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Interaction in the Ternary Complexes of HCl−Methanol−X, X = H_2O or NH_3: Ab Initio Calculations and On-the-Fly Molecular Dynamics

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Dynamics, structures, energetics, and vibrational spectra of the ternary complexes of hydrogen chloride with either methanol and water or methanol and ammonia were investigated by on-the-fly molecular dynamics and ab initio and density functional theory (DFT) with aug-cc-pvDZ basis sets. Addition of CH_3OH to the HCl−NH_3 system catalyzes the proton transfer from HCl to NH_3. However, the dynamics of the system show that the proton is not localized on NH_3; rather, it is shared between N and Cl.

1. Introduction

In recent years, there has been considerable interest in the structure and dynamics of molecular clusters in which a variable number of molecules are usually bound by hydrogen bonds. The reason for such intensive studies is that this type of interaction force plays a crucial role in many physical, chemical, and biological phenomena.[1,2] A concept that is generally associated with hydrogen bonding is the cooperativity effect that arises when the molecular clusters have more than two molecules. Cooperativity simply implies the enhancement of the hydrogen bond in the presence of another H bond with either the donor or acceptor of the first H bond. Therefore, it is very important to understand such intensified stability of some hydrogen-bonded clusters.

Because of the cooperativity effect, the total interaction energy becomes larger that the sum of the molecular pair interaction energies. Furthermore, this form of effect changes the dipole moments and vibration frequencies of the clusters. The hydrogen bonding in molecular clusters does not always increase the total interaction energies, that is, it does not make a positive contribution to cooperativity. If two proton-donating groups, for example, A−H and B−H, are giving their protons to one accepting group, for example, X in the A−H···X···H−B arrangement, a negative cooperativity, called anticooperativity, effect may take place. Consequently, the total interaction energy generally becomes less than the sum of the molecular pair interaction energies.[3] This effect also changes the properties of molecular clusters, such as the dipole moment and vibrational frequencies. Cooperativity and anticooperativity effects are both nonadditive features of molecular clusters.

Solvation and ionization of HCl in small clusters (see, for example, refs 4−9) and on/in the surface (see, for example, refs 10−15) have been the subjects of many investigations. Among them, the most studied system is HCl on/in water clusters and ice surface (see refs 4, 5, and 10−13 and references therein) due to the fact that these processes play an important role in the depletion of stratospheric ozone.[16,17] Moreover, since the proton-transfer reactions participate in a wide range of chemical and biological reactions, HCl ionization has been also studied with other H-bonded systems, such as NH_3,[5,8,9,18,19] CH_3OH,[3,6,14,15] CH_3SH,[7] and dimethylether.[20,21] The main questions in these studies are how many “solvent” molecules are necessary to ionize HCl and which solvent molecules promote proton transfer between the HCl and solvent molecules.

In this study, HCl solvation and ionization were investigated in ternary complexes, namely, HCl−CH_3OH−H_2O and HCl−CH_3OH−NH_3 complexes. The main tools for this search are ab initio calculations at the MP2/aug-cc-pvDZ level and on-the-fly molecular dynamics as implemented in the density functional code Quickstep,[22] which is the part of the CP2K package.[23] Ab initio calculations were performed to search the hydrogen bonding behavior of these complexes by calculating nonadditive effects on structures, binding energies, and vibrational modes of the molecular clusters. On-the-fly MD simulations were performed to understand the dynamics of these systems at low temperatures. The reason for such low-temperature studies is that the systems can be analyzed in a more rigid environment.

Investigations of CH_3OH−H_2O and CH_3OH−NH_3 complexes with HCl in different perspectives are very interesting for several reasons; first, one can calculate the preferential adsorption site for HCl on/in these complexes. Second, the extent of HCl solvation can be studied by searching potential energy surfaces of these ternary complexes, and this also responds to the question of which molecule can catalyze HCl ionization in these complexes. Third, since some of the structures contain the proton-transfer mechanism, it will be also useful to study the dynamics of the proton motion as well as the accompanying infrared spectrum. For such highly anharmonic systems, it is difficult to calculate both the dynamics and the spectra at the same time by using the standard computational methodologies, such as classical ab initio techniques and molecular dynamics simulations. The former one is often used for normal-mode analysis within the harmonic approximation, and the latter one is generally limited to an analytical potential function describing the bond formation and breaking. Therefore, on-the-fly molecular dynamics has advantages for the investigation of fluxional

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systems. Moreover, as will be explained in the Computational Details section, spectral calculations have been provided by the dipole−dipole correlation function as described in ref 24 and successfully applied to other systems (for example, refs 14, 15, 21, and 25). With this methodology, one does not need to worry about the anharmonicity of the system since it is automatically included.[24]

It should be very instructive to note at this point that the binary complexes of $HCl-CH_3OH$,[3,6] $HCl-H_2O$,[4,5,11] CH_3OH-H_2O,[26−30] and $HCl-NH_3$[5,8,9,18,19] have been the subject of much research. To the best of the authors' knowledge, there is no study related to the NH_3-CH_3OH complex.

Among these heterodimers, the most interesting case is the CH_3OH-H_2O dimer. This is because in the dimer structures, there are two isomers in which the H_2O molecule acts as either the proton acceptor or proton donor. The global minimum contains the structure in which methanol is the proton-accepting unit, and the energy difference between these two isomers was calculated as less than 1 kcal/mol with different levels of theory.[26−30]

The other interesting dimer is $HCl-NH_3$.[5,8,9,18,19] This dimer contains molecular HCl, and the inclusion of small molecules, such as H_2O or CH_3OH, catalyzes the proton transfer from HCl to NH_3 to form the NH_4^+ and Cl^- ion pair.[8] Moreover, the proton transfer could also be promoted by extra HCl or HF.[31] Although the structures and energetics of these proton-transferred systems were analyzed by quantum mechanical calculations, the dynamics of the proton has not been studied. It will be show in the Results and Discussion section that although the minimized structure gives ionized HCl, the acid proton undergoes large amplitude fluctuations between Cl and N during the trajectory run at an average temperature of 99 K.

The paper is organized as following; first, the details of ab initio calculations and on-the-fly MD simulations are given. In section 3, the structure, energetics, and three-body decomposition energies are discussed in terms of the nonadditivity effect. Then, the vibrational analysis calculated with ab initio calculations and finally the dynamics of the system are given in terms of the structure and spectra which are calculated from the dipole−dipole correlation function and compared with the ones that are obtained from ab initio calculations.

2. Computational Details

2.1. Details of Ab Initio Calculations. Ab initio calculations consist of three stages: first, the geometry and energy calculations for the complexes; second, calculations of IR spectra for the related system; and third, the nonadditive (three-body effects) computations. The configurations of the ternary complexes of $HCl-CH_3OH-H_2O$ and $HCl-CH_3OH-NH_3$ were optimized by using DFT/B3LYP and MP2 level calculations with aug-cc-pvDZ basis sets[32] at the frozen core approximation. Different starting geometries were constructed according to chemical intuition to search several regions of the intermolecular potential energy surface (IPES). All optimized configurations were also subjected to vibrational analysis to determine the correspondence with a minimum on the IPES.

The interaction energies of the complexes, $\Delta E_{\mathrm{int}}^{\mathrm{SM}}$ (where the superscript SM represents the method used in the calculations, B3LYP, MP2, and CCSD(T)) are defined as the difference between the energy of the isolated subunits and that of the supermolecule, corrected for basis set superposition error (BSSE) due to the deficiencies of a finite basis set by using the counterpoise procedure (CP),[33] which was employed for the final structures (viz., the optimized ones). It was shown by Hobza et al. for the water dimer that the corrected surface intermolecular distances are a little longer than the values evaluated by the standard gradient optimization (ca. 0.1−0.2 Å).[34] The interaction energies have also been corrected for the deformation error ΔE_{def}, that is, the energy needed to deform the monomers from their optimal equilibrium geometries to their geometries in the complex. The corrections were calculated at the MP2 level. Finally, the dissociation energies were also calculated from the interaction energies corrected for BSSE and deformation error by adding the difference of the energies of the zero-point motion obtained from the MP2 level within the harmonic approximation. All calculations were performed with the Gaussian 03 program.[35]

The nonadditivity effect is calculated as

$$\Delta E_{\mathrm{nonadd}} = E_{\mathrm{int}}^{\mathrm{SM}} - \Delta E_{\mathrm{int,AB}} - \Delta E_{\mathrm{int,BC}} - \Delta E_{\mathrm{int,AC}} \quad (1)$$

where $\Delta E_{\mathrm{int,AB}}$, $\Delta E_{\mathrm{int,BC}}$, and $\Delta E_{\mathrm{int,AC}}$ are the interaction energies (including BSSE) of the respective dimers. Monomer and dimer energies are calculated by using the full basis of the complex. The anticooperative interaction of the three monomers is present when $\Delta E_{\mathrm{nonadd}}$ is positive, that is, the sum of all pair interaction energies is more favorable than the total interaction energy.

2.2. On-the-fly Molecular Dynamics Simulations. The electronic structure code as implemented in the CP2K/QUICKSTEP package[22,23] was employed in this study. The Kohn−Sham formulation of density functional theory (DFT) with the Gaussian plane wave method[36] was implemented in the QUICKSTEP. The Kohn−Sham orbitals were expanded using a linear combination of atom-centered Gaussian-type orbital functions. The electronic charge density was described using an auxiliary basis set of plane waves. Energies and forces from on-the-fly ab initio molecular dynamics simulation sampling of the Born−Oppenheimer surface were calculated for each MD step using pseudopotentials of the Goedecker, Teter, and Hutter type,[36] a Gaussian valence basis set of quadruple-ζ quality augmented by three sets of polarization functions (QZV3P), and the exchange−correlation functional of Becke, Lee, Yang, and Parr (BLYP).[37,38]

The most stable two isomers of each ternary complex $HCl-CH_3OH-H_2O$ and $HCl-CH_3OH-NH_3$ were subject to trajectory calculations using on-the-fly molecular dynamics. Each system has been subjected to a minimization procedure by using QUICKSTEP before constant energy MD simulations were performed. The time scale for each system will be given in the related results section. The cluster spectra were obtained from the Fourier transform of the dipole−dipole correlation function,[24] as was applied successfully to other systems especially in the condensed phase.[14,15,21,25]

3. Results and Discussions

3.1. Structure, Energetics, and Three-Body Effects from Ab Initio Calculations. *Ternary Complexes of* $HCl-CH_3OH-H_2O$. Three stationary points have been found on the IPES. The structures are illustrated in Figure 1, and energy values corresponding to all minima are given in Table 1. In all minima, HCl binds strongly to the oxygen of either methanol (Figure 1a and c) or water (Figure 1b). The global minimum, shown in Figure 1a and denoted as $HCl-CH_3OH-H_2O$-1a, contains a cyclic structure formed by O1···O2···Cl atoms, in which methanol accepts a hydrogen bond from hydrogen chloride, H1···O1, and donates its hydrogen to water, H2···O2. In the other minima, shown in Figure 1b and represented as $HCl-CH_3OH-H_2O$-1b, the water molecule accepts hydrogen from hydrogen chloride, H1···O2 and donates its hydrogen to methanol,

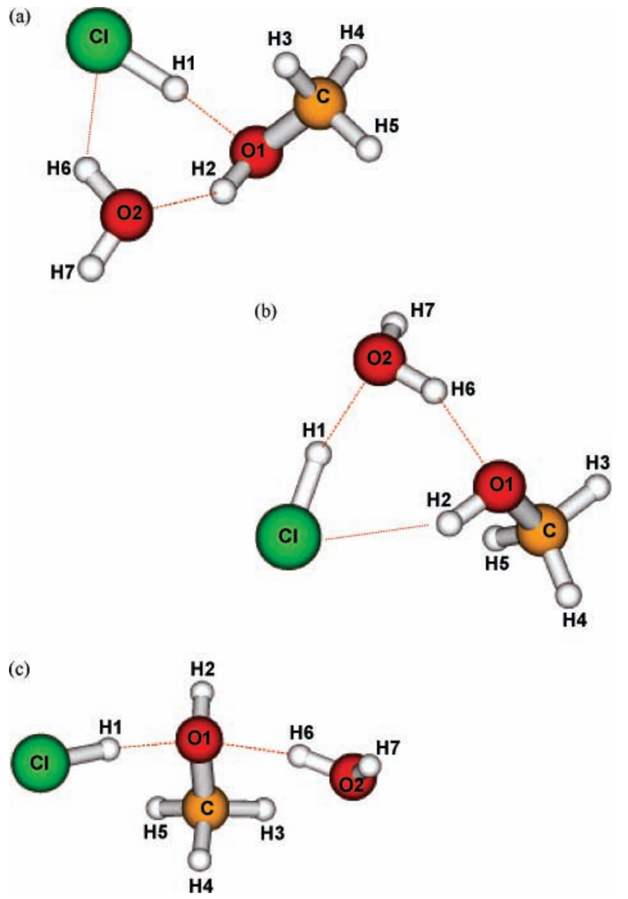

Figure 1. Structures of the of $HCl-CH_3OH-H_2O$ ternary complexes: (a) global minimum denoted as $HCl-CH_3OH-H_2O$-1a, (b) local minimum as $HCl-CH_3OH-H_2O$-1b, and (c) local minimum as $HCl-CH_3OH-H_2O$-1c.

H6···O1. The dissociation energy difference (ΔD_0^{MP2}) between these two minima is about 1 kcal/mol. For the water−methanol dimer in which methanol is either donating a proton to water or accepting a proton from water, a less than 1 kcal/mol energy difference was also obtained at different levels of calculation.[26−29] In addition to two cyclic structures, a third noncyclic structure was found, denoted as $HCl-CH_3OH-H_2O$-1c and shown in Figure 1c, in which HCl and H_2O are both donors and form hydrogen bonds H1···O1 and O1···H6 with methanol. Energetically, this configuration is less stable than cyclic 1a and 1b. The same initial configuration in which H_2O accepts protons from both CH_3OH and HCl was considered also, but it was converged to the cyclic structure shown in Figure 1a.

Let us now discuss the nonadditivity effect on geometric parameters. Geometric parameters of all structures are given in Table 2. The results for heterodimers were published recently;[3,6] therefore, the available literature data will be used for comparison. In the HCl···CH_3OH heterodimer calculated at the MP2/aug-cc-pvDZ level of theory,[3,6] the global minimum structure resembles the one that is shown in Figure 1a. Adding one water molecule to the heterodimer of $HCl-CH_3OH$ causes an elongation of the HCl bond length by about 0.028 Å. The H-bond length between H of HCl and O of methanol in the trimer given in Figure 1a (1.576 Å) becomes shorter than that in the dimer (1.756 Å). The C−O distance elongates by going from the dimer (1.437 Å) to the trimer (1.445 Å) shown in Figure 1a.

TABLE 1: The Interaction Energies (in kcal/mol) for $HCl-CH_3OH-H_2O$ and $HCl-CH_3OH-NH_3$ Conformers Calculated at the B3LYP, MP2, and CCSD(T) Levels with aug-cc-pvDZ

	$HCl-CH_3OH-H_2O$	$HCl-CH_3OH-H_2O$	$HCl-CH_3OH-H_2O$
	1a	1b	1c
E_{int}^{B3LYP}	−15.02	−13.97	−9.76
E_{int}^{MP2}	−15.63	−13.69	−10.79
$E_{int}^{CCSD(T)}$	−13.95	−12.56	−9.90
ΔZPE^{MP2}	3.98	4.07	3.53
ΔE_{def}^{MP2}	1.83	0.91	0.44
D_0^{MP2}	9.83	8.71	6.82
$D_0^{CCSD(T)a}$	8.15	7.57	5.93
	$HCl-CH_3OH-NH_3$	$HCl-CH_3OH-NH_3$	$HCl-CH_3OH-NH_3$
	2a	2b	2c
E_{int}^{B3LYP}	−54.36	−17.76	−9.65
E_{int}^{MP2}	−56.11	−17.75	−10.57
$E_{int}^{CCSD(T)}$	−50.67	−15.91	−9.35
ΔZPE^{MP2}	5.68	3.83	3.14
ΔE_{def}^{MP2}	40.32	2.37	0.84
D_0^{MP2}	10.11	11.55	6.59
$D_0^{CCSD(T)a}$	4.67	9.71	5.37

[a] The value D_0 was corrected by ΔZPE and ΔE_{def} calculated for MP2/aug-cc-pvDZ.

The water molecule acts as a proton donor in the global minimum of the heterodimer CH_3OH···H_2O. On the other hand, adding one HCl molecule to the system favors the HCl···CH_3OH interaction, and therefore, methanol donates its hydrogen to a water molecule to have a cyclic structure (see Figure 1a). This might be explained by using the argument that methanol is a stronger base than water in the gas phase;[39] therefore, it prefers HCl, which is more acidic than water as a proton donor. The O···O distances in dimers where water is either the proton donor or acceptor are calculated at the MP2/aug-cc-pvDZ level of theory as 2.844 and 2.912 Å, respectively. Inclusion of one HCl molecule to either dimer (i.e., complexes shown in Figure 1a and b) changes the O···O distances to 2.757 Å in Figure 1b and 2.762 Å in Figure 1a. The H···O bond in the water−methanol interaction shortens by 0.081 Å in going from the dimer (1.942 Å), where water is the proton acceptor, to the trimer (1.861 Å), illustrated in Figure 1a.

Table 3 shows the decomposition of the interaction energies into three-body as well as two-body contributions for all conformers shown in Figure 1a−c. As one can see from the table, the nonadditivity effects depend on the configuration of the three interacting molecules. The three-body nonadditive effect leads to stabilization of the trimer energies for conformers $HCl-CH_3OH-H_2O$-1a and $HCl-CH_3OH-H_2O$-1b, with the contributions calculated as ∼22 and ∼20%, respectively. The anticooperativity effect destabilizes the $HCl-CH_3OH-H_2O$-1c conformer energy by ∼4%. This conclusion is in agreement with the results for the water trimer where the cooperative effect strongly stabilizes the cyclic trimer, while this effect has less influence in trimers where molecules do not adopt a cyclic pattern.[40] On the basis of the two-body terms alone, the isomers would be quite similar in energy. Upon inclusion of the three-body terms, the situation changes; the 1c isomer with a double acceptor methanol would be less stable than the cyclic ones because of the quite small value of this term in the 1c structure.

Ternary Complexes of $HCl-CH_3OH-NH_3$. The ternary complex also has three minima on the IPES, which are all shown in Figure 2. The energy values are presented in Table 1, and the structural parameters are listed in Table 2. The global minimum, shown in Figure 2a and represented as $HCl-CH_3$-

TABLE 2: The Distances (*r*, Å) and the Angles (*a*, deg) between Atoms in the Ternary Complexes of HCl−CH_3OH−H_2O and HCl−CH_3OH−NH_3 and Their Monomers[a]

monomer HCl		monomer CH_3OH		monomer H_2O		monomer NH_3	
r(H−Cl)	1.287	*r*(O−H)	0.965	*r*(O−H)	0.965	*r*(N−H)	1.020
		r(C−O)	1.434	*a*(HOH)	103.8	*a*(HNH)	106.3
		a(HOC)	107.8				

	HCl−CH_3OH−H_2O				HCl−CH_3OH−NH_3		
distances	1a	1b	1c	distances	2a	2b	2c
r(H1−Cl)	1.356	1.328	1.312	*r*(H1−Cl)	1.755	1.361	1.330
r(O1−H2)	0.980	0.970	0.968	*r*(O−H2)	0.985	0.994	0.967
r(O1−C)	1.445	1.442	1.454	*r*(O−C)	1.435	1.441	1.453
r(O2−H6)	0.972	0.983	0.971	*r*(N,H1)	1.130		
r(O2−H7)	0.965	0.966	0.965	*r*(N,H6)	1.038	1.022	1.021
r(Cl···O2)	3.331	3.012		*r*(N,H7)	1.019	1.020	1.020
r(O1···O2)	2.761	2.757	2.879	*r*(N,H8)	1.019	1.019	1.020
r(O1···Cl)	2.918	3.390	3.093	*r*(O,Cl)	3.114	2.904	3.002
r(H1···O1)	1.576		1.785	*r*(Cl,N)	2.863	3.590	3.609
r(H2···O2)	1.860			*r*(N,O)	2.711	2.768	3.837
r(H6···Cl)	2.560			*r*(H2···Cl)	2.203		
r(H1···O2)		1.710		*r*(H6···O)	1.828		
r(H2···Cl)		2.689		*r*(H6···Cl)		2.875	2.668
r(H6···O1)		1.834	1.989	*r*(H3,N)			2.443
angles				angles			
a(H2,O1,C)	107.5	106.7	108.1	*a*(H2,O,C)	108.2	107.7	108.6
a(H6,O2,H7)	104.9	105.9	104.7	*a*(H6,N,H7)	110.7	106.6	106.0
a(Cl,H1,O1)	168.5		173.8	*a*(H7,N,H8)	110.0	106.5	105.9
a(Cl,H1,O2)	-	164.8		*a*(H6,N,H8)	111.1		106.2
a(O1,H2,O2)	151.3			*a*(N,H6,O)	140.5		
a(O2,H6,O1)		154.9	151.2	*a*(O,H2,Cl)	153.0		
a(O2,H6,Cl)	136.2			*a*(Cl,H1,N)	165.1		

[a] All values were calculated at the MP2 level with the aug-cc-pvDZ basis set.

TABLE 3: The Decomposition of Binding and Nonadditivity Energies ΔE_{nonadd} (kcal/mol) for the Ternary Complexes of HCl−CH_3OH−H_2O and HCl−CH_3OH−NH_3 Shown in Figures 1 and 2[a]

	HCl−CH_3OH−H_2O				HCl−CH_3OH−NH_3		
system	1a	1b	1c	system	2a	2b	2c
HCl···CH_3OH				HCl···CH_3OH			
E_{int}^{MP2}	−6.395	−2.185	−6.756	E_{int}^{MP2}	−	−6.436	−6.860
CH_3OH···H_2O				CH_3OH···NH_3			
E_{int}^{MP2}	−3.718	−4.161	−5.140	E_{int}^{MP2}	−	−5.150	−1.283
HCl···H_2O				HCl···NH_3			
E_{int}^{MP2}	−2.054	−4.576	0.626	E_{int}^{MP2}	−	−2.238	−1.237
ΔE_{nonadd}	−3.465	−2.770	0.481		−	−3.930	−1.184
$\Delta E_{nonadd}/E_{int}^{MP2}$ (%)	22.2	20.2	4.4		−	22.1	11.2

[a] All values calculated with MP2/aug-cc-pvDZ.

OH−NH_3-2a, contains a methanol-shared NH_4^+ and Cl^- ion pair, stabilized by a cyclic structure form of Cl···N···O atoms. It has been shown both experimentally and theoretically that the dimer of NH_3−HCl is molecular (see, for example, refs 5 and 18). However, addition of CH_3OH to the system promotes proton transfer, as was also observed for NH_3−HCl−X, where X is a small molecule such as H_2O, CH_3OH, and so forth.[8] This trimer is characterized by a very big interaction energy, which corrects for the deformation error and becomes −15.78 kcal/mol at the MP2 level.

The other minimum shown in Figure 2b and denoted as HCl−CH_3OH−NH_3-2b contains a cyclic structure in which HCl donates its hydrogen to methanol, ClH1···O, and accepts hydrogen from ammonia, NH6···Cl. Contrary to the first configuration, NH_3 does not catalyze the proton transfer. This might be because NH_3 is a good proton acceptor but a poor proton donor. The MP2 interaction energy corrected for deformation error is comparable to the one that was calculated for isomer 2a (−15.39 kcal/mol). The last configuration illustrated in Figure 2c and denoted as HCl−CH_3OH−NH_3-2c is similar to structure shown in Figure 2b, differing only in the methanol−ammonia interaction in which methyl hydrogen is interacting with ammonia (i.e., C−H···N). The MP2 interaction energy is the smallest one in this case (−9.72 kcal/mol).

The nonadditivity effect on geometric parameters can be discussed again by comparing the heterodimer values to the trimer values. Addition of one NH_3 molecule to the HCl−CH_3OH heterodimer changes the interaction site of HCl from methanol to ammonia in the global minimum. As was reported in the work of Li et al.,[8] methanol was one of the proton-transfer catalyzing molecules for HCl. Since the configuration of the global minimum of the HCl−CH_3OH heterodimer changes in the global minimum of the ternary complex of HCl−CH_3OH−NH_3, it is not appropriate to compare the geometrical parameters for structure HCl−CH_3OH−NH_3-2a. On the other hand, the second conformer shown in Figure 2b has a HCl−CH_3OH interaction that can be compared to the HCl−CH_3OH heterodimer.[3,6] Adding one ammonia molecule to the heterodimer

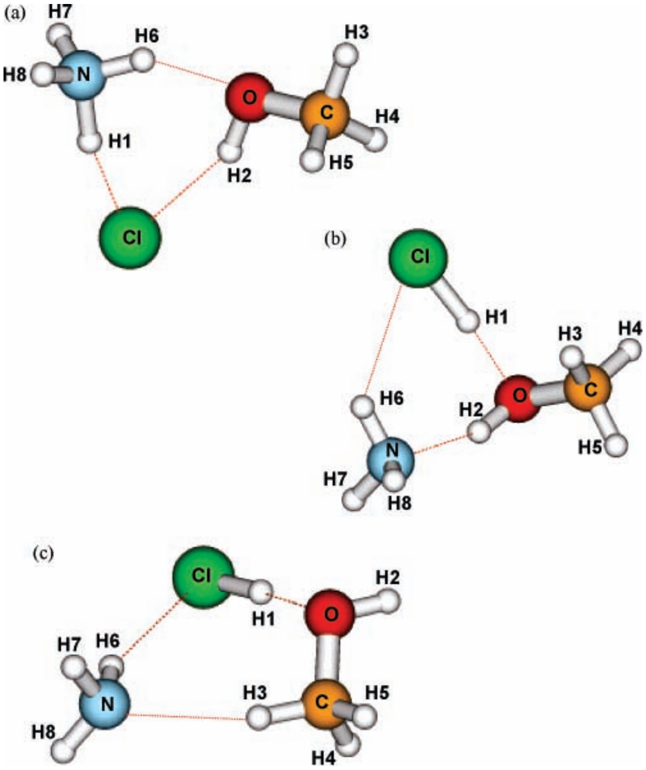

Figure 2. Structures of the of $HCl-CH_3OH-NH_3$ ternary complexes: (a) global minimum denoted as $HCl-CH_3OH-NH_3$-1a, (b) local minimum as $HCl-CH_3OH-NH_3$-1b, and (c) local minimum as $HCl-CH_3OH-NH_3$-1c.

of $HCl-CH_3OH$ causes an elongation of the HCl bond length by about 0.034 Å, which is higher than the one that has H_2O instead of NH_3.

Finally, let us discuss the decomposition of the interaction energies into three-body contributions and nonadditive effects for all conformers shown in Figure 2a−c. Table 3 summarizes the results. The nonadditive effect leads to stabilization of the trimer energies for conformers $HCl-CH_3OH-NH_3$-2b and $HCl-CH_3OH-NH_3$-2c, with the contributions calculated as ∼22 and ∼11%, respectively. However, the energy decomposition for two-body terms shows a different pattern; the dimer CH_3OH-NH_3-2b contributes more to stabilization than the dimer CH_3OH-NH_3-2c, where the CH of the CH_3 of methanol donated a hydrogen to the nitrogen atom of NH_3. The three-body effect is also much less in the 2c than that in the 2b isomer. Because of the ionization of HCl, the nonadditive effect for the isomer shown in Figure 2a was not considered.

3.2. Ab Initio Vibrational Analysis. The normal-mode frequencies within the harmonic approximation were calculated at the MP2/aug-cc-pvDZ level of theory for the optimized structures shown in Figures 1a−c and 2a−c. The results are listed in Table 4, which also contains the changes in the parameters caused by formation of the complexes—the shifts of the intramolecular frequencies and the ratios of IR intensities with respect to monomer values.

The calculated frequencies of the ternary complexes of $HCl-CH_3OH-H_2O$ are strongly perturbed as compared to frequencies of the binary complexes such as $HCl-CH_3OH$,[3,6] $HCl-H_2O$,[4,5,11] and H_2O-CH_3OH.[27−30] The most interesting intramolecular modes, namely, the ν(HCl) and ν(OH) frequencies, are discussed and compared to the respective mixed parental dimers on the basis of Table 4.

The $HCl-CH_3OH$ system is present in all complexes studied in this work. HCl is the proton donor in all of the trimers. The HCl frequency is sifted by -425 cm^{-1} in the $HCl-CH_3OH$ dimer relative to the HCl monomer calculated at the same level of theory.[6] Let us now discuss what happens when the water or ammonia molecule is added to this dimer. Addition of one water molecule to the $HCl-CH_3OH$ dimer shifts the HCl mode by -910 cm^{-1} in the ternary complex shown in Figure 1a relative to the monomer with a bigger intensity enhancement (I_{IR} in the dimer is equal to 1173 km mol^{-1}, and that in the ternary complex shown in Figure 1a is 2044 km mol^{-1}). The red shift in the case of the other isomer shown in Figure 1c is smaller, -350 cm^{-1}. Thus, we can describe the cooperativity effects in terms of the shifts of the HCl stretch where HCl is the proton donor to methanol by comparing the shifts in the trimers (Figure 1a and c) to the shift in the $HCl-CH_3OH$ dimer. These ratios are 2.2 and 0.8 for 1a and 1c, respectively. Two complexes with ammonia also contain the donor HCl, and the respective ratios of the HCl shifts are 2.3 and 1.4 for 2b and 2c complexes, corresponding well with the estimated nonadditivity effects. In summary, the red shifts of the HCl stretch frequencies increase in magnitude for the studied trimers in the sequence of 1c < 2c < 1a < 2b.

The question can be asked concerning the extent of the change of the ν(HCl) frequency with respect to the parental $HCl-H_2O$ dimer also. The HCl frequency in the $HCl-H_2O$ dimer is shifted by -185 cm^{-1} at the MP2/DZP level,[4] whereas in the ternary complex, it is found to be -551 cm^{-1} in 1b.

The frequency of the intramolecular OH mode of methanol, similar to the ν(HCl) frequency, is changed from its monomer value upon complexation in comparison to the dimer discussed above. The OH frequency of methanol is shifted by -25 cm^{-1} only in the $HCl-CH_3OH$ dimer relative to the methanol monomer.[6] It is much less than the shift of the HCl frequency in this dimer. However, the addition of a water molecule to the trimers increases the shift to -262 cm^{-1} in 1a, where the OH group of methanol is the acceptor (from HCl) and the donor of the proton (to OH_2), to -75 cm^{--} in 1b (OH donates a proton to Cl and accepts a proton from water), and -34 cm^{-1} in the 1c trimer (OH group double acceptor). Thus, the ratio of the shift for the trimer/dimer is now 10.5, 3.0, and 1.4 for 1a, 1b, and 1c, respectively, which illustrates the strong cooperative effects. Much higher shifts of the ν(OH) stretching frequency (-370 cm^{-1} for 2a, -560 cm^{-1} for 2b) can be found for the 2a and 2b trimers, while only -26 cm^{-1} is found for the 2c configuration.

The changes of the methanol ν(OH) stretching frequency in the trimers can be compared with this frequency mode in the dimer CH_3OH-H_2O also. In the methanol−water dimer, CH_3OH-H_2O, where methanol is donating its hydrogen to water, the red shift for the OH stretch frequency of methanol was calculated to be -120 cm^{-1} at the MP2/aug-cc-pvDZ level of theory. The most stable trimer 1a was predicted to have ν(OH) $= 3580$ cm^{-1}, while it is 3767 cm^{-1} for the 1b complex. Thus, the ratio of trimer/dimer shift is equal 2.1 for the ternary complex shown in Figure 1a and 0.6 for Figure 1b. Trimer 1c does not contains the OH-donating group. In summary, the red shifts of OH stretch frequencies increase in magnitude in the sequence of 2c < 1c < 1b < 1a < 2a < 2b.

3.3. Dynamics of the Ternary Complexes of HCl−Methanol−X, X = H_2O or NH_3. The trajectory calculations were carried out for two isomers of each ternary complex; namely, HCl is either connected to methanol (shown in Figure 1a) or H_2O (see Figure 1b) for the $HCl-CH_3OH-H_2O$ system and to NH_3 (Figure 2a) or methanol (Figure 2b) for the $HCl-CH_3OH-NH_3$ system. The calculated spectra from the dipole−

TABLE 4: The Important Frequencies (cm^{-1}), the Infrared Intensities (km mol^{-1}) for the Ternary Complexes of HCl−CH_3OH−H_2O and HCl−CH_3OH−NH_3 Shown in Figures 1 and 2 Calculated at the MP2/aug-cc-pvDZ Level

system	frequencies	ν_c	I_c	$\Delta\nu = \nu_c - \nu_m$	I_c/I_m
HCl	ν(HCl)	3023	42.7		
CH_3OH	$\nu(OH)_m$	3842	34.4		
	ν(CO)	1044	112.3		
H_2O	$\nu_{as}(OH)_w$	3928	67.0		
	$\nu_s(OH)_w$	3803	4.1		
	δ(HOH)	1622	67.5		
NH_3	$\nu_{as}(NH_2)$	3635	5.0		
	$\nu_{as}(NH_3)$	3635	5.0		
	$\nu_s(NH_3)$	3480	4.6		
	$\delta(NH_3)$	1648	13.3		
	$\delta(NH_3)$	1045	131.0		
HCl−CH_3OH[a]	ν(HCl)	2598	1173.7	−428	27.5
	$\nu(OH)_m$	3817	56.0	−25	1.6
	ν(CO)	1025	105.6	−20	0.9
CH_3OH−H_2O[b]	$\nu_{as}(OH)_w$	3900		−28	
(water is proton donor)	$\nu_s(OH)_w$	3658		−145	
	δ(HOH)	1646		24	
HCl−H_2O[c]	ν(HCl)	2929		−185	
	$\nu_{as}(OH)_w$	4041		−17	
	$\nu_s(OH)_w$	3901		−11	
	δ(HOH)	1666		1	
HCl−NH_3[d]	ν(HCl)	2403		−646	
	$\nu_{as}(NH_2)$	3681		−32	
	$\nu_{as}(NH_3)$	3681		−32	
	$\nu_s(NH_3)$	3533		0	
	$\delta(NH_3)$	1676		−13	
	$\delta(NH_3)$	1676		−13	
	$\delta(NH_3$, umbrella)	1170		115	
HCl−CH_3OH−H_2O-1a	ν(HCl)	2113	2044.4	−910	47.9
	$\nu(OH)_m$	3580	424.3	−262	12.3
	ν(CO)	1044	79.1	0	0.7
	$\nu_{as}(OH)_w$	3896	133.3	−32	2.0
	$\nu_s(OH)_w$	3733	100.8	−70	24.6
	δ(HOH)	1625	79.6	3	1.2
HCl−CH_3OH−H_2O-1b	ν(HCl)	2472	1167.5	−551	27.3
	$\nu(OH)_m$	3767	102.8	−75	3.0
	ν(CO)	1034	79.7	−10	0.7
	$\nu_{as}(OH)_w$	3873	105.6	−55	1.6
	$\nu_s(OH)_w$	3510	480.8	−293	117.3
	δ(HOH)	1644	30.6	22	0.5
HCl−CH_3OH−H_2O-1c	ν(HCl)	2673	1031.2	−350	24.1
	$\nu(OH)_m$	3808	63.8	−34	1.9
	ν(CO)	1005	97.1	−39	0.9
	$\nu_{as}(OH)_w$	3905	130.8	−23	1.9
	$\nu_s(OH)_w$	3725	176.3	−78	43.0
	δ(HOH)	1635	52.6	13	0.8
HCl−CH_3OH−NH_3-1a	$\nu(OH)_m$	3472	775.7	−370	22.5
	ν(CO)	1055	111.7	11	0.9
	ν_{as}(free NH)	3633	62.5		
	ν_s(free NH)	3547	137.7		
	ν(bonded NH)	3240	347.0		
	ν(bonded NH)	1904	2175.5		
	$\delta(NH_2)$	1680	13.0		
	$\delta(NH_2)$	1642	537.6		
	$\delta(NH_3$, umbrella)	1221	92.4		
HCl−CH_3OH−NH_3-1b	ν(HCl)	2035	2035.7	−988	47.6
	$\nu(OH)_m$	3282	993.0	−560	28.8
	ν(CO)	1020	90.6	−24	0.8
	ν_{as}(free, NH)	3629	15.5	−6	3.1
	$\nu_{as}(NH_3)$	3605	32.2	−30	32.2
	$\nu_s(NH_3)$	3463	14.7	−17	3.1
	$\delta(NH_3)$	1652	9.9	4	0.7
	$\delta(NH_3)$	1642	14.8	−6	1.1
	$\delta(NH_3$, umbrella)	1139	152.8	94	1.1
HCl−CH_3OHNH_3-1c	ν(HCl)	2435	1531.8	−588	35.8
	$\nu(OH)_m$	3816	54.6	−26	1.6
	ν(CO)	1010	101.3	−34	0.9
	ν_{as}(free, NH)	3627	5.7	−8	3.1
	ν_{as}(bonded, NH)	3614	35.5	−21	7.1
	$\nu_s(NH_3)$	3466	16.3	−14	3.5
	$\delta(NH_3)$	1655	7.1	7	0.5
	$\delta(NH_3)$	1647	8.1	−1	1.6
	$\delta(NH_3$, umbrella)	1096	126.0	51	0.9

[a] Ref 6. [b] Ref 29. [c] Ref 4. [d] Ref 5.

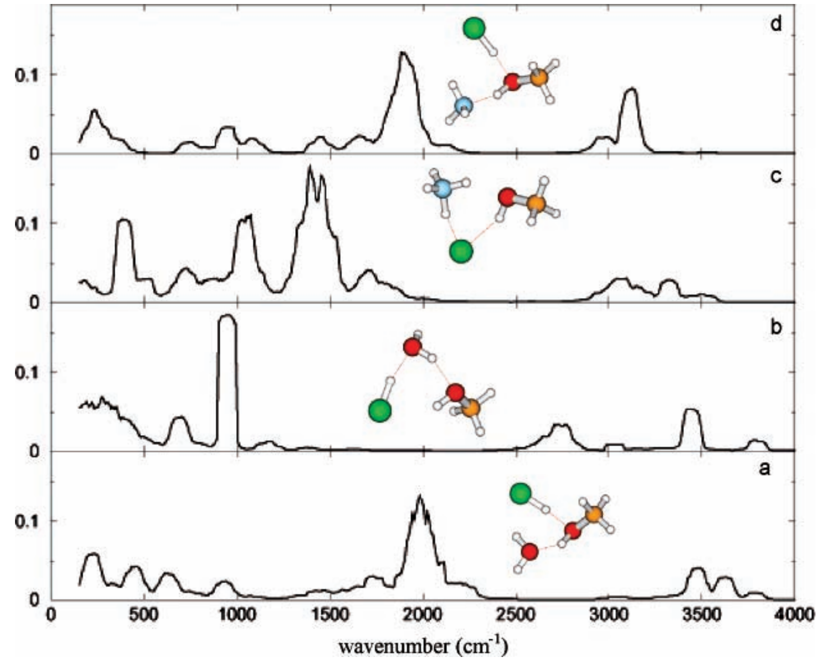

Figure 3. Calculated spectra from on-the-fly MD simulated trajectories of (a) HCl−CH_3OH−H_2O-1a, (b) HCl−CH_3OH−H_2O-1b, (c) HCl−CH_3-OH−NH_3-2a, and (d) HCl−CH_3OH−NH_3-2b. The same relative intensity units are used in all calculations. The inserted structures are also shown in Figures 1a,b and 2a,b.

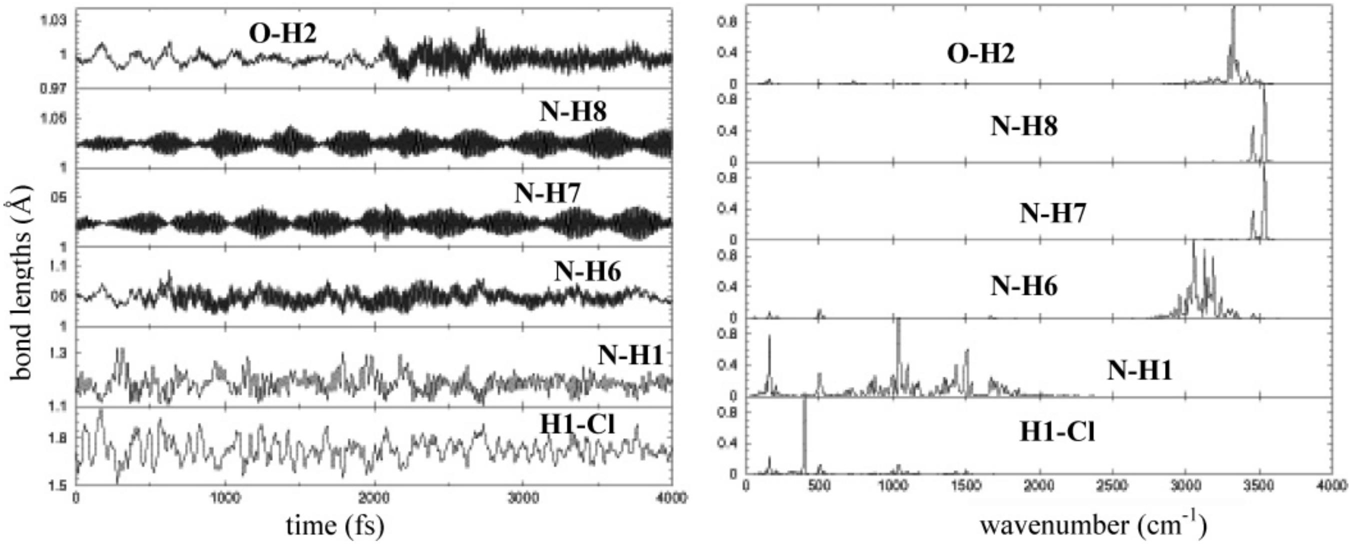

Figure 4. The time evolution of HCl, NH, and OH bond lengths (left) and the corresponding frequencies from Fourier transformation of the bond lengths for the ternary complex of HCl−CH_3OH−NH_3-2a (right) during a 4 ps run at an average temperature of 80 K. The atom labels are shown in Figure 2a.

dipole correlation function for each ternary complex subjected to on-the-fly MD calculations are shown in Figure 3 and will be discussed in detail in the following sections.

Ternary Complex of HCl−CH_3OH−H_2O-1a. The QUICKSTEP-optimized structure has a similar structure as that shown in Figure 1a. The trajectory calculation was run for 4 ps at an average temperature of 99 K. During the trajectory run, the average HCl bond length was 1.368 Å with a standard deviation (SD) of 0.154 (the MP2/aug-cc-pvDZ level gave 1.356 Å). The average O−H bond length of methanol was 0.988 Å (SD = 0.100) as compared to 0.980 Å calculated at the MP2 level. The average O−H bond length of water, which has a coordination to the Cl atom, was 0.981 Å (SD = 0.093), and the free O−H one was 0.975 Å (SD = 0.084). The Fourier transform of the HCl bond trajectory gave a peak at around 1995 cm^{-1} (which is calculated as 2113 cm^{-1} at the MP2/aug-cc-pvDZ level). The frequencies calculated from the Fourier transform of the O−H bond trajectories are 3485 cm^{-1} for methanol and 3625 cm^{-1} for the bonded OH of H_2O and 3790 cm^{-1} for the free OH of H_2O. A similar trend was found for OH stretch frequencies with MP2 level calculations (see Table 4)

Ternary Complex of HCl−CH_3OH−H_2O-1b. The QUICKSTEP-optimized structure has a similar structure as that shown in Figure 1b. The trajectory was run for 4 ps at an average temperature of 99 K. The calculated spectrum from the dipole−dipole correlation function is also given in Figure 3b. During the trajectory run, the average HCl bond length was 1.306 Å (SD = 0.117), and the corresponding HCl stretch frequency calculated from the Fourier transform of the bond length was 2760 cm^{-1}. The OH bond distances were 0.990 Å (SD = 0.076) for bonded OH of H_2O, 0.973 Å (SD = 0.083) for free OH of H_2O, and 0.974 Å (SD = 0.056) for methanol. The corresponding frequencies calculated from the Fourier transform of the O−H bond trajectories are 3445, 3796 and 3747 cm^{-1}, respectively.

Ternary Complex of HCl−CH_3OH−NH_3-2a. The optimized structure is similar to the one shown in Figure 2a. The trajectory was run for 4 ps at an average temperature of 80 K. The calculated spectrum from the dipole−dipole correlation function is also given in Figure 3c, and the time evolution of the H−Cl, N−H, and O−H bond lengths and the corresponding frequencies from their Fourier transforms are given in Figure 4. It is seen that the acid proton undergoes large amplitude fluctuations between Cl and N. During the MD run, the average N−H distance (connected to Cl) was 1.186 Å (SD = 0.185), and the H−Cl distance was 1.726 Å (SD = 0.265). The other N−H bond length connected to the methanol oxygen was 1.048 Å (SD = 0.105), and the free N−H bond lengths were around 1.024 Å (SD = 0.081). It seems that these results correspond to proton sharing between Cl and N rather than proton transfer to N. Reflection of proton sharing can also be seen from the calculated spectra (shown in Figure 3c) as an underlying continua which is a characteristic of proton-sharing systems.[41] The transient proton-sharing species had short lifetimes of <0.1 ps. A similar conclusion was reached by Asada et al.[9] by computing the quantum effect of the proton motion of the NH_3−HCl−H_2O ternary complex, which has a similar structure to the one shown in Figure 2a. Because of the quantum delocalization of the proton, the ionic isomer is weakened.

Ternary Complex of HCl−CH_3OH−NH_3-2b. The optimized structure is shown in Figure 2b. The trajectory was run for 4 ps at an average temperature of 80 K. The calculated spectrum from the dipole−dipole correlation function is also given in Figure 3d. During the MD run, the average N−H distance (connected to Cl) was 1.024 Å (SD = 0.061), the free N−H bond length was 1.024 Å (SD = 0.067), the H−Cl bond length was around 1.376 Å (SD = 0.125), and the average methanol O−H bond length was 1.007 Å (SD = 0.081). The Fourier transform of bond lengths gives the following: 1890 cm^{-1} for the HCl stretch, 3110 cm^{-1} for the OH stretch of methanol, and the 3410 and 3530 cm^{-1} doublet for the N−H stretch, which is not observed in the spectrum calculated from the dipole−dipole correlation function shown in Figure 1d.

4. Conclusions

Structure, energetics, dynamics, and spectra of the HCl−CH_3OH−X, X = H_2O or NH_3, ternary complexes have been investigated in terms of the nonadditivity effect with MP2/aug-cc-pvDZ level calculations by ab initio and on-the-fly molecular dynamics at low temperatures. Our results can be summarized as follows:

1. Investigation of the intermolecular potential energy surface of ternary complexes shows three minima on the IPES for the HCl−CH_3OH−H_2O (Figure 1a,b,c) and HCl−CH_3OH−NH_3 (Figure 2a,b,c) complexes. The global minima (Figures 1a and 2a) correspond to cyclic structures, in which the methanol molecule is the donor and acceptor of the hydrogen bond, respectively. Among all isomers of each ternary complex, only one isomer gave ionized HCl, Cl^-−CH_3OH−NH_4^+, as shown in Figure 2a.

2. The characteristics of the complexes, such as bond lengths, interaction energies, and a red shift of the O−H or HCl stretch frequencies, depend not only on the nature of the monomer subunit but also on the donor or acceptor role played by these monomers. In particular, for trimers where methanol is the donor (i.e., 1a, 1b, 2b), the interaction energy and the nonadditive three-body effect are very close in the case of both types of trimers.

3. Supermolecular calculations of the three-body energies show that the structure and properties of the trimers could not be accurately described by assuming pairwise additivity. The three-body term is representing as much as ∼20% of the total MP2 interaction energy of the cyclic 1a, 1b, 2b trimers. A sizable part of this effect contributes to the reinforcement of hydrogen bonds in cyclic structures.

4. Furthermore, the two isomers of each ternary complex were also subjected to on-the-fly MD simulations at low temperatures. Among the four ternary complexes shown in Figures 1a,b and 2a,b, only the trimer shown in Figure 2a gave the ionized form of HCl. However, the dynamics of this system showed the proton sharing of hydrogen between Cl and N.

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