for our complexes in Table 3. At very low temperatures (i.e. 10K), the entropic effect is negligible and $\Delta_r G_{10}^0$ is basically identical to the reaction enthalpy. The influence of the entropic factor increases with the temperature and turns positive slightly over 200K, an analogous behavior to that observed in ref. [33] (see their Table 8).

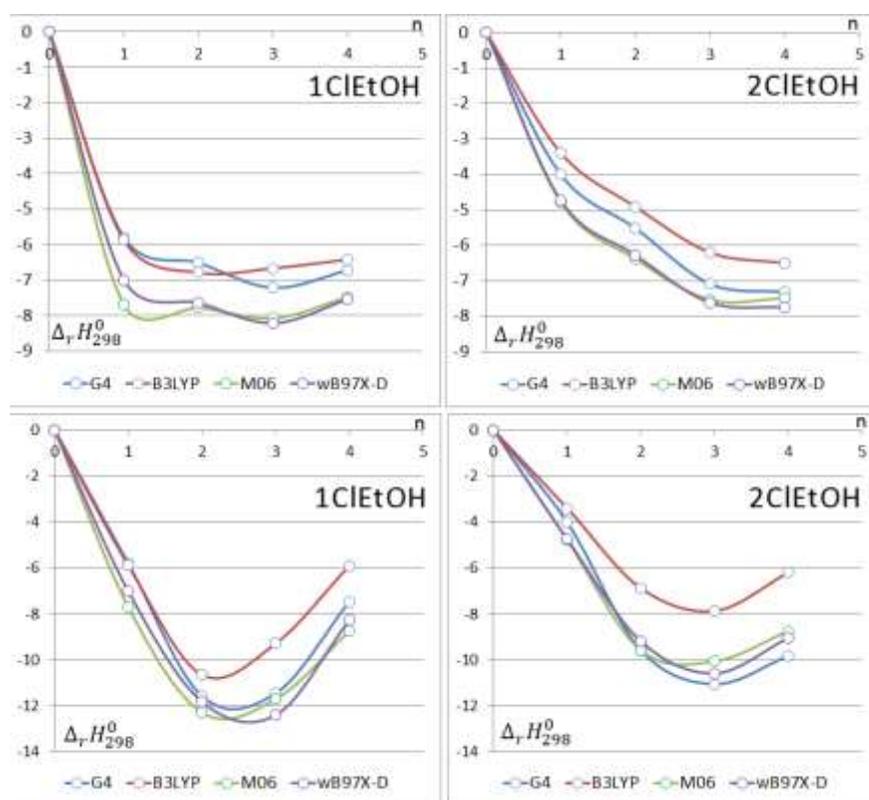


Figure 6. Plot of the enthalpy of reaction at 298.15 K (in kcal/mol) according to equation (1) (upper panels) and equation (2) (lower panels) for 1ClEtOH (left) and 2ClEtOH (right), with respect to the number of water molecules n

The second important piece of information in Table 2 is the larger stabilization energy of the water complexes for 1ClEtOH than for 2ClEtOH when $n=1$, and 3, but the reversion of stability when $n=4$. This behavior can be rationalized in terms of local vs global solvation. While the 1ClEtOH species has a very hydrophobic end (with the $-Cl$ and $-OH$ substituents) and a hydrophobic end (the methyl group), 2ClEtOH has two relatively hydrophilic ends, one with the chlorine atom, the other with the hydroxyl group. Therefore, when there is a small number of molecules, local solvation of the more hydrophilic $-CHClOH$ group favors a larger stability of the complexes. For a larger number of water molecules, the whole molecule becomes important and then the balance between hydrophilic and hydrophobic regions favors the solvation of 2ClEtOH over that of 1ClEtOH. One presumes then that the enthalpy of solvation of 2ClEtOH will be larger than the enthalpy of solvation of 1ClEtOH.

Looking at the graphs, it is noticeable the convergence of the complexation energy per water molecule to a value around 8 kcal/mol. Again, the larger facility for saturation of the solvation sites in the case of 1ClEtOH than 2ClEtOH is apparent. A glance at the curves of stabilization energies with respect to the water clusters reveals that 1ClEtOH starts to behave like fully solvated already with 2 water molecules, while 2ClEtOH needs 3 to exhibit the same effect. In both cases, the 4-water complex has already the first solvation shell complete, so that the complexation energy with respect to the 4-water cluster is comparable to the energy of complexation of the 1 water complex for 1ClEtOH and the 2-water complex for 2ClEtOH. A four-water complex should then be enough to study meaningfully dehalogenation of these complexes in water solution.

TABLE 2 Energies of complexation (in kcal/mol) for the different clusters with 1 to 4 water molecules. The upper two group of values correspond to the energies of complexation with respect to the water clusters for 1ClEtOH and 2ClEtOH respectively. The second two groups correspond to the complexation energies with respect to *n* isolated water molecules divided by the number of water molecules in each complex. For MP2, B3LYP, M06 and ω B97X-D methods, the values reported are those obtained with the aug-cc-pVTZ basis set

Method	$\Delta_r H_0^0$	$\Delta_r H_{298}^0$	$\Delta_r G_{298}^0$	$\Delta_r H_0^0$	$\Delta_r H_{298}^0$	$\Delta_r G_{298}^0$	$\Delta_r H_0^0$	$\Delta_r H_{298}^0$	$\Delta_r G_{298}^0$	$\Delta_r H_0^0$	$\Delta_r H_{298}^0$	$\Delta_r G_{298}^0$
	1_W_A			1_2W_A			1_3W_A			1_4W_A ^a		
MP2	-6.9	-7.3	1.3	-11.4	-11.9	-0.7	-12.4	-12.5	-1.8			
G4	-5.3	-5.8	3.1	-10.9	-11.6	0.1	-11.4	-11.5	-0.3	-7.7	-7.5	3.5
B3LYP	-5.5	-5.9	2.7	-10.0	-10.6	0.9	-9.2	-9.3	1.2	-6.2	-5.9	4.4
M06	-7.3	-7.7	1.1	-11.8	-12.3	-0.9	-11.7	-11.7	-0.9	-8.9	-8.7	2.5
ω B97X-D	-6.6	-7.0	1.5	-11.2	-11.8	0.0	-11.9	-12.4	-0.2	-8.5	-8.3	1.9
	2_W_A			2_2W_A			2_3W_A			2_4W_A ^a		
MP2	-5.2	-5.5	2.6	-8.9	-9.5	1.6	-10.9	-11.1	0.1			
G4	-3.6	-4.0	4.4	-8.8	-9.6	2.3	-11.0	-11.1	0.1	-10.0	-9.8	1.1
B3LYP	-3.2	-3.4	4.1	-6.4	-6.9	4.0	-7.8	-7.9	2.3	-6.3	-6.2	4.5
M06	-4.4	-4.8	3.5	-8.9	-9.6	2.2	-10.1	-10.1	0.5	-8.7	-8.7	3.3
ω B97X-D	-4.5	-4.7	3.1	-8.6	-9.2	2.2	-10.3	-10.6	1.0	-9.1	-9.0	2.0
	1_W_A			1_2W_A			1_3W_A			1_4W_A ^a		
MP2	-6.9	-7.3	1.3	-7.2	-7.7	0.9	-7.7	-8.4	0.7			
G4	-5.3	-5.8	3.1	-5.9	-6.5	2.5	-6.5	-7.2	2.3	-6.0	-6.7	2.7
B3LYP	-5.5	-5.9	2.7	-6.3	-6.8	2.0	-6.0	-6.7	2.3	-5.8	-6.4	2.6
M06	-7.3	-7.7	1.1	-7.2	-7.8	1.1	-7.5	-8.1	1.1	-6.9	-7.5	1.6
ω B97X-D	-6.6	-7.0	1.5	-7.1	-7.6	1.1	-7.4	-8.2	1.4	-6.9	-7.6	1.5
	2_W_A			2_2W_A			2_3W_A			2_4W_A ^a		
MP2	-5.2	-5.5	2.6	-8.9	-9.5	1.6	-10.9	-11.5				
G4	-3.6	-4.0	4.4	-4.8	-5.5	3.6	-6.3	-7.1	2.5	-6.6	-7.3	2.1
B3LYP	-3.2	-3.4	4.1	-4.4	-4.9	3.6	-5.6	-6.2	2.7	-5.9	-6.5	2.6
M06	-4.4	-4.8	3.5	-5.8	-6.4	2.6	-6.9	-7.5	1.5	-6.8	-7.5	1.8
ω B97X-D	-4.5	-4.7	3.1	-5.7	-6.3	2.5	-6.9	-7.6	1.8	-7.1	-7.7	1.5

^a No MP2/aug-cc-pVTZ results were obtained for the complexes with 4 water molecules

TABLE 3 Reaction Gibbs free energies (in kcal/mol) at each temperature given, for 1ClEtOH and 2ClEtOH, using reaction (2).

Method	T=10K				T=100K				T=200K			
	n=1	n=2	n=3	n=4	n=1	n=2	n=3	n=4	n=1	n=2	n=3	n=4
1ClEtOH.nH ₂ O												
MP2 ^a	-7.3	-11.6	-12.2	---	-6.9	-8.2	-8.9	---	-6.4	-4.4	-5.3	---
G4	-5.7	-11.2	-11.1	-7.1	-4.8	-7.7	-7.7	-3.8	-3.7	-3.7	-4.0	-0.1
B3LYP	-5.8	-10.3	-8.9	-5.6	-5.0	-6.8	-5.8	-2.5	-4.1	-2.9	-2.3	1.0
M06	-7.7	-11.9	-11.3	-8.4	-7.3	-8.5	-8.1	-5.0	-6.9	-4.7	-4.5	-1.2
ωB97X-D	-7.0	-11.4	-12.0	-7.9	-6.5	-7.9	-8.3	-4.8	-6.0	-3.9	-4.2	-1.4
Avg.^b	-6.7	-11.3	-11.1	-7.2	-6.1	-7.8	-7.8	-4.0	-5.4	-3.9	-4.1	-0.4
2ClEtOH.nH ₂ O												
MP2 ^a	-5.4	-9.1	-10.7	---	-4.6	-5.8	-7.3	---	-3.8	-2.0	-3.6	---
G4	-3.9	-9.2	-10.7	-9.5	-2.5	-5.6	-7.3	-6.1	-1.0	-1.6	-3.6	-2.5
B3LYP	-3.3	-6.5	-7.5	-5.8	-2.0	-3.2	-4.5	-2.6	-0.7	0.4	-1.0	1.0
M06	-4.7	-9.2	-9.7	-8.3	-3.6	-5.6	-6.5	-4.7	-2.4	-1.7	-3.0	-0.7
ωB97X-D	-4.6	-8.8	-10.2	-8.7	-3.7	-5.4	-6.7	-5.3	-2.6	-1.5	-2.8	-1.7
Avg.^b	-4.4	-8.6	-9.8	-8.1	-3.3	-5.1	-6.5	-4.7	-2.1	-1.3	-2.8	-0.9

^a The MP2/aug-cc-pVTZ for n=4 are not available.

^b The arithmetic average was performed over all methods (the largest basis set result was considered in each case).

The upper panel in Fig. 6, which represents the average energy per added water molecule both to 1ClEtOH and 2ClEtOH, shows an interesting difference between the species. While in 1ClEtOH the additional water contributes with approximately the same energy to the complex, this is not the case for 2ClEtOH, which shows a marked decrease toward stabilization with the additional molecules. This is another manifestation of the already mentioned effect of the more distributed hydrophilic and hydrophobic regions in 2ClEtOH with respect to 1ClEtOH. This effect is not so noticeable if one uses equation (2) where the energy difference is recorded against the n-water complex. In this case it is clear that the curves exhibit similar behavior, although the ones for 1ClEtOH are more acute and reach lower energies than those for 2ClEtOH. One can notice also that the B3LYP DFT method is the one giving the worse results (i.e. largest difference with respect to the more exact G2 results) of the three DFT methods, most probably because of the lack of dispersion energy, present in the other two and important for these loose hydrogen-bonded complexes.

3.4 | IR spectra

The comparison of the C-Cl and O-H stretching in 1ClEtOH and 2ClEtOH is shown in Table 4. Solvatochromism is present in both bands as a hypsochromic effect (blue shift) in 1ClEtOH and 2ClEtOH as well. While the effect on the OH stretching is monotonical for both species, with a total shift of about 600 cm⁻¹, the C-Cl band has a different behavior. In 2ClEtOH the band suffers practically no shift, while in 1ClEtOH varies more slowly than the OH band, does not decrease monotonically and even splits in two bands in the case of the 3W and 4W complexes. This fact is shown in Table 4 by listing the pair of frequencies at which these bands appear, involving the C-Cl stretching and several OH stretching from the water molecules. Both

for the 3- and 4-water complexes the lower wavelength band is less intense, about one third of the intensity of the band at the longer wavelength.

TABLE 4 Wavelength (in cm^{-1}) of the C-Cl and O-H bands in the free 1ClEtOH and 2ClEtOH molecules, as well as in the clusters with up to four water molecules

N	1ClEtOH		2ClEtOH	
	CCl	OH	CCl	OH
0	644	3885	681	3866
1	596	3682	683	3849
2	580	3557	684	3565
3	603/620	3441	682	3501
4	547/596	3266/3387	675	3357

The superimposed IR spectra of free and 4-water complexed 1ClEtOH is presented in Figure 7. The most important bands involving some movement of the solute have been marked in the figure.

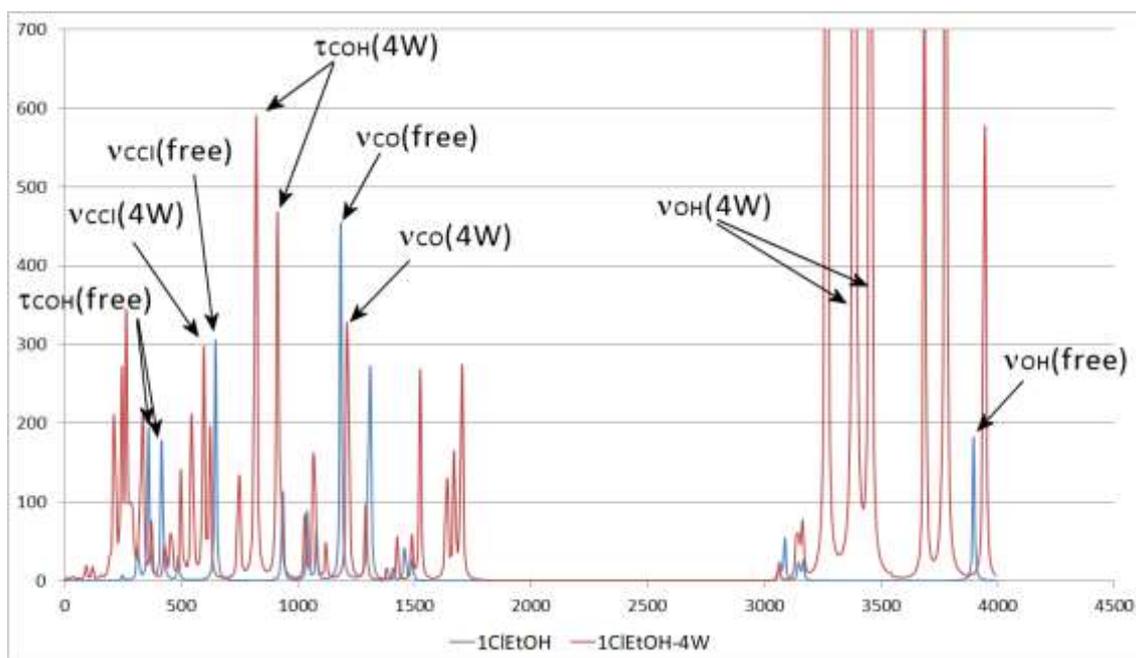


Figure 7. Superimposed IR spectra of 1ClEtOH free (blue) and complexed with four water molecules (red). Wavelengths in cm^{-1} .

The hypsochromic effect on the C-Cl stretching band is significant and should be possible to identify it experimentally. Moreover, there is an important bathochromic effect on the torsion band of the COH group and a smaller one on the stretching band of the CO group. Taking into account both the hypsochromic and bathochromic effect, an interesting

phenomenon results. While in the free 1ClEtOH the C-Cl band should be observed at longer wavelengths than the COH torsion, the opposite should be true in solution. All these spectral characteristics should be helpful to identify the presence of the 1ClEtOH isomer and distinguish it from the 2ClEtOH isomer.

4 | CONCLUSIONS

In this work we report a computational study of the two isomers of chloroethanol, namely 1ClEtOH and 2ClEtOH, both free and complexed with up to four water molecules. Both the density function M06 method, with several basis sets, and composite methods CBS-QB3 and G4 have been employed for the calculation of structures, energetics and spectra.

The results indicate that there are important differences in the way that water affects both isomers. On the one side, the water complexes of 1ClEtOH are more stable than those of 2ClEtOH. About three molecules of water are enough to saturate the first solvation shell of both isomers, but the chlorine atom is more involved in the interactions with water in the case of 1ClEtOH than in the case of 2ClEtOH. An increase in the length of the C-Cl bond as well as a blue shift of the C-Cl stretching band supports the view that water solvation weakens the C-Cl bond, therefore favoring dehalogenation. These results agree with those of Philips et al [13] in their study of dehalogenation of chloromethanol. This is not the case in 2ClEtOH where water addition does not affect neither the C-Cl bond distance nor the stretching frequency. The OH stretching frequency, on the contrary, is affected similarly in both molecules. Although experimentally this frequency will be masked by those of the solvent water molecules, it is possible to observe in the theoretical spectra the hypsochromic effect associated to solvation.

The study of the IR spectra allows to identify separately the 1ClEtOH and 2ClEtOH isomers, both in gas phase and solution. The C-Cl stretching band shows a gap of about 40 cm^{-1} between both isomers. Therefore, the presence of two C-Cl stretching bands in gas phase would give away the presence of the second isomer. The relative intensities could provide an estimation of the relative concentrations. What is more, it was shown that in the presence of water the combination of a hypsochromic shift of the OH stretching band and a bathochromic shift of the COH torsion band reverses the order of these transitions with respect to gas phase, therefore providing clues about the presence or not of this isomer.

It is known that many reactions that occur in cold regions of the atmosphere and the interstellar medium (ISM) are produced by heterogeneous catalysis on dust particles and ice clusters. Binding of small molecules to the water in these clusters or, conversely, binding of small water clusters to those species, is an important feature to be understood for studies in the ISM. This paper sheds light on one such phenomenon, in the same spirit than other very recent publications [35]. The binding energies of the chloroethanols to the water clusters, as well as their variation with the number of water molecules contacted, give clues as to the extent in which a small ISM water particle can participate in the reaction of dehalogenation of these species.

Work is under way on the participation of water molecules in the dehalogenation reaction properly, which involves a hydrogen transfer from oxygen in the case of 1ClEtOH, while demanding a transfer from a hydrogen on carbon in 2ClEtOH. The determination of the relation between both isomers in the reaction path for the obtention of acetaldehyde will be published elsewhere.

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KEYWORDS: Microhydration, 2-chloroethanol, 1-chloroethanol, dehalogenation, thermodynamics

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