

Theoretical Study of the CH \cdots O Interaction in Fluoromethanes \cdot H $_2$ O and Chloromethanes \cdot H $_2$ O Complexes

Eugene S. Kryachko and Th  r  se Zeegers-Huyskens*

Department of Chemistry, University of Leuven, 200F Celestijnenlaan, B-3001 Heverlee, Belgium

Received: March 8, 2001; In Final Form: May 15, 2001

MP2/6-31+G(d,p) calculations are used to analyze the CH \cdots O interaction between X $_n$ H $_{3-n}$ CH ($n = 1, 2, 3$, X = F, Cl) as proton donors and H $_2$ O as acceptor. Only the constrained linear structures are considered, although they do not correspond, for the CH $_3$ X and CH $_2$ X $_2$ complexes, to any global minima on the potential energy surface. The interaction energies range from 0.29 to 3.68 kcal mol $^{-1}$ and are correlated to the intermolecular H \cdots O distances and the acidities of the proton donors, similar to conventional OH \cdots O hydrogen bonds. Interaction with H $_2$ O results in a contraction of the CH bond and an elongation of the external CH and CX ones. The CH stretching vibrations are analyzed for the fully or partially deuterated isotopomers in order to decouple them from the other vibrational modes. The CH(D) stretching vibrations are blue-shifted and the CH(D) stretching vibrations of the external CH bonds are red-shifted. Linear correlations are established between the shifts of the CH(D) stretching vibrations and the variations of the distances in the corresponding CH bonds. Complex formation results in a substantial decrease in intensity of the CH(D) stretching vibrations in the methane or fluoromethanes complexes and an increase in intensity in the chloromethanes complexes. In all the studied complexes, the charge transfer from the proton acceptor to the proton donor goes mainly to the lone pair of the X atom(s). By analogy with the conventional hydrogen bonds, there is also an increase in the population of the recipient antibonding molecular orbital, in the present case the $\sigma^*(\text{CH})$ orbital. The interaction energies are correlated to the percentage of s character of the CH bonds in the isolated monomers. The results suggest that the interaction in the CH \cdots O and OH \cdots O systems is characterized by several similar properties, in relatively good agreement with the statements of Gu, Kar and Scheiner (*J. Am. Chem. Soc.* **1999**, *121*, 9411). In many aspects, the CHCl $_3\cdot$ H $_2$ O complex appears as a precursor of the standard hydrogen bonds.

Introduction

It is increasingly recognized that CH \cdots O interactions play an important role in determining molecular conformation and crystal packing,^{1–15} supramolecular architecture,^{16,17} and the structure of biological systems such as nucleic acids.^{18–21} Much of the evidence for CH \cdots O interactions stems from the observation of close H \cdots O contacts in crystal structures. The standard hydrogen bonds AH \cdots B result from the approach of a proton donor AH toward an acceptor B. The donor atom A is electronegative, e.g., O or N, and the acceptor atom B contains at least one lone pair of electrons. The formation of such classical hydrogen bonds is accompanied by an elongation of the AH bond, by a red shift of the AH stretching frequency and a substantial increase of the infrared intensity compared to the noninteracting species. In the case of CH \cdots B interactions involving C(sp) (alkynes) or C(sp 2) (alkenes), a red shift of the CH stretching vibration has been observed.^{11,22–24} In RC \equiv CH \cdots O systems, the CH stretching frequencies are correlated to the intermolecular C \cdots O distances.¹³ Similar correlations have been found in conventional hydrogen bonds.

However, there is a rather limited number of systems where the CH \cdots B interactions result in a blue shift of the relevant CH stretching frequency. This has been already observed in 1980 for fluoroparaffin derivatives dissolved in mixtures of

diethyl ether/methylcyclohexane.²⁵ In these systems, the CH stretching band is shifted to higher frequencies on cooling to lower temperatures or by increasing the concentration of the proton acceptor.²⁵ A blue shift has been also observed for the CH stretching vibration of chloroform in the presence of triformylmethane²⁶ and in mixed solvents containing proton acceptors.²⁷ Recently, a blue shift in the gas phase has been detected in the chloroform–fluorobenzene complex by double-resonance infrared ion-depletion spectroscopy.²⁸ Blue shifts have also been observed in the dimers of 4-methoxybenzaldehyde²⁹ and hydrated CH groups in dimethyl sulfoxide.³⁰ All these interactions are thought to be rather weak. However, it should be emphasized that when chloroform or bromoform are complexed by strong proton acceptors such as dimethylsulfoxide,³¹ ammonia or aliphatic amines,³² pyridine³³ or amidines,³⁴ a red shift of the CH stretching vibration has been detected in solution^{31,33,34} and in the gas phase as well.³² Recently, theoretical studies have been conducted to elucidate the nature of these weak CH \cdots O interactions resulting in a blue-shifted CH stretching vibration. High-level ab initio treatments of CH $\cdots\pi$,^{28,35} CH \cdots O,^{36–46} or CH \cdots N⁴⁷ interactions predict a contraction of the CH bond and a blue shift of the corresponding CH stretching vibration. The question arises, however, whether all CH \cdots O contacts might refer to standard hydrogen bonds. The theoretical studies on methane and its fluoro-derivatives complexed with water support the viewpoint that CH \cdots O

* Corresponding author.

interactions can be categorized as true hydrogen bonds, although they of course tend to be weaker due to the normally lesser proton donor ability of CH as compared to that of OH.³⁷ Nevertheless, on the basis of mainly vibrational data and natural bond orbital (NBO) analysis,⁴⁸ it has been concluded that the hydrogen bonding in the fluoroform–water, chloroform–benzene, or fluoroform–oxirane complexes is essentially different from that present in the water dimer. The term “anti-hydrogen bond”,³⁵ later replaced by “improper, blue-shifting hydrogen bonds”⁴⁸ has been then proposed.

There still remain a number of important and fundamental questions that the present article is intended to address. They are the following. For the conventional AH \cdots B hydrogen bonds, correlations have been established between the interaction energies, the intermolecular distances, the elongation of the AH bond, the changes in frequencies or intensities of the AH stretching vibration, and the acidities/basicities of the AH and B species.^{49,50} The current situation with the CH \cdots B interaction is different. Theoretical studies in this area refer to different systems, so that no systematic correlations could be deduced from these data. The present work aims to undertake a systematic study of the interaction between fluoro- and chloro-methanes and a water molecule. In the first section, we discuss the interaction energies along with the geometric changes resulting from the interaction with one water molecule. The second one deals with an analysis of the vibrational frequencies and infrared intensities using the different isotopomers of the proton donors. In the last section, we present the results of the NBO analysis of the charge transfer along with the changes in the population of the antibonding orbitals of the proton donors. This analysis is particularly relevant in the present study because, as generally admitted in the conventional hydrogen bonds, the decrease in the AH stretching frequencies is consistent with the bond weakening associated with an increasing occupation of the $\sigma^*(\text{AH})$ orbital. To the best of our knowledge, the occupation of the $\sigma^*(\text{CH})$ orbital for the CH \cdots O interactions investigated in the present work has been only estimated for methane–water⁴⁰ and fluoroform–water⁴⁸ complexes. These results are, however, in complete disagreement. Indeed, in the former case, an increase whereas in the second one, a decrease of the $\sigma^*(\text{CH})$ population were predicted.

Computational Methods

The geometries of the isolated molecules CH $_4$, CH $_n$ F $_{4-n}$, and CH $_n$ Cl $_{4-n}$ ($n = 1, 2, 3$) and their complexes with a water molecule were optimized at the MP2/6-31+G(d,p) computational level. The characteristics of the CH $_3$ F \cdot H $_2$ O complex were further refined at the higher MP2/6-311+G(d,p) level. Interaction energies were obtained as the difference in energy between the complex, one one hand, and the sum of isolated monomers, on the other hand. Basis set superposition errors (BSSE) were corrected by the counterpoise procedure.⁵¹ It is worth stressing that, for these weak interactions, failure to correct the BSSE would have resulted in erroneous conclusions.^{35,44} Harmonic vibrational frequencies and intensities of the isolated proton donors, their deuterated counterparts, and the corresponding complexes with a water molecule were calculated at the MP2/6-31+G(d,p) level. Charges on individual atoms, populations of molecular orbitals, and coefficients of the hybrid orbitals were obtained by using the natural bond population scheme.⁵² The GAUSSIAN 98 package of programs⁵³ was used for all calculations reported in the present work. The BSSE corrections for the hydrogen bond distances, energies, and frequencies were obtained according to the methods described in refs 54 and 55.

It must be stressed that the main objective of the present work is not to compare the data obtained at different computational levels. This has been discussed in refs 37 and 46.

Results and Discussion

Energetics and Geometries. Initially, the geometry of the complexes of CH $_4$, CH $_n$ F $_{4-n}$, and CH $_n$ Cl $_{4-n}$ ($n = 1, 2, 3$) with a water molecule was fully optimized without any constraint. They are labeled by **A** and displayed in Figure 1. In the complexes involving CH $_4$, CHF $_3$, and CHCl $_3$, the CH \cdots O bond is nearly linear, the CH \cdots O angle ranging between 179.6° and 179.9°. In the CH $_4$ ·H $_2$ O complex, the C $_2$ axis of the water molecule and one of the C $_3$ axes of methane become collinear. The dihedral angle H'OH is equal to 180°. Such structure fairly agrees with the V–O structure reported in ref 41 and disagrees with that found in ref 56 where the CH' approach of one of the lone pair of the water molecule was thought to be preferential. For the CHF $_3$ ·H $_2$ O complexes, the dihedral angles of 179.4° and 177.4°, respectively, indicate that the C $_2$ axis of the water molecule nearly coincides with the C $_3$ axis of the proton donor. The present structure **A** of the CHF $_3$ ·H $_2$ O complex where, as we admit from the valence-bond theory, the CH bond bisects the lone pair of oxygen is in agreement with earlier studies⁴³ performed via the MP2/6-31G(d,p) method.

The **A** complexes involving mono- and dihalogeno derivatives show a strong departure from linearity. In the structures shown in Figure 1, the halogen atom is weakly bonded to one of the hydrogen atoms of the water molecule forming a cyclic form. The corresponding H \cdots F bond lengths vary from 2.016 and 2.249 Å in CH $_3$ F·H $_2$ O and CH $_2$ F $_2$ ·H $_2$ O (**A** $_1$), respectively. Similarly, we have 2.599 and 3.388 Å for the H \cdots Cl lengths in the complexes CH $_3$ Cl·H $_2$ O and CH $_2$ Cl $_2$ ·H $_2$ O (**A** $_1$). In these cyclic structures, the CH \cdots O bond is not linear, the CH \cdots O angle ranging between 116° and 142°. Cyclic structures for the interaction of CH $_3$ Cl and CH $_2$ Cl $_2$ with a water molecule were also found at a lower computational level⁵⁷ and, recently, in the complexes of triflylmethane with CHCl $_3$.⁴⁸ Actually, the potential energy surface (PES) for the CH $_2$ X $_2$ ·H $_2$ O interaction includes another minimum corresponding to the **A** $_2$ structure also displayed in Figure 1. In this structure, the distance of 2.346 Å indicates a weak interaction between the F and H atoms. Two weak CH \cdots O interactions cannot be ruled out, despite the large H \cdots O distance of 2.738 Å and the unfavorable angle of 87.6°. The **A** $_2$ form of the CH $_2$ F $_2$ ·H $_2$ O complex is slightly more stable, by 0.26 kcal mol $^{-1}$, than the **A** $_1$ form.

Figure 1 also includes the transition structure **A** $_F^{\text{tr}}$ on the PES of the CH $_3$ F·H $_2$ O dimer. In fact, such PES possesses three equivalent minima of the **A**-type. **A** $_F^{\text{tr}}$ is the transition structure between each pair of these minima with an activation barrier of 1.71 kcal mol $^{-1}$. Such small transition barrier indicates a relative flatness of the mentioned PES. Interestingly, in **A** $_F^{\text{tr}}$, the CH \cdots O angle is equal to 179.4° showing in that way a strong tendency to linearity.

For the purpose of comparison between the nature and strength of the CH \cdots O interaction in all the studied complexes, the geometry was further reoptimized with the single restriction of a linear CH \cdots O bond. These structures are labeled by **B** in Figure 1. It is interesting to notice that such constrained optimization provides structures where one of the lone pair of the oxygen atom of the water molecule is pointed directly to the hydrogen atom of the CHX $_3$ or CH $_2$ X $_2$ molecule. The H'OH dihedral angles are equal to 135° for the CH $_3$ X complexes and 146.1° for the CH $_2$ X $_2$ complexes. However, previous calculations carried out at the MP2/6-31G(d,p) level

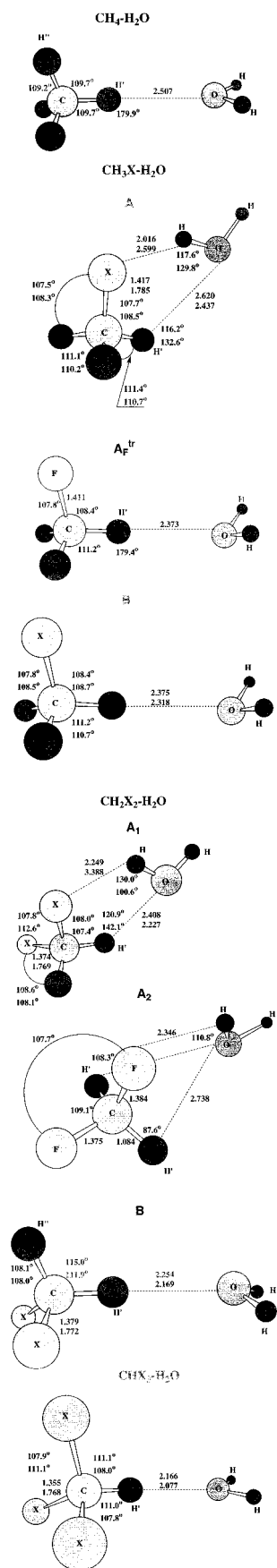


Figure 1. MP2/6-31+G(d,p) geometries of the optimized (A) and constrained (B) structures in methane, fluoromethanes, and chloromethanes complexed with a water molecule (distances in Å, angles in degrees). The top values correspond to X = F and the bottom ones to X = Cl.

TABLE 1: MP2/6-31+G(d,p) Interaction Energy (kcal mol⁻¹) Calculated with Counterpoise Correction of BSSE, Intermolecular Distance H···O, and Variation of the CH', CH'', and CX Distances (mÅ) in the A and B Complexes between Methane, Fluoro- and Chloromethanes, and Water

system	<i>E</i>	<i>r</i> (H···O)	Δr (CH') ^a	Δr (CH'')	Δr (CX)
CH ₄ ·H ₂ O	0.29	2.507	-0.4	+0.8	
CH ₃ F·H ₂ O A	3.76	2.620	-1.2	+1.0	+12.4
CH ₃ F·H ₂ O B	1.57 ^b	2.364 ^b	-1.9 ^b	+0.4 ^b	+6.5 ^b
CH ₂ F ₂ ·H ₂ O A	3.40	2.408	-2.2	+0.5	+14.6 ^c
CH ₂ F ₂ ·H ₂ O B	2.62 ^d	2.254	-2.4	+0.2	+5.7
CHF ₃ ·H ₂ O	3.72 ^d	2.164	-1.6		+4
CH ₃ Cl·H ₂ O A	2.76	2.437	-0.5	+0.1	+3.1
CH ₃ Cl·H ₂ O B	1.74	2.305	-1.3	+0.1	+5.8
CH ₂ Cl ₂ ·H ₂ O A	3.78	2.227	-1.1	0	+5.8 ^c
CH ₂ Cl ₂ ·H ₂ O B	3.22	2.169	-1.1	0	+3.2
CHCl ₃ ·H ₂ O	3.68	2.077	-0.6	-	+2.7
H ₂ O·H ₂ O	4.8	1.946	+6.6 ^e	-0.7 ^e	

^a The CH distances in the isolated molecules are: CH₄: 1.08622 Å; CH₃F: 1.08669 Å; CH₂F₂: 1.08596 Å; CHF₃: 1.08489 Å; CH₃Cl: 1.08474 Å; CH₂Cl₂: 1.08369 Å; CHCl₃: 1.08357 Å. ^b Calculations carried out at the MP2/6-311+G(d,p) level gave the following values: *E* = 1.41 kcal mol⁻¹, *r*(H···O) = 2.413 mÅ, Δr (CH') = -1.7 mÅ (in good agreement with values of ref 37, Δr (CH'') = 0.5 mÅ, Δr (CX) = +5.5 mÅ. ^c X atom not participating in the formation of the closed structure. ^d Calculations carried out at the 6-31++G(d,p) level (including BSSE) provide *E* values equal to 1.56 and 2.65 kcal mol⁻¹ for the CH₂F₂ and CHF₃ complexes.⁴⁴ The fact that these values differ from those of the present work may be due to other choices of the geometries of the monomer, more specifically, the CC, CH, and CF distances. ^e The two values represent the variation of the OH distances of the bonded and free OH groups of the proton donor in the water dimer.

have shown that for the CH₃F·H₂O complex, the interaction is slightly more favorable if both lone pairs of water share their contribution to the interaction.⁴³

Thus, the linear structures for the complexes involving the mono- and dihalogeno-derivatives, do not correspond to any local minima on the corresponding potential energy surfaces and are characterized by imaginary frequencies of 21i cm⁻¹ and 9i cm⁻¹ for the dimers of CH₃F and CH₂F₂ with water and 44i cm⁻¹ and 21i cm⁻¹ for the water complexes involving CH₃Cl and CH₂Cl₂, respectively. It must be stressed that the high-frequency modes do not differ substantially in the optimized and constrained structures. For example, in the CH₂F₂·H₂O complex, the two ν (CH₂) vibrations are predicted at 3309 and 3199 cm⁻¹ in the optimized structure; these frequencies are lower by 1 and 5 cm⁻¹ than the frequencies obtained for the constrained structure. Similar differences are obtained for the other complexes.

Table 1 reports the interaction energies, the intermolecular H···O distances along with the variations of the CH distances involved in the interaction of water (Δr (CH')) and of the free CH group (Δr (CH'')). The variations of the CX (X = F, Cl) distances are indicated as well. The data for the classical OH···O hydrogen bond in the water dimer are also shown there for the comparison. The interaction energies are larger for the optimized structures but this is not unexpected because they result from a double interaction involving the hydrogen and oxygen atoms of water. This has been shown recently for other systems.⁵⁸ These structures are not very relevant for the present study because only a consistent geometry allows a fair comparison between the systems. Except otherwise stated, the following discussion will only refer to the constrained structures. It is also worth noticing that the effect of BSSE on the optimized geometries and energies is weak. For the CH₄·H₂O complex, the BSSE-corrected CH' distance is 1.08576 Å and the contraction of the CH' bond is larger by 0.06 mÅ than the uncorrected

one. Also, the BSSE-corrected energy is larger by 0.0005 kcal mol⁻¹ than the uncorrected one.

The present results demonstrate that inclusion of each fluorine atom strengthens the interaction energy by about 1 kcal mol⁻¹ and shortens the H...O distance by ca. 0.1 Å in agreement with literature data.³⁷ Substitution of hydrogen by chlorine atoms leads to less systematic variations.

By analogy with conventional hydrogen bonds, the interaction energies correlate with the intermolecular distances. As shown recently for a large number of hydrogen-bonded systems⁵⁹ the interaction energies are correlated to the third power of the hydrogen bond length. However, in the small range investigated in the present work, such correlation takes the following linear form:

$$E = 21.9 - 8.60 r(\text{H}\cdots\text{O}) \quad (r = 0.9774) \quad (1)$$

As shown in Table 1, all the changes in CH' bond length are negative, taking a maximum of -2.4 mÅ for the CH₂F₂·H₂O complex. The contraction of the CH' bond further decreases with the number of chlorine atoms implanted on methane and the smallest value of -0.6 mÅ is predicted for the CHCl₃·H₂O complex. These results clearly demonstrate that, in contrast to the conventional hydrogen bonds, the changes in the CH distances are not correlated to the intermolecular distances nor to the strength of the interaction. Notice that for the standard OH...O bonds, the correlation has been recently discussed in ref 60. Inspection of the data of Table 1 shows further that the CH'' and CX bonds are elongated in comparison with the free methane derivatives and moreover, such elongation appears to be significantly larger for the CX bonds than for the CH'' ones. These changes are contrary to the pattern in the conventional water dimer where the OH' bond undergoes a stretch of 6.6 mÅ and the OH'' bond a contraction of only -0.7 mÅ.

As in the conventional hydrogen bonds,⁶¹ the CH...O interaction strength depends on the acidity of the hydrogen donor. We deduce a correlation between the interaction energies and the experimental gas-phase proton affinities⁶² (PA(A⁻)) for the conjugate anions of the different hydrogen donors. However, in contrast to the results of ref 39, the correlation is not linear and the best interpolation takes a form of the second-order polynomial:

$$E = -79.4 + 0.48 (\text{PA}^-) - 0.7 (\text{PA}^-)^2 \quad (r = 0.9697) \quad (2)$$

Vibrational Spectra. One of the most characteristic features of the conventional hydrogen bonds is related to their vibrational spectrum. In OH...O hydrogen bonds, the OH stretching vibration is typically red-shifted and its intensity is larger than in the monomer. In contrast, in all the complexes investigated in the present work, the CH' stretching vibration becomes blue-shifted. This has been outlined in ref 37 where the frequency shifts and intensities of the CH' stretching vibration in fluoromethanes complexed with water have been calculated at the same level as in the present work. However, no correlation between the contraction of the CH' bond and the corresponding blue shift could be deduced from these results. In the CH₄·H₂O complex, the frequency shift of the antisymmetrical CH' stretching vibration is equal to +10 cm⁻¹ and the ratio of intensity in the complex and the isolated subunit equal to 0.07,³⁷ which is in agreement with the present calculations. Nevertheless, there exists some ambiguity concerning the concept of the "antisymmetrical" vibration in the complexed molecules. Indeed, in isolated CH₄, the triply degenerate vibration F is predicted at 3265 cm⁻¹ with an intensity of 21.7 km mol⁻¹. In the

TABLE 2: Frequency Shift (cm⁻¹) and Intensity (km mol⁻¹) of the ν(CH) and ν(CD) Vibrations for the Interaction between the Isotopomers of Fluoro- and Chloromethanes and Water in the Constrained Structures B

system	Δν(CH'(D'))	I(CH'(D ^f))	I(CH'(D'))	Δν(CH''(D''))	I(CH''(D''))
CHD ₃ ·H ₂ O	+12	17	0	-10	22
CH ₃ D·H ₂ O	+9	5.9	0.4	-7	8.7
CHD ₂ F·H ₂ O	+32	27.9	1.3	-7	32.4
CH ₂ DF·H ₂ O	+25	21.2	4.1	-6	24.0
CHDF ₂ ·H ₂ O	+43	32.4	1.8	-4	36.4
CHDF ₂ ·H ₂ O	+34	32.6	12.5	-4	36.4
CHF ₃ ·H ₂ O	+33	24.9	5.3		
CD ₃ F·H ₂ O	+27	35.1	0.9		
CHD ₂ Cl·H ₂ O	+27	11.4	11	-4	14.7
CH ₂ DCl·H ₂ O	+19	9.9	6.9	-3	11.2
CHDCl ₂ ·H ₂ O	+26	3.9	50.4	+1	6.0
CHDCl ₂ ·H ₂ O	+18	4.1	20.8	-1	4.1
CHCl ₃ ·H ₂ O	+23	0.2	103		
CDCl ₃ ·H ₂ O	+16	0.1	45.6		
DOH·H ₂ O ^a	-124	3	370	+5	12.3 ^a

^a The OH group of HOD acts as proton donor in the water dimer; the intensity of the ν(OD) vibration in free HOD is 19.2 km mol⁻¹. For the dimer of the normal isotopomer H''OH'...OH₂, the decrease in the ν(OH') frequency of the proton donor (specifically the bond involving the bridging hydrogen) is -79 cm⁻¹. The value of -31 cm⁻¹ erroneously cited in ref 37 corresponds to the stretching frequency of the non-bonded OH'' group. Also, the value of 1.89 corresponds to the ratio of intensity of the ν(OH'') vibration in the complex/isolated subunit.

CH₄·H₂O complex, the A₁ vibration is calculated at 3275 cm⁻¹ and the doubly degenerate E vibration at 3254 cm⁻¹, with respective intensities of 1.5 and 6.8 km mol⁻¹. The high-frequency component, blue-shifted by 10 cm⁻¹ from the free molecule, involves mainly the CH' stretching mode but includes also some contribution of the external CH'' bond, not participating in the bonding with a water molecule. More significant are the blue shifts in the fully or partially deuterated proton donors where the CH or CD stretching vibrations are decoupled from the other vibrational modes. The ν(CH) vibration, predicted at 3234 cm⁻¹ with an intensity of 17 km mol⁻¹ in the free CHD₃ isotopomer, is computed at 3246 cm⁻¹ with a nearly vanishing intensity in the complex with water. The blue shift is now 12 cm⁻¹ instead of 10 cm⁻¹ and the decrease of the corresponding intensity appears to be larger than in the normal isotope. It is also worth noticing that in the CHD'₃ complex where one of the D atom acts as a proton donor, the ν(CH) frequency of the external CH bond decreases by 10 cm⁻¹ and its intensity rises to 22 km mol⁻¹. The difference between the coupled and uncoupled vibrational modes is still larger in the CH₂F₂ complex where the frequency shift is 28 cm⁻¹ in the normal isotopomer and rises to 43 cm⁻¹ in the CDF₂H' one. As already mentioned, the contraction of the CH' bond takes the maximum value of -2.4 mÅ precisely for this complex.

We must also notice that the effect of BSSE on the frequencies is weak. The corrected ν(CD') frequency in the H₃CD'·H₂O complex is 1 cm⁻¹ higher and the corrected ν(CH') frequency in the D₃CH'·H₂O complex is only 2 cm⁻¹ higher than the uncorrected one.

The spectroscopic data are summarized in Table 2 which includes the frequency shifts of the CH' and CH'' stretching vibrations along with the infrared intensities of the CH or CD stretching vibrations in the free molecules (I(CH^f)(D^f)) and in their corresponding complexes with water. For each complex, the first and second rows refer to the corresponding characteristics of the CH and CD stretching vibrations. The results for the water dimer, also reported in Table 2, indicate that for the normal isotopomer, the decrease in the OH frequency of the

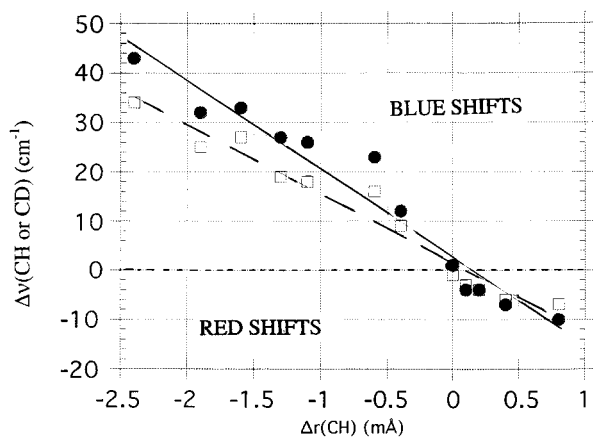


Figure 2. Frequency shifts $\Delta\nu(\text{CH})$ (●) and $\Delta\nu(\text{CD})$ (□) as a function of the variation of the corresponding CH' or CH'' distances. The upper part refers to $\Delta\nu(\text{CH}')(\text{D}')$ and the lower part to $\Delta\nu(\text{CH}'')(\text{D}'')$.

proton donor (specifically the bond involving the bridging hydrogen) is -79 cm^{-1} . In the $\text{DOH}\cdots\text{H}_2\text{O}$ dimer, the red shift of -124 cm^{-1} is in good agreement with literature data⁶³ calculated at approximately the same level. The value of the red shift in the water dimer appears to be substantially larger than the blue shift of 33 cm^{-1} predicted for the $\text{CHF}_3\cdots\text{H}_2\text{O}$ complex, in contradiction with the statements of ref 37.

We notice that all the studied complexes are characterized by blue shifts of the CH' or CD' stretching vibrations, ranging from 9 to 43 cm^{-1} , and smaller red shifts of the CH'' or CD'' stretching vibrations, ranging from -1 to -10 cm^{-1} . The method of isotopic substitution allows us to deduce quantitative correlations between the frequency shifts of the CH and CD stretching vibrations and the variations of the distance in the corresponding to the CH' and CH'' bonds:

$$\Delta\nu(\text{CH}) = 2.69 - 17.91 \Delta r(\text{CH}) \quad (r = 0.9747) \quad (3)$$

$$\Delta\nu(\text{CD}) = 1.44 - 14.07 \Delta r(\text{CH}) \quad (r = 0.9787) \quad (4)$$

These correlations are illustrated in Figure 2 where the upper part refers to the blue shifts of the CH' or CD' stretching vibration and the lower one to the red shifts of the CH'' or CD'' stretching vibration.

It must be mentioned that all the vibrational frequencies have been calculated at the harmonic level. For the complex $\text{CH}_4\cdots\text{H}_2\text{O}$, the frequency shift of the $\nu(\text{CH}')$ vibration calculated within the one-dimensional model is 1 cm^{-1} higher. The difference between harmonic and anharmonic frequency shifts must be larger for the stronger complexes. We have shown in a previous work⁶⁴ that the anharmonicity roughly increases with the hydrogen bond strength. These considerations suggest that the slopes of eqs 3 and 4 will be somewhat larger when considering the anharmonic frequency shifts instead of the harmonic ones.

The infrared intensities may also shed some light on the bonding pattern. In the complexes involving the fluoromethanes, the CH' stretching vibrations show a strong intensity decrease. Calculations carried out at the MP2/6-31++G(d,p) level indicate a similar intensity decrease in the fluoroform–ethylene oxide complex, viz., from 25 to 8 km mol^{-1} .²⁸ This behavior appears to be in contrast with the chloromethanes complexes where the intensity does not change significantly in the monochloro-isotopomers but is greatly enhanced in the di- or trichloro-isotopomers. A similar intensity increase has also been predicted in the chloroform–benzene complex.^{35,65} The intensity patterns,

TABLE 3: Charge Transfer and Change in Natural Population Atomic Charge (me) of the Different Atoms Relative to Monomers

system	CT ^a	$\Delta q_{\text{H}'}^b$	δq_{C}	$\Delta q_{\text{H}''}$	Δq_{X}	Δq_{O}
$\text{CH}_4\cdots\text{H}_2\text{O}^c$	2.3	+27	-8	-7, -7, -7	-	-3.4
$\text{CH}_3\text{F}\cdots\text{H}_2\text{O}^c$	4.0	+29	-10	-7, -10	-9	-8.3
$\text{CH}_2\text{F}_2\cdots\text{H}_2\text{O}^c$	6	+34	-15	-9	-8, -9	-12.5
$\text{CHF}_3\cdots\text{H}_2\text{O}^c$	7.5	+37	-21	-	-8, -8, -8	-17.7
$\text{CH}_3\text{Cl}\cdots\text{H}_2\text{O}$	5.1	+30	-3	-7, -7	-19	-8.7
$\text{CH}_2\text{Cl}_2\cdots\text{H}_2\text{O}$	7.8	+34	0	-6	-18, -18	-14.3
$\text{CHCl}_3\cdots\text{H}_2\text{O}$	9.6	+36	0	-	-14, -16, -16	-19.2
$\text{H}_2\text{O}\cdots\text{H}_2\text{O}$	12.6	+26 ^c	-31 ^c	-7 ^c	-	-18.1

^a Charge transfer (CT) defined as the sum of atomic charges on the proton acceptor molecule. ^b By convention positive values indicate a loss of charge and negative values a gain of charge. ^c The CT values calculated at the same level³⁷ are somewhat different being 4, 6, 8, and 11 me in the same order. The present of 7.5 me for the CHF_3 complex is in good agreement with the data of ref 48. ^c Variation of the charges on the H' , O and H'' atoms of the proton donor in the $\text{H}''\text{OH}'\cdots\text{OH}_2$ dimer. MP2/6-311+G(d,p) calculations give respective values of +33, -36 and -7 me.

calculated at the present level, are not so clear as those of the frequency shifts and no quantitative correlation could be deduced between the frequency shifts and intensity changes. Nevertheless, it is interesting to notice that the interaction between chloroform and water results in a weak contraction of the CH' bond, a very small blue shift, and a large intensity increase of the corresponding CH' stretching vibration. From this point of view, the CHCl_3 complex with water can be considered as the “precursor” of the conventional hydrogen bonds.

It is worth noticing that in the **A** structures, the CH' bond is also contracted and the corresponding CH' stretching vibration blue-shifted, although to a lesser extent than in the constrained structures.

As mentioned above, complex formation of fluoro- and chloromethanes with water is accompanied by a significant elongation of the CX bond. The CX stretching vibrations appear to be coupled with the CH_3 or CH_2 out-of-plane deformation modes. Deuteration does not affect the coupling to a great extent. Therefore, no correlation between the variation of the distances and the corresponding frequency shifts could be established. It is however worth noticing that in free CH_2Cl_2 , the modes predicted at 812 and 750 cm^{-1} can be assigned predominantly to the $\nu^{\text{as}}(\text{CCl})$ and $\nu^{\text{s}}(\text{CCl})$ vibrations. In the water complex, these two vibrations are red-shifted, by -8 and -5 cm^{-1} , respectively. These values are qualitatively in agreement with the values of -13 and -10 cm^{-1} measured experimentally for the stronger complex between CH_2Cl_2 and diethyl ether.²⁵

NBO Analysis of the Electronic Structure. The formation of a hydrogen-bonded complex implies that a certain amount of electronic charge is transferred from the proton acceptor to the proton donor molecule. In addition, there is a rearrangement of electron density within each monomer. Such charge transfer has been recently discussed for the interaction between fluoromethanes and a water molecule but the changes in natural charges have been computed only for the atoms of the $\text{CH}'\cdots\text{O}$ triad.³⁷ Table 3 lists the charge transfer (CT) along with the changes in natural atomic charges of each atom of the proton donor. A comparison of the data of Tables 1 and 3 reveals that the charge transfer is roughly proportional to the strength of the interaction. The bridging proton becomes more positive and the gain in positive charge slightly increases with the interaction energies. In the $\text{CH}_4\cdots\text{H}_2\text{O}$ complex, the charge transfer to the carbon atom and each of the external hydrogen atoms is nearly identical. Further, a common feature of the fluoromethanes and

TABLE 4: Change in the Occupation of the $\sigma^*(CH')$, $\sigma^*(CH'')$, and $\sigma^*(CX)$ Orbitals and of the Lone Pairs of X (me). %s Character of the CH Bond in the Free Halomethanes

system	$\sigma^*(CH')^a$	$\sigma^*(CH'')$	$\sigma^*(CX)$	LP(X)	%s(CH)	%s(CH')
CH $_4$ ·H $_2$ O	+2.4	0			25.0	24.7
CH $_3$ F·H $_2$ O	+2.4	-0.2	0	+3.4	26.5	26.5
CH $_2$ F $_2$ ·H $_2$ O	+2.7	-0.4	-0.6, -0.6	+3.1, +3.9	29.0	28.5
CHF $_3$ ·H $_2$ O	+2.3		-1.2, -1.2, +3.3, +3.3, -1.4	+3.6	32.0	33.5
CH $_3$ Cl·H $_2$ O	+3.9	-0.3	+0.1	+2.6	26.9	26.5
CH $_2$ Cl $_2$ ·H $_2$ O	+4.7	-0.5	-0.5, -0.5	+3.1, +3.1	28.7	28.2
CHCl $_3$ ·H $_2$ O	+4.6		-0.5, -0.5, +2.9, +3.3, -0.1	+3.3	32.3	32.3
H $_2$ O·H $_2$ O ^b	+13.1	0			24.5	28.0

^a Positive values indicate an increase in the occupation of the considered orbital. ^b Change in the occupation of the $\sigma^*(OH')$ and $\sigma^*(OH'')$ orbitals in the H $'OH''\cdots OH_2$ dimer; %s(OH) character in isolated water and the dimer.

chloromethanes complexes is the large charge transfer to the fluorine or chlorine atoms. In the fluoromethanes complexes, we observe an increase of the charge density on the carbon atom, leading to a larger C $^-$ H $^+$ polarization of the CH bond. In the chloromethanes complexes, the charge gain on the carbon atoms is nearly zero, the larger part of the charge transfer taking place to the chlorine atom(s). In none of the complexes investigated in the present work, there exists an indication of a reversed C $^+$ H $^-$ polarity.⁴ However, such conclusion must be taken with some caution. Indeed, whereas the hydrogen atom acquires a positive charge in all the monomers, the natural charges of the carbon atom in CH $_3$ F, CH $_2$ F $_2$, and CHF $_3$ are, respectively, equal to -0.115, +0.530, and +1.083 e and, in CH $_3$ Cl, CH $_2$ Cl $_2$, and CHCl $_3$, -0.632, -0.461, and -0.374 e, covering a wide range of values and reversed signs. In the water dimer, a larger amount of charge is transferred to the more electronegative oxygen atom, leading, as expected, to a larger O $^-$ H $^+$ polarization.

The NBO analysis of several typical hydrogen-bonded systems has demonstrated a charge transfer from the lone pairs of the proton acceptor to the antibonding orbital(s) of the proton donor.⁵² The decrease in the AH stretching frequencies is consistent with the bond weakening associated with an increasing occupancy of the $\sigma^*(AH)$ antibonding molecular orbital (MO). For the CH $'\cdots O$ interaction, the occupation of the $\sigma^*(CH)$ antibonding MO has been discussed for CH $_4$ ^{40,52} and CHF $_3$ ⁴⁸ complexed with a water molecule. The results seem to be, however, contradictory. In the first case, the NBO analysis indicated a net transfer of charge into the $\sigma^*(CH')$ antibonding MO whereas in the second case, a small decrease of electron density in this orbital was predicted. The results of the NBO analysis for the present complexes are gathered in Table 4 which indicates the change in occupation of the $\sigma^*(CH')$, $\sigma^*(CH'')$, and $\sigma^*(CX)$ antibonding MOs. The results for the water dimer are also shown there for the comparison.

Let us now analyze these results. In the water dimer, the dominant part of the charge transfer originates from the oxygen lone pairs (-12.7 me) and mainly goes into the $\sigma^*(OH)$ antibonding MO of the proton donor whose population increases by 13.1 me. The situation for the fluoro- and chloromethanes complexed with water is, however, different. The electronic charge transfer goes dominantly into the lone pairs of the fluorine or chlorine atoms. There is also, for all the studied complexes, a smaller but significant decrease of the population of the $\sigma^*(CX)$ antibonding MO and a rather small decrease of the occupation of the $\sigma^*(CH'')$ one. According to ref 48, in the CHF $_3$ ·H $_2$ O complex, the electronic transfer goes dominantly into

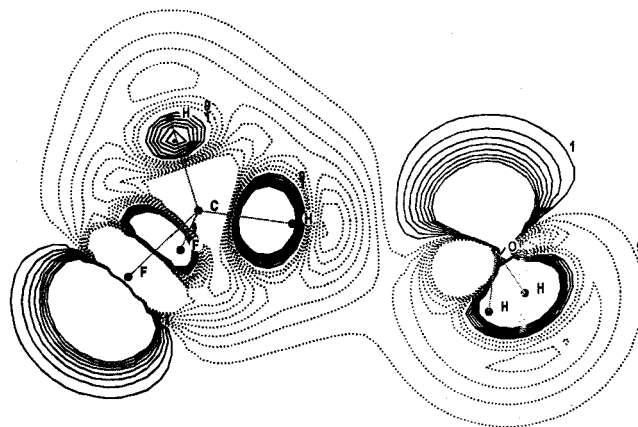


Figure 3. Density difference section of the CH $_2$ F $_2$ ·H $_2$ O complex **B** using MOLDEEN program⁷⁰ with the keywords “bonds” and “orient”. The contour spacing is 0.00125 e/au 3 . The value of contour 1 is chosen at 0.00125 e/au 3 . Contour 9 has the value of -0.00125 e/au 3 . Dotted lines represent a loss of electron density relative to the isolated monomers. Dark regions refer to increased density.

the lone pairs of the fluorine atoms (3.3, 4.6 and 4.6 me) and there is also a smaller decrease of the population in all three $\sigma^*(CF)$ orbitals (-1.8, -1.0, -1.0 me). Although the level of the calculations was not indicated in that work, the present results dealing with the occupation of the lone pairs and the $\sigma^*(CH)$ orbitals are in relatively good agreement. However, contrary to the statements of ref 48, we observe an *increase* of the $\sigma^*(CH)$ population by 2.3 me and not a decrease by 1.7 me. This increase is also systematically found in the other complexes investigated in the present work. It is worth noticing that our results are in good agreement with MP2/6-31G(d) study of the CH $_4$ ·H $_2$ O interaction where the NBO analysis demonstrates a net transfer of charge into the $\sigma^*(CH)$ antibonding MO typical for standard hydrogen bonds.⁵² The amount of charge transfer was not indicated in ref 52. Anyway, even at the lower MP2/6-31G(d,p) computational level, the n $_O$ - $\sigma^*(CH')$ interaction appears as the dominant contribution to the bonding in the CH $_4$ ·H $_2$ O complex.⁵²

To visualize the formation of the CH $'\cdots O$ bond in terms of the MO pattern, we present in Figure 3 the density difference section of the complex CH $_2$ F $_2$ ·H $_2$ O (**B**). Contours displayed there by dotted lines show a loss of electron density. On the other hand, the continuous lines cover the regions with a gain of electron density. We clearly observe in this Figure that the CH $'\cdots O$ bonding region is divided into two parts, one of which, in the close vicinity of the hydrogen atom H', loses electron density whereas the other one, nearby the oxygen atom gains electron density. A similar pattern exists within the CH' bonding area: close to H' there is a significant gain of density and farther a loss. This loss of density is largely compensated by its gain in the neighborhood of the fluorine atoms.

Interestingly, a comparison of the data of Tables and 4 reveals that the amount of charge transfer does not exactly match the sum of the changes in the population of the antibonding orbitals. In the CHF $_3$ ·H $_2$ O complex, as for example, these changes are equal to 7.5 me and 8.7 me, respectively. The small difference of 1.2 me can be accounted for by a small decrease of the occupation of the Rydberg orbitals of the C atom that, in the present case, amounts to 1.1 me. In the water dimer, the decrease in occupation of the Rydberg orbital of the oxygen atom of the proton donor is still smaller, being about 0.2 me. This provides only a negligible contribution to the total charge transfer of 12.6 me.

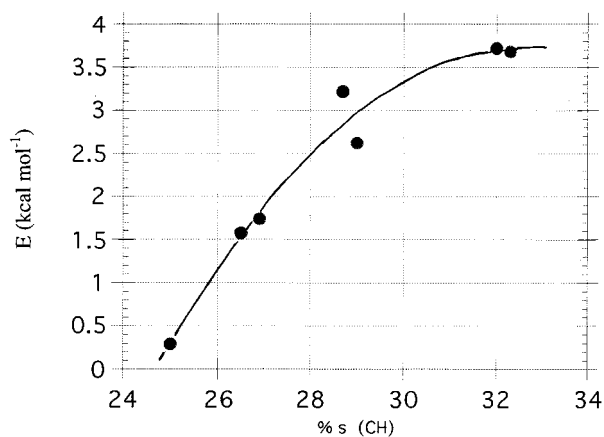


Figure 4. Interaction energies as a function of the %s character of the CH bond in the proton donor monomers.

For all the complexes, the increase in the occupation of the $\sigma^*(\text{CH}')$ orbitals remains moderate, viz., between 2.4 and 4.7 me. In absence of any other effects, an increase of the $\sigma^*(\text{CH})$ population must result in an increase of the CH' bond length. Inspection of the present results indicate that this is actually not the case. It is however worth stressing that in the three chloromethanes complexes, the contraction of the CH' bond decreases with increasing occupation of the corresponding antibonding orbital. In the water dimer, the change in occupation of the $\sigma^*(\text{OH}')$ is significantly larger (13.1 me), corresponding to an elongation of the OH' bond by 6.6 mÅ.

Table 4 also reports the percentage s character of the CH bond in the isolated proton donors and in their water complexes. The results indicate a significant influence of the substitution of the hydrogen by fluorine or chlorine atoms on the hybridization of the CH bond which is of sp^3 type in isolated CH_4 and nearly of the sp^2 type in the isolated tri-halogeno derivatives. As illustrated in Figure 4, the interaction energies increase with the s character of the CH bonds in the isolated molecules. This is in good agreement with the experimental or theoretical gas-phase acidities of the CH bonds which depend on the hybridization of the C atom and increase in the order $\text{sp} > \text{sp}^2 > \text{sp}^3$.^{66–68}

As indicated in Table 4, the s character of the CH' bond is not significantly altered in the complexes. The situation is rather different in the water dimer, where the %s character of the bonded OH' group increases by 3.5% in agreement with the value of 3.2% calculated at the RHF/6-31G(d) level.⁵² Therefore, it can be concluded that the contraction of the CH' bond resulting from the interaction with water is not due to the rehybridization of the CH' bond and a strengthening of its s character as suggested in ref 27. According to ref 26, the recipient CH' orbital in CHCl_3 is a Rydbergised CH^* MO expanded outside the CH region. So, it can be concluded that the repulsion between the electron pair responsible for the $\sigma(\text{CH})$ bond and the electron pair donated from water results in a compression of the CH bond. This must lead to a strengthening of the CH' bond, compensating only partly its weakening due to hydrogen bond formation. The two effects are difficult to separate but they nearly cancel each other in the $\text{CHCl}_3 \cdot \text{H}_2\text{O}$ complex, where the change of occupation of the $\sigma^*(\text{CH}')$ antibonding MO of +4.6 me corresponds to a very weak contraction of the CH' bond. From this point of view also, such complex appears as a "precursor" of the standard hydrogen bonds. In the three fluoromethane complexes, the repulsion effect predominates largely.

A previous theoretical study has shown that the dipole moment of the isolated proton donor CHF_3 lowers if the CH

bond stretches.²⁸ The authors has taken this dipole reduction as evidence that the electrostatic attraction between the proton donor and proton acceptor would likewise decrease by the CH bond stretch. However, a Morokuma partitioning analysis of the energy contributions to the total complexation energy has been performed for the fluoromethanes complexed with water.³⁷ This analysis shows that the electrostatic components of the interaction energies in the $\text{CH} \cdots \text{O}$ and $\text{OH} \cdots \text{O}$ systems are both stabilized by a stretch of the bond, although to a lesser extent for the former systems. It was concluded³⁷ that the forces pushing toward contraction in the $\text{CH} \cdots \text{O}$ systems are slightly larger than the elongation forces, while the opposite is true in the $\text{OH} \cdots \text{O}$ systems.

The present calculations of the occupation of the σ^* antibonding MO reinforce the aforementioned statement. It is also interesting to notice that when CH_4 is complexed with the strong proton acceptor Cl^- , the CH' bond is elongated by 6 mÅ and the two components of the doubly degenerate vibrations CH' vibration are red-shifted by -60 and -34 cm^{-1} .⁶⁹ In this case, the large electronic density on the Cl^- anion will likely result in a charge transfer accompanied by a larger occupation of the $\sigma^*(\text{CH})$ antibonding orbital.

Finally, we would like to mention that we have obtained rather similar results for the interaction between CHF_3 and H_2S . In this case, complex formation results in a contraction of the CH' bond by -1.4 mÅ and a blue shift of the corresponding CH' stretching vibration by $+12 \text{ cm}^{-1}$.

Concluding Remarks. The present work deals with a theoretical study of the interaction between fluoro- and chloromethanes and water. The optimized geometries, interaction energies, and the vibrational properties of the fully or partially deuterated proton donors are discussed.⁷¹ In all the studied complexes, the interaction leads to a contraction of the CH' bond and a blue shift of the corresponding stretching vibration. The most important results of the present work concern actually the NBO analysis. The charge transfer taking place from water to the proton acceptor goes mainly to the lone pair of the halogen atom(s). Interestingly, there is also an increase in the population of the $\sigma^*(\text{CH}')$ antibonding orbital which increases on going from the CH_4 to the CHCl_3 complexes. Comparison of all the properties investigated in the present work allows us to conclude that the nature of the interaction in the $\text{CH} \cdots \text{O}$ and the conventional $\text{OH} \cdots \text{O}$ hydrogen bonds present several similar characteristics, in relative good agreement the statements of ref 37. In many aspects, the $\text{CHCl}_3 \cdot \text{H}_2\text{O}$ complex appears as a precursor of the conventional hydrogen bonds. Water is a proton acceptor of moderate strength. If it is replaced by stronger proton acceptors, the CH' stretching vibration of CHCl_3 becomes red-shifted as mentioned in the Introduction.

Acknowledgment. The authors thank Professor C. Sandorfy for fruitful discussions. E.K. acknowledges the grant of the University of Leuven.

References and Notes

- (1) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Co: San Francisco, London, 1960.
- (2) Green, R. D.; *Hydrogen Bonding by CH groups*; MacMillan: London, 1974.
- (3) Taylor, R. B.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.
- (4) Wiberg, K. B.; Waldron, R. F.; Schulte, G.; Saunders, M. *J. Am. Chem. Soc.* **1991**, *113*, 971.
- (5) Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1990**, 454.
- (6) Steiner, T.; Saenger, W. *J. Am. Chem. Soc.* **1992**, *114*, 10146.
- (7) Steiner, T.; Saenger, W. *Acta Cryst.* **1992**, *B48*, 819.
- (8) Steiner, T. *Cryst. Rev.* **1996**, *6*, 1.

- (9) Chaney, J. D.; Goss, C. R.; Folting, B. D.; Santarsiero, B. D.; Hollingsworth, M. D. *J. Am. Chem. Soc.* **1996**, *118*, 9432.
- (10) Steiner, T.; Kanters, J. A.; Kroon, J. *Chem. Commun.* **1996**, 1277.
- (11) Kariuki, B. M.; Harris, K. M. D.; Philip, D.; Robinson, J. M. A. *J. Am. Chem. Soc.* **1997**, *119*, 12679.
- (12) Kuduva, S. S.; Craig, D. C.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1999**, *121*, 1936.
- (13) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, U.K., 1999, and references therein.
- (14) Jeffrey, G. A. *J. Mol. Struct.* **1999**, *485*, 293.
- (15) Steiner, T. *J. Phys. Chem. A* **2000**, *121*, 1479.
- (16) Houk, K. N.; Menzer, S.; Newton, S. P.; Raymo, F. M.; Fraser Stoddart, J.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 1479.
- (17) Mehta, G.; Vidya, R. *J. Org. Chem.* **2000**, *65*, 3497.
- (18) Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1996**, *118*, 12467.
- (19) Sigel, R. K. O.; Freisinger, E.; Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1998**, *120*, 12000.
- (20) Hobza, P.; Šponer, ; Cubero, E.; Orozco, M.; Luque, J. *J. Phys. Chem. B* **2000**, *104*, 6286, and references therein.
- (21) Hocquet, A.; Ghomi, A. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5351.
- (22) Engdhal, A.; Nelander, B. *Chem. Phys. Lett.* **1983**, *100*, 129.
- (23) DeLaat, A. M.; Ault, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 4232.
- (24) Jeng, M.-L.; DeLaat, A. M.; Ault, B. S. *J. Phys. Chem.* **1989**, *93*, 3997.
- (25) Trudeau, G.; Dumas, J.-M.; Dupuis, P.; Guérin, M.; Sandorfy, C. *Top. Curr. Chem.* **1980**, *93*, 91.
- (26) Budšinsky, M.; Fiedler, Arnold, Z. *Synthesis* **1989**, 858.
- (27) Boldeskul, I. E.; Tsymbal, I. F.; Ryltsev, E. V.; Latajka, Z.; Barnes, A. J. *J. Mol. Struct.* **1997**, *436*, 167.
- (28) Hobza, P.; Havlas, Z. *Chem. Phys. Lett.* **1999**, *303*, 447.
- (29) Karger, N.; Amorin da Costa, A. M.; Ribeiro-Claro, P. J. A. *J. Phys. Chem. A* **1999**, *103*, 8672.
- (30) Mizumo, K.; Imafuji, S.; Ochi, T.; Ohta, T.; Maeda, S. *J. Phys. Chem. B* **2000**, *104*, 11001.
- (31) Allerhand, A.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1963**, *85*, 1715.
- (32) Hussein, M. A.; Millen, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 693.
- (33) Devaure, J.; Turrell, G.; Van Huong, P.; Lascombe, J. *J. Chim. Phys.* **1968**, *65*, 1064.
- (34) Oszczapowicz, J.; Jaroszewska-Manaj, J.; Golimowska, K. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2343.
- (35) Hobza, P.; Spirko, V.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem. A* **1998**, *102*, 2501.
- (36) Masella, Flament, J. P. *J. Chem. Phys.* **1999**, *110*, 7245.
- (37) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411.
- (38) Choi, H. S.; Kim, K. S. *J. Phys. Chem. B* **2000**, *104*, 11006.
- (39) Vargas, R.; Garza, J.; Dixon, D. A.; Hay, B. P. *J. Am. Chem. Soc.* **2000**, *122*, 4750.
- (40) Seiler, P.; Weisman, G. R.; Glendening, E. D.; Weinhold, F.; Jonhson, van B.; Dunitz, J. D. *Angew. Chem.* **1987**, *99*, 1216.
- (41) Szczesniak, M. M.; Chalasinski, G.; Cybulski, S. M.; Cieplak, P. *J. Chem. Phys.* **1993**, *98*, 3078.
- (42) Woon, D. E.; Zeng, P.; Beck, D. R. *J. Chem. Phys.* **1990**, *93*, 7808.
- (43) Alkorta, J.; Maluendes, S. *J. Phys. Chem.* **1995**, *99*, 6457.
- (44) Van Mourik, T.; Van Duijneveldt, F. B. *J. Mol. Struct. (THEOCHEM)* **1995**, *341*, 63.
- (45) Giribet, C. G.; Vizioli, C. V.; Ruiz de Azúa, Contreras, R.; Dannenberg, J. J.; Masunov, A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3029.
- (46) Novoa, J. J.; Mota, F. *Chem. Phys. Lett.* **1997**, *266*, 23.
- (47) Gu, Y.; Kar, T.; Scheiner, S. *J. Mol. Struct.* **2000**, *104*, 11006.
- (48) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.
- (49) Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond. Recent Developments in Theory and Experiments*; North-Holland Publ. Co.: Amsterdam, New York, Oxford, 1976.
- (50) Ratajczak, H.; Orville-Thomas, W. J. *Molecular Interactions*; John Wiley & Sons: Chichester, New York, Brisbane, Toronto, 1980.
- (51) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1979**, *19*, 553.
- (52) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
- (53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ciolowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Repogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (54) Hobza, P.; Havlas, Z. *Theor. Chem. Acc.* **1998**, *99*, 372.
- (55) van Mourik, T.; Price, S. L.; Clary, D. C. *Chem. Phys. Lett.* **2000**, *331*, 253.
- (56) Novoa, J. J.; Tarron, B.; Whangbo, M.-H.; Williams, J. M. *J. Chem. Phys.* **1991**, *95*, 5179.
- (57) Hobza, P.; Sandorfy, C. *Can. J. Chem.* **1984**, *62*, 606.
- (58) Chandra, A. K.; Nguyen, M. T.; Zeegers-Huyskens, Th. *Chem. Phys.* **2000**, *225*, 149.
- (59) Rozenberg, M.; Loewenschuss, A.; Marcus, Y. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2699.
- (60) Gilli, G.; Gilli, P. *J. Mol. Struct.* **2000**, *552*, 1, and references herein.
- (61) Zeegers-Huyskens, Th. *Chem. Phys. Lett.* **1986**, *129*, 172.
- (62) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas-Phase Ion and Neutral Thermochemistry*; *J. Phys. Ref. Data, Suppl. 1*, 1988, 17. Experimental $PA(A^-)$ values of the corresponding anions (kcal mol^{-1}): CH_4 : 418, CH_3F : 409, CH_2F_2 : 389, CHF_3 : 376, CH_3Cl : 396, CH_2Cl_2 : 374, CHCl_3 : 358.
- (63) Ojamäe, L.; Hermansson, K. *J. Phys. Chem.* **1994**, *98*, 4271.
- (64) Pawelka, Z.; Zeegers-Huyskens, Th. *Vibr. Spectrosc.* **1998**, *18*, 41.
- (65) The values of the intensities in the isolated state and in the complex must be likely interchanged in ref 35, Table 2). At any level of calculation, the infrared intensity of the $\nu(\text{CH})$ vibration in CHCl_3 is indeed very low (0.2 to 0.3 km mol^{-1}) and must correspond to the free molecule and the value of 39 km mol^{-1} to the benzene complex.
- (66) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 3399.
- (67) Olivella, S.; Urpi, F.; Vilarrasa, J. *J. Comput. Chem.* **1984**, *5*, 230.
- (68) Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075.
- (69) Wild, D. A.; Loh, Z. M.; Wolyne, P. P.; Weiser, P. S.; Bieske, E. *Chem. Phys. Lett.* **2000**, *332*, 531.
- (70) Schaftenaar, G. MOLDEN, CAOS/CAMM Center of Nijmegen (Nijmegen) 1991.
- (71) All optimization outputs can be provided by the authors on request.