4-1-1999

Hydrogen bonding and cooperative effects in mixed dimers and trimers of methanol and trifluoromethanol: An *ab initio* study

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Hydrogen bonding and cooperative effects in mixed dimers and trimers of methanol and trifluoromethanol: An *ab initio* study

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Ab initio calculations are used to provide information on the mixed dimers and cyclic trimers of the methanol-trifluoromethanol system. In order to better understand the systems, the monomers and their corresponding dimers and trimers are also investigated. Molecular structures and harmonic frequencies are obtained at the B3LYP/6-311++G(d,p) level. Interaction energies are calculated with the MP2 and B3LYP methods using the 6-311++G(d,p), 6-311++G($2d,2p$), and 6-311++G($3d,2p$) basis sets for the dimers and heterodimers. The 6-311++G(d,p) basis set was used to calculate the interaction energies for the trimers and heterotrimers. Because the primary goal of this study is to examine cooperative effects, particular attention is given to parameters such as O...O distances, electronic charge densities at the bond critical points, enhanced dipole moments, shifts in the stretching frequencies of the donor O–H bond, and the length of the donor O–H bond. © *1999 American Institute of Physics.* [S0021-9606(99)30613-9]

I. INTRODUCTION

Hydrogen bonding plays a significant role in a wide range of chemical and biological processes.[1,2] The hydrogen bond (HB) is typically defined as an attractive interaction between a proton donor D–H and a proton acceptor A in the same or in a different molecule,

D–H...A,

where D and A are normally electronegative atoms such as N, O, or F. The magnitude of the interaction ranges between 2 and 20 kcal/mol. An important structural characteristic of a hydrogen bond is a shortening of the D...A distance along with a stretching of the D–H bond. The amount of these geometrical changes is usually correlated with the strength of the interaction.

A very relevant concept associated with hydrogen bonding is cooperativity, considered as the enhancement of a HB by the formation of another HB with either the donor or acceptor of the first HB.[3] Cooperativity is frequently applied in theoretical work and for the interpretation of experimental data.[4] It helps explain the behavior of hydrogen bonded systems.

Alcohols possess the ability to form clusters (self-association) in the liquid phase via hydrogen bonding.[5] Theoretical calculations have been supportive of this picture.[6–16] Of particular interest are the recent studies of the structural and energetic properties of hydrogen-bonded water,[7,8] methanol,[9–14] and water–methanol complexes.[15,16] It has been found that the dimers have linear hydrogen-bonded structures, while the results for higher oligomers are consistent with cyclic structures. Less attention has been paid to the hydrogen-bonded complexes of perfluoroalcohols.[17–23]

CF$_3$OH is the simplest perfluoroalcohol that can be studied by *ab initio* methods. In addition, it plays an important role in the atmospheric degradation of CF$_3$CFH$_2$ (HFC-134a)

and other hydrofluorocarbons, and is therefore a compound that requires some attention.[24–27] Our group has recently studied cooperativity effects in cyclic trifluoromethanol trimer at the Hartree–Fock (HF) level and different basis sets.[23] In contrast to the linear structure of the methanol dimer, we found that the analogous dimer of CF$_3$OH involves a secondary hydrogen bond between one of the fluorine atoms of the donor and the hydrogen atom of the acceptor molecule.

From a fundamental standpoint, it appears interesting to study the nature of alcohol–perfluoroalcohol interactions since such study can contribute to the current understanding of the proton-donor (acid) and proton-acceptor (base) character of alcohols and perfluoroalcohols. It is well known that methanol behaves like a bifunctional molecule since it can behave both as a proton donor and as a proton acceptor simultaneously.[9–14] On the other hand, the proton-acceptor character of CF$_3$OH is very weak because the CF$_3$ group removes electron density from the OH group, so that the extent of self-association is expected to be relatively small; however, the increased acidic property of trifluoromethanol makes it an excellent candidate as a proton donor in the studies of hydrogen-bonded systems.

The purpose of this work is to investigate the hydrogen-bonding interactions and cooperativity in the dimers and trimers as well as in the mixed dimers and trimers of methanol and trifluoromethanol molecules.

As an aid in referring to the various structures studied, the following shorthand notation will be used. For the methanol and trifluoromethanol monomers we will use the symbols M and T, respectively. For the dimers and trimers we will use the notation T_n and M_n, $n=2,3$. For the mixed dimers we have two possibilities, TM and MT. In each case, the first symbol corresponds to the donor, while the second to the acceptor moiety. For the mixed trimers, T_2M represents a cyclic trimer with two CF$_3$OH units and one CH$_3$OH unit,

whereas M_2T stands for a cyclic trimer with two CH_3OH molecules and one CF_3OH molecule.

II. COMPUTATIONAL DETAILS

All *ab initio* density functional results were calculated using the GAUSSIAN 94 program.[28] The MP2 calculations were carried out with the GAUSSIAN 98 program.[29] We used the Becke3LYP nonlocal exchange correlation functional,[30] which has been extensively used in studies of hydrogen-bonded clusters and tested against MP2, MP4, and G2 *ab initio* calculations.[13,14,31–38] See for instance Novoa and Sosa.[36] These authors found that the B3LYP functional predicts hydrogen-bonding geometries that are in very good agreement with MP2 geometries. See also the very relevant paper of Hagemeister *et al.*[14] and that of Mó *et al.*[13] These researchers have used the B3LYP functional to study methanol clusters. In particular Mó *et al.* have found that the B3LYP/6-311+G(d,p) optimized geometries are not significantly different from the MP2 optimized geometries.

However, Novoa and Sosa[36] have shown that density functional theory (DFT) is not a good model for the study of the energetics of hydrogen-bonded complexes. To illustrate this, one can look at the interaction energies for the H_2O-H_2O, NH_3-NH_3, and $C_2H_2-H_2O$ systems in the work by Novoa and Sosa.[36] The counterpoise corrected interaction energies were calculated by the authors using the different basis sets cc-pVDZ, 6-31++G($2d,2p$), aug-cc-pVTZ at the HF, MP2, and B3LYP levels. These energies can be used to determine the correlation contribution from the MP2 and the B3LYP models. For the dimer of water, it is found that the B3LYP model estimates a correlation contribution which is nearly independent of the basis set. For the NH_3 dimer, the B3LYP model underestimates the correlation contribution by more than a factor of 2. For the $C_2H_2-H_2O$ system the situation is even worse.

In this work, the interaction energies are calculated at the MP2/6-311++G(d,p) level for the trimers and mixed trimers of methanol and trifluoromethanol. For the dimers and mixed dimers, the interaction energies are calculated with the MP2 and the B3LYP models using the 6-311++G(d,p), 6-311++G($2d,2p$), and 6-311++G($3d,2p$) basis sets. We investigate whether our results of the DFT-B3LYP model with respect to the correlation contribution to the interaction energies parallel those of Novoa and Sosa.[36]

The geometries of the different systems under investigation were optimized at the B3LYP/6-311++G(d,p) level. The so optimized geometries were used to obtain the harmonic vibrational frequencies at the same level of theory. These harmonic frequencies were scaled by an empirical factor of 0.98[39] and the scaled frequencies were used to evaluate zero-point energy (ZPE) and thermal corrections to the interaction energies. It has been shown that a very good correlation exists between the charge density at the HB critical point and the strength of the interaction.[8,12,13,23] For this purpose the charge densities at the bond critical points for all systems were located at the HF/6-311++G(d,p) level of theory.[40]

Total interaction energies for the various clusters are calculated as

$$\Delta E = E(\text{cluster}) - \Sigma E_i, \qquad (1)$$

where the sum runs over all the monomers in the cluster. All interaction energies have been corrected for basis-set superposition error (BSSE) using the full counterpoise procedure.[41] The negative of the interaction energy gives the dissociation energy D_e. D_0 would refer to the this quantity, after correction for zero-point energies. The enthalpy of formation of a given cluster is equal to ΔE with a ΔPV correction (assuming ideal gas behavior).

Finally, the cooperative effects themselves will be highlighted using several different indications. In order to quantitatively determine the cooperativity factor, the same method will be used as Mó *et al.* highlighted in previous work.[12] It is defined as the relative shifts in the frequency of the donor O–H stretching mode:

$$A_b = \Delta \nu_{OH} / \Delta \nu_{OH'}, \qquad (2)$$

where the $\Delta \nu_{OH'}$ and $\Delta \nu_{OH}$ represent the variation of the stretching frequency in the dimer and trimer with respect to the monomer, respectively.

It is important to point out that Mó *et al.*[13] have carried out large basis set Hartree–Fock, MP2, and DFT/B3LYP calculations on the dimer and cylcic trimer of methanol. In particular, geometry optimizations and frequency calculations at the B3LYP/6-311+G(d,p) level and interaction energies at the B3LYP/6-311++G($3df,2p$) for the $(CH_3OH)_2$ and $(CH_3OH)_3$ were performed by these authors.

III. RESULTS AND DISCUSSION

A. Geometries

The hydrogen bonded optimized structures for the different dimers and trimers studied in this work are shown in Figs. 1(A)–1(D) and 2(A)–2(D), respectively. The structural parameters for the methanol and trifluoromethanol monomers along with their corresponding changes upon complexation are summarized in Table I. Some relevant intermolecular parameters for the complexes are given in Table II.

1. Intramolecular geometry

The internal structure of each subunit is altered upon complexation. The extent of the structural change is an indication of the donor–acceptor behavior of the monomers in the complexes. This behavior may be traced to changes in the O–H and C–O bond lengths. An increase of the O–H distance concomitant with a decrease in the C–O distance would indicate a donor character whereas a lengthening of the C–O bond would reflect an acceptor behavior.

Dimerization produces a noticeable increase in the length of the acceptor C–O bond, while decreasing the donor C–O bond. The magnitude of these changes for both donor and acceptor follows the order $TM>T_2>M_2>MT$. This sequence indicates that the donor character of trifluoromethanol and the acceptor character of methanol are enhanced in the TM system relative to their corresponding dimers. This observation is supported also by the sequence of the donor
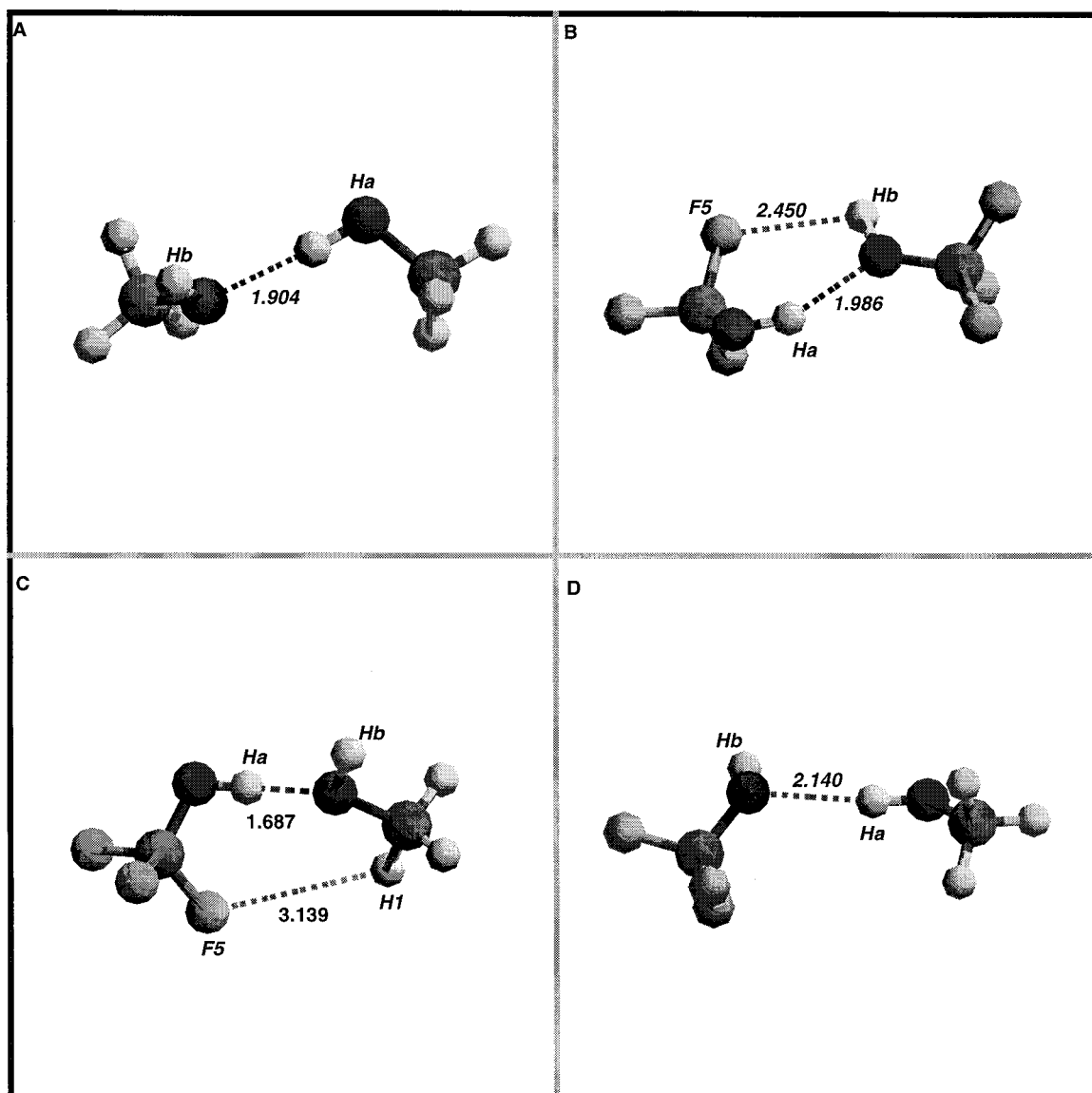
FIG. 1. B3LYP/6-311++G(d,p) optimized structures of dimers and mixed dimers of methanol and trifluoromethanol: (A) methanol dimer; (B) trifluoromethanol dimer; (C) mixed dimer with trifluromethanol as donor; (D) mixed dimer with methanol as donor.

O–H elongation, i.e., TM>M_2≈T_2>MT. It is seen also that the poor acceptor behavior of CF_3OH is more pronounced in the MT complex.

The donor O–H bonds are significantly lengthened upon trimerization. In fact, cooperative effects may be quantified by these Δr values. A comparison of Δr between the methanol and trifluoromethanol trimers shows larger cooperativity for methanol (see Table V). Regarding the mixed trimers, we notice that the O–H bond in the methanol moiety that is acting as H donor to CF_3OH in both T_2M and M_2T is slightly increased. This is consistent with the already mentioned poor acceptor nature of CF_3OH. However, the increase of the O–H bond of the methanol that is H donor to methanol in M_2T is comparable to that in methanol trimer. With respect to the CF_3OH unit, we see that the O–H bond elongation is very large. In fact, the largest O–H bond lengthening is found in the M_2T system (0.041 Å) followed by the T_2M trimer (0.038 Å) where methanol is the acceptor molecule.

For the case in which the acceptor molecule is CF_3OH (T_2M), we also notice an increase of the O–H bond which is comparable to that in the T_3 system.

2. Intermolecular structural parameters

Among the key features of a hydrogen bond are the typically short O...O distance and the near linearity of the O–H...O arrangement. We find that in the dimers the O...H and the O...O intermolecular distances follow the order TM<M_2<T_2<MT, while for the O–H...O angle the order is TM>M_2>MT>T_2 (Table I). It is also apparent when looking at Fig. 1 that a long-range electrostatic interaction is taking place in TM between one of the fluorine atoms of the donor and the hydrogen atom *trans* to the OH group in the acceptor molecule.

It is worth mentioning that the dimer of CF_3OH has some significant differences compared to methanol. The
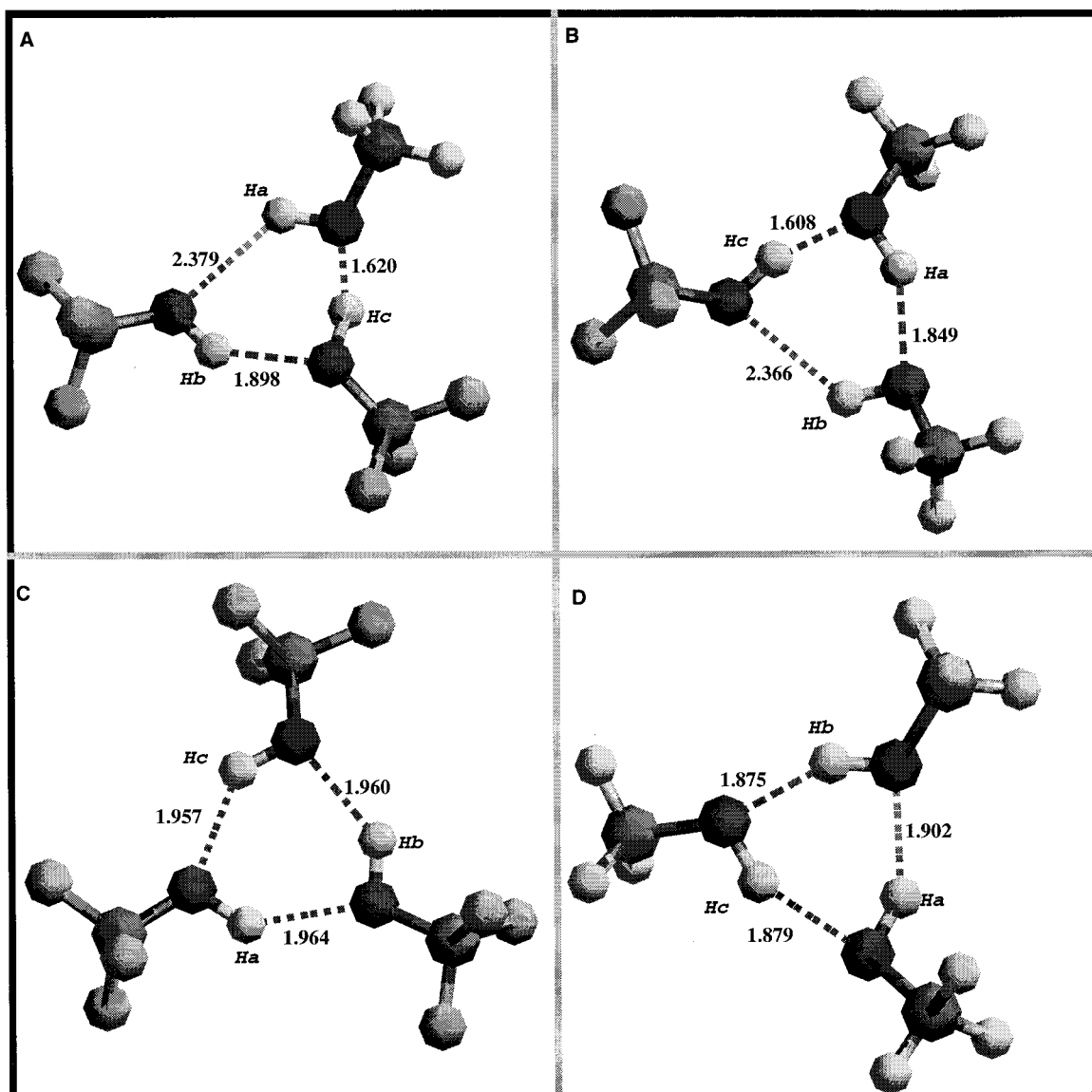
FIG. 2. B3LYP/6-311++G(d,p) optimized structures of trimers and mixed trimers of methanol and trifluoromethanol: (A) mixed trimer with two molecules of trifluromethanol and one molecule of methanol; (B) mixed trimer with two molecules of methanol and one molecule of trifluoromethanol; (C) trimer of trifluromethanol; (D) trimer of methanol.

most striking feature is the deviation in linearity of the hydrogen bond (see Table I). Trifluoromethanol has a hydrogen-bond angle of 152°, while the hydrogen-bond angle of methanol is 176°. In addition, the hydrogen atom of the acceptor points preferably toward one of the fluorine atoms of the donor group. In fact, the distance between these two atoms is 2.450 Å [Fig. 1(B)]. The corresponding C–F distance in the donor is lengthened by 0.019 Å and the acceptor O–H distance is lengthened by 0.003 Å. These geometrical features suggest the existence of a secondary hydrogen bond between a fluorine atom in the donor monomer and the OH group of the acceptor.[23] This secondary hydrogen bond helps to overcome the poor acceptor ability of CF_3OH.

Trimerization produces a noticeable reduction of the O...O distances. Similar results are found for the O...H distances, although in the T_2M and M_2T clusters the O...H distance is actually lengthened for the M(donor)–T(acceptor) arrangement. Nevertheless the shortest O...H and O...O dis-

tances are found in the heterotrimers for the T(donor)–M(acceptor) arrangement.

We observe that the three hydrogen bonds in T_3 are practically equivalent as reflected by the similar bond lengths (≈ 1.960 Å) and the charge density at the corresponding critical points (see Table III). In contrast, the three hydrogen bonds in the other trimers are not strictly equivalent, but two are much stronger than the third one. Moreover, one of the hydrogen bonds in T_2M and M_2T is significantly stronger than the other two. This is seen in the shorter bond length and a greater charge density at the corresponding critical points. A common feature for all trimers is the position of the methyl (trifluoromethyl) groups with respect to the O–O–O plane. We see that in all cases two groups are on the same side of the O–O–O plane, while the third one is found with an approximate *trans* conformation with respect to the other two. For methanol, this result is coherent with recent experimental studies.[42]

TABLE I. Structural parameters for the methanol and trifluoromethanol monomers and their corresponding changes upon complexation.[a]

	Methanol unit					
	C–O	O–H	C–H	C–H	C–H	H–O–C
M	1.424	0.961	1.097	1.097	1.090	108.8
M_2	−0.006	0.008	0.002	0.002	0.002	0.1
	0.008	0.001	−0.002	−0.002	−0.001	0.5
M_3	−0.001	0.014	0.000	−0.001	0.001	1.3
	0.000	0.015	−0.001	−0.001	0.001	1.1
	−0.001	0.015	0.000	−0.001	0.001	1.3
TM	0.012	0.001	−0.003	−0.004	−0.001	1.6
MT	−0.001	0.001	0.000	0.000	0.000	0.1
T_2M	0.013	0.005	−0.004	−0.004	−0.001	1.7
M_2T	0.007	0.016	−0.002	−0.003	0.000	2.1
	0.007	0.005	−0.002	−0.003	0.000	0.9

	Trifluoromethanol unit					
	C–O	O–H	C–F	C–F	C–F	H–O–C
T	1.346	0.966	1.354	1.354	1.331	109.5
T_2	−0.011	0.007	0.019	0.000	−0.001	−0.4
	0.011	0.003	−0.008	−0.008	−0.001	1.3
T_3	0.006	0.010	−0.005	−0.008	0.002	2.4
	0.006	0.010	−0.005	−0.007	0.002	2.3
	0.006	0.010	−0.006	−0.007	0.002	2.6
TM	−0.020	0.024	0.012	0.006	0.008	1.2
MT	0.006	0.001	−0.005	−0.005	0.000	1.4
T_2M	−0.008	0.038	0.000	0.000	0.007	−0.1
	−0.004	0.012	0.000	−0.003	0.006	−0.8
M_2T	−0.019	0.041	0.008	0.004	0.012	0.3

[a]In M_2 and T_2 the first row is for donor, second for acceptor; in M_2T and T_2M the first row is for donor to methanol, the second for donor to trifluoromethanol; distance in Å, angles in degrees.

TABLE II. Relevant intermolecular parameters. Distance is in Å, angles in degrees.[a]

	M_2	T_2	TM	MT
r_{O--H}	1.904	1.986	1.687	2.140
r_{O--O}	2.873	2.881	2.677	3.074
A_{O--HO}	176.2	151.7	179.6	163.0
	M_3	T_3	T_2M	M_2T
r_{Ob--Ha}	1.902	1.965	2.379	1.849
r_{Oc--Hb}	1.875	1.959	1.898	2.366
r_{Oa--Hc}	1.879	1.958	1.619	1.608
r_{Oa--Ob}	2.779	2.759	3.012	2.733
r_{Ob--Oc}	2.769	2.760	2.737	3.070
r_{Oc--Oa}	2.769	2.763	2.594	2.588
A_{O--HaO}	148.2	136.9	122.6	149.1
A_{O--HbO}	150.9	137.6	142.2	129.3
A_{O--HcO}	150.3	138.2	162.4	163.0
$A_{COa--Hc}$	133.3	140.6	126.1	124.1
$A_{COb--Ha}$	136.2	143.3	150.1	131.5
$A_{COc--Hb}$	128.8	139.7	136.3	134.8
$\tau_{CaOcObOa}$	14.0	6.0	13.8	17.8
$\tau_{CcObOaOc}$	−16.5	−7.4	−12.5	−14.2
$\tau_{CbOaOcOb}$	13.5	3.8	5.0	−12.7

[a]See Figs. 1 and 2 for labeling convention.

A structure where the three methyl groups lie in the O–O–O plane in the methanol trimer was found to be a saddle point of third order by Mó *et al.*[13] They found this structure to be 1.46 kcal/mol less stable than the global

TABLE III. Charge densities (in e au^{-3}) at the bond critical points (ρ_c) and calculated dipole moment (μ) and dipole moment enhancements ($\Delta\mu$); dipole units in debyes.[a]

	$\rho_{C–O}$	$\rho_{O–H}$	ρ_{HB}	μ	$\Delta\mu$
M	0.249	0.372		1.69	
M_2	0.255	0.359	0.025	3.01	0.82
	0.240	0.370			
M_3	0.251	0.350	0.029	0.75	−0.03
	0.250	0.350	0.030		
	0.251	0.349	0.027		
T	0.329	0.360		2.00	
T_2	0.339	0.349	0.019	1.70	0.27
	0.317	0.354			
T_3	0.321	0.343	0.020	0.05	0.00
	0.321	0.343	0.020		
	0.321	0.343	0.020		
TM	0.344	0.325	0.041	5.22	1.36
	0.234	0.368			
MT	0.249	0.369	0.014	1.00	0.11
	0.323	0.357			
T_2M	0.332	0.307	0.050	4.16	1.31
	0.330	0.341	0.024		
	0.233	0.363	0.009		
M_2T	0.343	0.304	0.052	4.13	1.38
	0.239	0.347	0.029		
	0.240	0.364	0.009		

[a]In the dimers the results are given in the donor–acceptor order; in T_2M they are given in the TM, TT, MT order, while in M_2T the results are given in the TM, MM, MT sequence; densities calculated at the HF/6-311++G(d,p); dipole moments calculated at the B3LYP/6-311++G($3d,2p$).

minimum. A similar result was found for the trimer of trifluoromethanol by Doering *et al.*[23] at the HF/6-311++G($2d,2p$) level. We also investigated the existence of these symmetric trimers. Our results for the methanol trimer are essentially the same as those found by Mó *et al.*[13] Regarding the symmetric trifluoromethanol trimer, we found this structure, using our highest basis set, to be only 0.19 kcal/mol less stable than the nonplanar T_3 system. This result clearly indicates that the potential energy surface associated with the out-of-plane displacements of the CF_3 groups of a trifluoromethanol trimer is very flat, even flatter than that of the corresponding CH_3 groups in the methanol trimer.

B. Charge densities

The observations made on the structural features of the complexes are mirrored in the charge densities shown in Table III. Upon dimerization, ρ_c for C–O increases for the donor and decreases for the acceptor. An increase in ρ_c signals a stronger bond, and thus a shorter bond length. This effect is more pronounced in TM and negligible in MT. Upon trimerization, the charge density for the C–O bond in M_3 and T_3 moves closer to that of the monomer. However, the charge densities for the C–O bond of the methanol moiety in T_2M and M_2T are even smaller than those of the corresponding donor in the dimers and heterodimers.

Charge densities as calculated at the bond critical points are an indication of cooperative effects. One important trend to look for is the decrease of ρ_c for the donor O–H bond

upon dimerization and trimerization. Because charge density is an indication of bond strength, this decrease implies that the O–H bond is being slightly weakened. The weakening of this bond is due to the favorable hydrogen bonding. Cooperativity lowers the charge density even more, which is why ρ_c is lower in the trimer than in the dimer for the O–H bond. Another indication of cooperativity is seen in the strengthening of the hydrogen bond in the trimer as opposed to the dimer. This is observed as an increase in ρ_c at the hydrogen bond upon trimerization. These cooperative effects are more significant in the heterotrimers.

C. Dipole moment enhancement

The formation of a first hydrogen bond in a dimer will distort the charge distribution of each monomer. This polarization leads to a dipole moment in the dimer that is larger than the vector sum of the individual monomers. This enhanced dipole moment is an expression of the cooperative nature of hydrogen bonds. To investigate this property, we have evaluated the variation of the dipole moment upon dimerization and trimerization as the difference between the dipole moment of the corresponding cluster and that obtained by vector sum of the individual dipole moments. To calculate the dipole moment of each subunit, the complete set of basis functions of the clusters was used and the geometry of each monomer was frozen in that of the optimized cluster. The results so obtained are listed in Table III. We see that dimerization is accompanied by a significant enhancement of the dipole moment. The magnitude of this enhancement parallels the strength of the hydrogen bond in the clusters, TM$>$M$_2$$>T_2$$>$MT. For the M$_3$ and T$_3$ clusters there is no dipole enhancement, due to the fact that these trimers have a cyclic structure. However, the T$_2$M and M$_2$T systems show a significant dipole enlargement (M$_2$T$>$T$_2$M) because these trimers are formed with different monomers and the cyclic structure does not necessarily counteract the possible enhancements on each molecule.

D. Vibrational frequencies

The optimized geometries of the clusters were used to calculate the normal mode frequencies within the harmonic oscillator approximation. The results are listed in Table IV. The shifts of some vibrational modes upon complexation are displayed in Table V. As one would expect, there is a sizable redshift in the stretching mode of the donor O–H bond upon formation of a dimer. The calculated redshifts for M$_2$ and T$_2$ are 158 and 124 cm^{-1}, respectively, while those for TM and MT are 478 and 22 cm^{-1}, respectively. It can be seen that the acceptor O–H stretching frequency in T$_2$ also undergoes a notable redshift of 35 cm^{-1}. This is a result of the secondary hydrogen bond found in this dimer.

Another mode of vibration that is affected is the C–O stretching mode. Table V shows that upon dimerization the donor C–O frequencies M$_2$ and T$_2$ are blueshifted by 21 and 29 cm^{-1}, respectively. Similarly, the donor C–O stretching mode in TM is blueshifted by 47 cm^{-1}, this is 18 cm^{-1} more than in T$_2$. The donor C–O mode in MT is blueshifted by 7 cm^{-1}, this is 14 cm^{-1} less than in M$_2$.

Dimerization also has strong effects upon the donor O–H torsion and bending modes; both modes are blueshifted by significant amounts. The torsion frequencies of the donor are blueshifted by 403 and 288 cm^{-1} for M$_2$ and T$_2$, respectively. The corresponding blue shift in TM is 581 cm^{-1}, which is significantly larger (more than 290 cm^{-1}) than that in T$_2$; however, the calculated blueshift of the torsion mode in MT is 281 cm^{-1} less than that in M$_2$. The donor O–H bending modes are shifted to higher frequencies by 62 and 40 cm^{-1} for M$_2$ and T$_2$, respectively. The corresponding frequency shifts in TM and MT are 68 and 36 cm^{-1}. In all cases, the shifts of the O–H group not involved in the hydrogen bond are considerably smaller.

Many of the same qualitative trends seen upon dimerization are also noted upon trimerization. The O–H stretching frequencies are affected by trimerization even more than dimerization. The redshift ranges from 233 to 299 cm^{-1} for M$_3$ and from 160 to 200 cm^{-1} for T$_3$. This increase in the redshift of the donor O–H stretch is one method of determining that cooperative effects are present. In fact, this frequency variation is actually used to quantify the cooperativity factor as seen in Eq. (2). The effect of trimerization also increases the shifts seen in the C–O stretching frequencies. Two of the C–O stretches in T$_3$ are redshifted by 36 cm^{-1}, while the other is blueshifted by 48 cm^{-1}. All three C–O stretches in M$_3$ are shifted to the blue.

It is worth mentioning that, in general, the shifts of the O–H stretching and torsion frequencies in the mixed trimers are considerably larger than in the trimers and heterodimers. For example, the O–H stretch frequency shift of the CF$_3$OH unit that acts as a H donor to the methanol unit in the T$_2$M cluster is 250 cm^{-1} larger than in TM and more than 3 times larger than in T$_3$.

E. Energetics and cooperativity

The electronic interaction energies (counterpoise corrected) for the B3LYP/6-311++G(d,p) optimized dimers and mixed dimers of methanol and trifluoromethanol were computed with the 6-311++G(d,p), 6-311++G($2d$, $2p$), and 6-311++G($3d,2p$) basis sets at the HF, MP2, and B3LYP levels. The results are shown in Table VI. Also shown in Table VI is the correlation contribution from the MP2 and the B3LYP models. The interaction energies for the optimized trimers and mixed trimers were obtained with the 6-311++G(d,p) at the MP2 level. The dissociation energies and dissociation enthalpies for the various clusters at 0 K and at room temperature are given in Table VII. There is good agreement between the calculated dissociation enthalpies and previous theoretical[13] and experimental[43,44] values.

From Table VI, we observe that the MP2 interaction energies are consistently improved as the size of the basis set is increased. The HF interaction energies calculated with the 6-311++G($2d,2p$) basis set are very similar to those obtained with the 6-311++G($3d,2p$) basis set although they are considerably smaller than those obtained with the 6-311++G(d,p) basis set. This is also the case for the B3LYP model.

We can see also that in each system the correlation contribution from the MP2 model is significantly improved with

TABLE IV. Harmonic vibrational frequencies (cm^{-1}) obtained at the B3LYP/6-311++G(d,p) level.[a]

	τ_{OH}	s_{CO}	b_{OH}	s_{OH}	Other normal modes							
M	298	1042	1356	3846	3112	3036	2989	1505	1494	1480	1168	1070
M$_2$	701	1063	1418	3688	3092	3014	2973	1508	1494	1480	1169	1113
	341	1035	1360	3843	3128	3070	3011	1505	1497	1479	1170	1075
					188	123	106	52	45	24		
M$_3$	645	1052	1408	3547	3104	3044	2994	1510	1496	1477	1172	1115
	742	1054	1418	3600	3106	3046	2996	1510	1497	1477	1172	1124
	815	1068	1465	3613	3106	3050	2999	1513	1497	1486	1173	1157
					210	208	188	176	118	116	107	91
					83	62	42	41				
T	242	1266	1392	3812	1131	1086	884	623	609	593	446	435
T$_2$	530	1295	1432	3688	1131	1101	877	621	608	597	399	433
	321	1248	1386	3777	1162	1068	890	632	613	605	458	445
					123	80	48	33	21	17		
T$_3$	499	1230	1403	3612	1164	1106	890	631	611	603	388	445
	518	1231	1407	3648	1154	1108	890	632	612	604	397	445
	592	1314	1409	3652	1152	1132	896	643	624	630	410	452
					122	121	117	98	41	38	33	30
					29	24	16	12				
TM												
T	826	1313	1460	3334	1125	1095	878	623	611	607	446	423
M	320	1030	1359	3850	3140	3090	3025	1507	1498	1482	1171	1077
					213	120	72	53	35	20		
MT												
M	420	1049	1392	3824	3108	3034	2988	1506	1494	1480	1168	1080
T	292	1254	1380	3796	1149	1106	887	627	612	596	463	443
					104	89	59	30	10	−15		
T$_2$M												
M	478	1030	1375	3795	3139	3095	3026	1507	1498	1492	1174	1092
T	915	1245	1464	3084	1156	1130	888	632	613	607	447	429
T	650	1311	1417	3589	1139	1107	884	627	611	580	445	410
					237	146	124	95	89	69	42	39
					35	25	24	20				
M$_2$T												
M	762	1048	1410	3571	3125	3078	3029	1510	1499	1490	1179	1092
M	481	1039	1385	3786	3124	3074	3014	1509	1497	1478	1172	1110
T	960	1303	1470	3001	1159	1119	879	626	614	610	447	427
					244	215	147	116	110	98	83	66
					47	42	28	18				

[a]τ, s, and b stand for torsional, stretching, and bending modes, respectively.

the basis set size. For instance, the correlation contribution for the TM system using the largest basis set is 2.5 times that obtained with the smallest basis set. However, the correlation contribution from the B3LYP model does not change much with the size of the basis set. The B3LYP model underestimates the correlation contribution in all systems. This is more pronounced in the T$_2$ and MT systems where the correlation contribution is underestimated by more than a factor of 2. These results are consistent with the results of Novoa and Sosa[36] and support their conclusion that the DFT model is not a reliable method to study the energetics of hydrogen-bonded systems.

The strength of the hydrogen-bonding interaction, in the various dimers and mixed dimers, follows the order TM>M$_2$>T$_2$>MT. This order is the same at all levels of theory. It is worth mentioning that the difference in interaction between the different complexes can be found already at the self-consistent field (SCF)-HF level, since its origin is in the electrostatic and induction interaction, which are well

described already at the SCF-HF level, and consequently also in the DFT-B3LYP model.

From Table VIII, we see that the strength of the hydrogen-bonding interaction, in the various trimers and mixed trimers, follows the order M$_2$T>T$_2$M>M$_3$>T$_3$. We observe also that except for T$_3$, the trimerization enthalpies are predicted to be more than that obtained from the constituent dimers. This fact indicates that cooperative effects as seen from considerations of the energetics must be important in the M$_3$, T$_2$M, and M$_2$T complexes. For instance, the dissociation enthalpy of M$_2$T at 0 K exceeds by 1.94 kcal/mol the sum of the corresponding enthalpies of the TM, MT, and M$_2$ dimers at the MP2/6-311++G(d,p). The cooperativity increases further at room temperature. The presence of a secondary hydrogen bond in the trifluoromethanol dimer is mainly responsible for the negative cooperativity observed in T$_3$.

A different way of measuring cooperative effects is through the computation of the three-body interaction en-

TABLE V. Cooperativity parameters. O--O distances, R_{00} (Å); elongation of the O–H bonds, Δr (Å); shifts of the C–O stretching and of the O–H stretching, bending, and torsional modes, $\Delta \nu (\text{cm}^{-1})$; and cooperativity factors, A_b.

	R_{00}	Δr	$\Delta \nu(\text{OH}_s)$	$\Delta \nu(\text{OH}_\tau)$	$\Delta \nu(\text{OH}_b)$	$\Delta \nu(\text{CO}_s)$	A_b
M_2	2.873	0.008	−158	403	62	21	
			−3	43	4	−7	
M_3	2.769	0.014	−299	517	109	16	1.9
	2.769	0.015	−246	444	62	12	1.6
	2.779	0.015	−233	347	52	10	1.5
T_2	2.881	0.007	−124	288	40	29	
			−35	79	−6	−18	
T_3	2.759	0.010	−200	350	17	48	1.6
	2.760	0.010	−164	276	15	−36	1.3
	2.763	0.010	−160	257	11	−35	1.3
TM	2.677	0.024	−478	581	68	47	
			4	22	3	−12	
MT	3.074	0.001	−22	122	36	7	
			−16	50	−12	−12	
T_2M[a]	3.012	0.005	−51	180	19	−12	2.3
	2.595	0.038	−728	673	72	−21	1.5
	2.737	0.012	−223	408	25	45	1.8
M_2T[b]	2.733	0.016	−275	464	44	6	1.7
	3.070	0.005	−60	183	29	−3	2.7
	2.588	0.041	−811	718	78	47	1.7

[a]Data given in the MT, TM, TT sequence.
[b]Data given in the MM, MT, TM sequence.

ergy, ΔE_3. This quantity is defined as the difference between the total interaction energy of the trimer, and the sum of the interaction energies of the different dimers we can find within the trimer, all computed as ΔE_{elec}. It is important to note that the three-body term is evaluated with the geometry of all species frozen in that of the optimized trimer, so the effects of any geometry distortion are present here too.

The resulting quantities for the various trimers are reported in Table VII. It is immediately clear that the formation of the trimers implies a significant net energy gain in all

cases, including T_3. We found that the average interaction energy of the different dimers of trifluoromethanol within the trimer is 3.36 kcal/mol. This gives an upper estimate of 1.40 kcal/mol for the secondary hydrogen bond present in the fully optimized dimer.

F. Basis set superposition error

The basis set superposition error (BSSE) on the interaction energies has been estimated for all the optimized com-

TABLE VI. Electronic interaction energies (kcal/mol) for the dimers and heterodimers at the HF, MP2, and B3LYP levels and different basis sets.

	M_2			T_2		
	HF	MP2	B3LYP	HF	MP2	B3LYP
6-311++G(d,p)	−4.19	−5.04	−5.16	−3.77	−4.76	−4.50
6-311++G($2d,2p$)	−3.74	−5.20	−4.74	−3.18	−4.83	−3.96
6-311++G($3d,2p$)	−3.77	−5.34	−4.78	−3.21	−5.04	−4.04

	TM			MT		
	HF	MP2	B3LYP	HF	MP2	B3LYP
6-311++G(d,p)	−9.76	−10.45	−10.77	−1.32	−2.08	−1.82
6-311++G($2d,2p$)	−8.90	−10.46	−10.01	−1.04	−2.16	−1.61
6-311++G($3d,2p$)	−8.92	−10.64	−10.01	−1.06	−2.27	−1.60

	Correlation contribution							
	M_2		T_2		TM		MT	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
6-311++G(d,p)	−0.85	−1.03	−1.01	−0.73	−0.69	−1.01	−0.76	−0.50
6-311++G($2d,2p$)	−1.46	−1.00	−1.65	−0.78	−1.56	−1.11	−1.14	−0.57
6-311++G($3d,2p$)	−1.57	−1.01	−1.83	−0.83	−1.72	−1.09	−1.21	−0.54

TABLE VII. Dissociation energies (D_e), dissociation enthalpies at 0 K (D_0) and at 298 K ($-DH_{298}$); cooperativity and three-body effects. All values are in kcal/mol.[a]

	Previous work					Cooperativity			
	D_e	D_0	$-\Delta H_{298}$	Theory	Expt	D_e	D_0	$-\Delta H_{298}$	$-\Delta E_3$
M_2T	18.94	16.16	15.92			1.40	1.94	2.50	2.34
T_2M	17.05	14.82	14.25			−0.24	0.37	0.65	1.95
T_3	11.57	9.80	8.86	8.1[b]		−2.71	−1.93	−1.31	1.56
M_3	15.34	11.84	12.27	11.52[c]	12.5[d]	0.22	0.80	2.10	2.34
M_2	5.34	3.98	3.70	3.55[c]	3.2[e]–3.5[f]				
T_2	5.04	4.19	3.67	3.09[b]					
TM	10.64	9.39	9.13						
MT	2.27	1.53	1.46						

[a]Values are calculated at the MP2/6-311++G($3d,2p$) level for dimers and heterodimers, and at the MP2/6-311++G(d,p) for trimers and heterotrimers. Cooperativity and three-body effects are obtained at the MP2/6-311++G(d,p). The scaled B3LYP/6-311++G(d,p) frequencies are used for zero-point energy and thermal corrections.
[b]Reference 23.
[c]Reference 13.
[d]Reference 44.
[e]Reference 11.
[f]Reference 43.

plexes using the full counterpoise correction procedure. The results are displayed in Table VIII. It can be seen that the BSSE at the MP2 level is much larger (by a factor of up to 2.7) than that at the HF level. It is also apparent that the BSSE at the B3LYP level is very similar to that estimated at the HF level. The BSSE is reduced by increasing the size of the basis set. For instance, the BSSE for M_2 at the MP2/6-311++G(d,p) amounts to 37% of the interaction energy, while at the MP2/6-311++G($3d,2p$) the BSSE amounts to 18% of the interaction energy.

It is important to mention that the BSSE affects the geometries (distances and angles) of the hydrogen-bonded systems. Even though we did not correct the optimized O...O distances for BSSE, we should expect the uncorrected O...O equilibrium distance to be somewhat shorter than the corresponding BSSE-corrected calculations. This is because in an AB system the energy lowering of A by using B's basis functions is helped by bringing B closer to A.

IV. CONCLUSIONS

This paper is, to our knowledge, the first *ab initio* study of hydrogen bonding and cooperativity of mixed dimer and trimer clusters of methanol and trifluoromethanol. The results were compared with those of the corresponding dimers and trimers of each molecule, i.e., CF_3OH and CH_3OH. The structures were systematically optimized, and harmonic vibrational frequencies were calculated from analytical second derivatives.

Dimerization and trimerization caused noticeable shifts in the frequencies of many vibrational modes. Not surprisingly, those involving the O–H bond were most dramatically affected. The donor character of CF_3OH, as indicated by the O–H frequency shifts, is more evident in the TM system than in T_2. The shifts of the O–H stretching and torsion frequencies in the mixed trimers are much larger than in the trimers and mixed dimers.

TABLE VIII. Basis set superposition error (BSSE) at the HF, MP2, and B3LYP levels of theory and different basis sets.[a]

	M_2			T_2			M_3		T_3	
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	HF	MP2
6-311++G(d,p)	0.69	1.86	0.78	0.86	1.92	0.74	1.55	4.37	1.93	4.27
6-311++G($2d,2p$)	0.43	1.11	0.42	0.92	1.80	0.76				
6-311++G($3d,2p$)	0.27	0.94	0.27	0.69	1.45	0.87				

	TM			MT			T_2M		M_2T	
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	HF	MP2
6-311++G(d,p)	0.97	2.50	1.05	0.52	1.20	0.54	2.00	5.09	1.85	5.07
6-311++G($2d,2p$)	0.69	1.73	0.65	0.52	1.00	0.44				
6-311++G($3d,3p$)	0.48	1.57	0.50	0.33	0.75	0.35				

[a]HF interaction energies (BSSE corrected) for the trimers are −12.28, −8.85, −14.54, and −16.28 kcal/mol for M_3, T_3, T_2M and M_2T, respectively.

Cooperative effects were also evidenced by shorter O...O distances, increased donor O–H bond lengths, enhanced dipole moments, and charge densities computed at the bond critical points. Dissociation enthalpies at 0 K and at room temperature were also used to measure cooperativity. Three-body effects were explored as an alternative way of measuring quantitatively cooperative effects.

Our results indicate that the strength of the hydrogen-bonding interaction, in the various clusters studied, follows the order $M_2T>T_2M>M_3>TM>T_3>M_2>T_2>MT$. We found the symmetric planar trimers of methanol M_{3s} and trifluoromethanol T_{3s} to be saddle points of third order.[13,23]

ACKNOWLEDGMENT

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