Stabilities of the C−H···O Bonded Complexes of the Haloforms $HCCl_nF_{3-n}$ ($n = 0-3$) with Dimethyl Ether, Oxirane, and Acetone: An Experimental and Theoretical Study

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Complexation enthalpies of the complexes of the haloforms $HCCl_nF_{3-n}$ ($n = 0-3$) with dimethyl ether, oxirane, and acetone have been determined in liquid krypton and/or liquid argon using infrared spectroscopy. The same quantities were derived starting from ab initio complexation energies, calculated at the MP2=FULL/aug-cc-VTZ level, and by correcting these energies for thermodynamic and solvent contributions. The two sets of data are compared and discussed.

Introduction

Because of their importance in various chemical and biochemical areas, weak intermolecular interactions involving C−H···O or C−H···N hydrogen bonds have been the subject of many theoretical and experimental studies.[1−20] Recently, we have investigated, using infrared spectroscopy, the behavior of the C−H stretch in the haloforms $HCCl_nF_{3-n}$ ($n = 0-3$) upon complexation with dimethyl ether (DME), oxirane (OX) and acetone (AC).[21,22] The results show that for these complexes, with one exception, the C−H stretch is blue shifted upon complexation, the shift decreasing from fluoroform to chloroform. The exception is the chloroform complex with DME, for which a small red shift is observed. Ab initio calculations show that for each of the Lewis bases the complexation energies are in the interval between 10 and 20 kJ mol^{-1} and that the energy increases, by 3−5 kJ mol^{-1}, from the fluoroform to the chloroform complex. Very few experimental data on the stabilities of these complexes have been published up to now,[6,23] and consequently, experimental evidence on the correlation of the complexation energies with the blue shift of the C−H stretch is also lacking. It is the purpose of the present contribution to fill this gap by reporting on the complexation enthalpies of the complexes in solution in liquid rare gases, using infrared spectroscopy. The comparison of the experimental data with the ab initio energies was made possible by transforming the latter, first into vapor phase enthalpies by applying statistical thermodynamics, and then into liquid-phase complexation enthalpies by correcting for solvation influences as estimated from Monte Carlo free energy perturbation[24] calculations. Further, the evolution of the ab initio complexation energies in the different series of complexes was analyzed using symmetry adapted perturbation theory.[25]

Experimental Section

The samples of DME, OX, and AC and the haloforms in the series CHF_3−$CHCl_3$, including $CDCl_3$, were obtained commercially (Aldrich Chemical Co.) and were used without further purification. The solvent gases, argon and krypton, were supplied by L'Air Liquide and had stated purities of 99.9999% and 99.998%, respectively.

The infrared spectra were recorded using a Bruker IFS 66v Fourier transform spectrometer, equipped with a Globar source, a Ge/KBr beam splitter, and a LN_2-cooled broad band MCT detector. Interferograms were averaged over 250 scans, Blackman-Harris 3-Term apodized and Fourier transformed with a zero filling factor of 2, to yield spectra at a resolution of 0.5 cm^{-1}. The experimental setup consists of a pressure manifold needed for filling and evacuating the cell and for monitoring the amount of gas used in a particular experiment, and the actual cell.[26] The cell has a path length of 10 mm and is equipped with wedged Si windows.

At similar monomer concentrations the fraction of weak complexes formed increases at lower temperatures. Therefore, initially attempts were made to determine the complexation enthalpies of the complexes studied here in liquid argon (LAr), as this solvent allows lower temperatures than liquid krypton. However, limited solubility, certainly at the lowest temperatures, in that solvent prevented usefull quantitative data to be obtained for complexes containing OX, AC, or $HCCl_3$. Therefore, the enthalpies of the complexes with OX and AC were determined in liquid krypton (LKr), while those of the DME complexes were measured, where possible, in both solvents. Typical monomer mole fractions used were in the range between 0.5×10^{-4} and 3×10^{-4}, and spectra were recorded at temperatures between 93 and 123 K in liquid argon, and between 123 and 153 K in liquid krypton. The complexation enthalpies were determined from these spectra using the Van't Hoff equation corrected for variations of solvent densities with temperature, as described before.[27,28]

Computational Details

Unless stated otherwise, the second-order perturbation calculations were performed using Gaussian03,[29] while BSSE was corrected using the CP-corrected gradient techniques developed by Simon et al.[30,31]

Information on the different attractive and repulsive contributions to the interaction energy was obtained by carrying out Symmetry Adapted Pertubation Theory (SAPT) calculations, using the SAPT2002 program,[25] in combination with GAMESS−US.[32] The underlying theory of SAPT calculations has been reviewed by several authors,[33−40] and it will not be discussed in detail here. The double perturbation approach of the SAPT analysis treats both the intramolecular correlation and the

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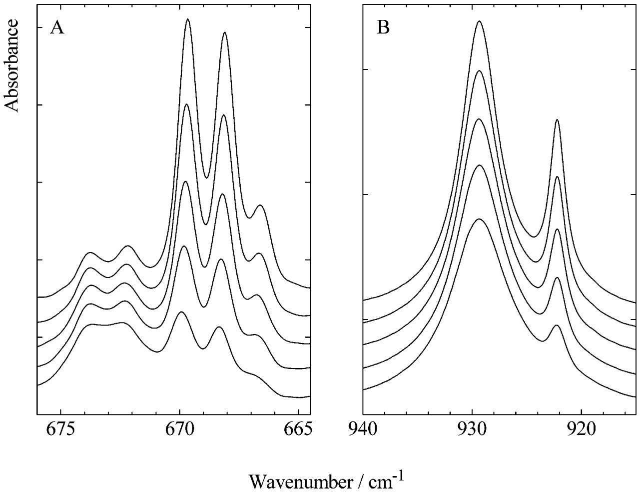

Figure 1. Symmetric CCl_3 stretching (A) and symmetric C−O−C stretching (B) regions for a solution in liquid krypton containing dimethyl ether and chloroform, with mole fractions equal to 2.9×10^{-4} and 1.0×10^{-4}, respectively. From top to bottom the temperature of the solution increases, from 123 to 150 K.

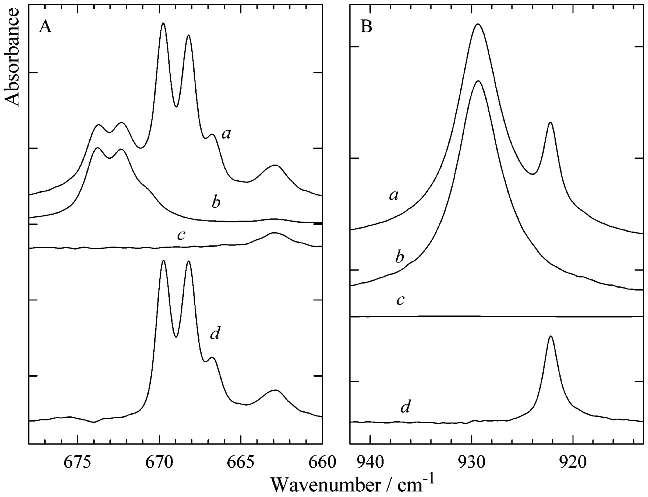

Figure 2. Decomposition of an experimental spectrum obtained for a solution in liquid krypton containing dimethyl ether and chloroform, at 135 K: (A) symmetric CCl_3 stretching region; (B) symmetric C−O−C stretching region. Traces *a* show the original spectra recorded for a solution with mole fractions 2.9×10^{-4} and 1.0×10^{-4} of dimethyl ether and chlorofom, respectively. Traces *b* and *c* are the rescaled monomer spectra showing the contributions of monomer dimethyl ether (*b*) and monomer chloroform (*c*). Traces *d* show the isolated spectra of the CH···O bonded complex obtained by subtracting traces *b* and *c* from traces *a*. The weak feature at 663 cm^{-1} observed in traces *a*, *c*, and *d* is due to a small amount of CO_2 present in the DME sample.

intermolecular interaction as perturbations, and results in a significant number of perturbation contributions.[38] For physical clarity, we have grouped these so that the interaction energy E_{int} can be described as a sum containing electrostatic (el), induction (in), dispersion (di), and exchange (ex) contributions together with a remainder δ in which all contributions not contained in the preceding terms have been collected:

$$E_{int} = E_{el} + E_{in} + E_{di} + E_{ex} + \delta$$

The relation of these terms to the more detailed SAPT terms has been described in the literature.[40]

To correct the experimental complexation enthalpies for solvent effects, solvation Gibbs energies of monomers and complexes were obtained from Monte Carlo perturbation calculations, using a modified version of BOSS 4.1, as described before.[41] The enthalpy of solvation $\Delta_{sol}H$ and the entropy of solvation $\Delta_{sol}S$ in LAr and in LKr were extracted from the Gibbs energies of solvation $\Delta_{sol}G$, using the expressions $\Delta_{sol}S = -\partial(\Delta_{sol}G)/\partial T$ and $\Delta_{sol}H = \Delta_{sol}G + T\Delta_{sol}S$. For each species, the Gibbs energies of solvation were calculated at 11 different temperatures between 88 and 138 K for LAr and between 120 and 175 K for LKr, at a pressure of 28 bar, i.e., the vapor pressure of LAr and LKr at the highest temperatures studied.

Results and Discussion

The application of the Van't Hoff relation to determine the experimental complexation enthalpies, ΔH°_{exp}(LAr) and ΔH°_{exp}(LKr), requires integrated intensities of monomer and complex bands. For the present purpose, band areas of absorption bands were used as integrated intensities. The complexes studied here are weakly bonded. Consequently, complexation shifts are small, which invariably results in important overlap of corresponding monomer and complex bands. To avoid inaccuracies inherently connected to resolving strongly overlapping bands with least squares band fitting, band areas were determined by subtraction techniques. This is illustrated in Figures 1 and 2 for the complex of DME with chloroform. Figures 1A and 1B give the region of $\nu_2^{HCCl_3}$ (symmetric CCl_3 stretching) and of ν_6^{DME} (symmetric C−O−C stretching), respectively, of mixed monomer solutions in LKr, as a function of temperature. Monomer bands can be seen in Figure 1A at 673.8 and 672.2 cm^{-1} (a third band in this region, at 670.9 cm^{-1}, does not give rise to a separate maximum in this figure) and at 929.5 cm^{-1} in Figure 1B. In addition, bands due to the complex are observed at 669.7, 668.1, and 666.6 cm^{-1} (Figure 1A) and at 922.1 cm^{-1} (Figure 1B). From the mixed monomer spectra, rescaled spectra of single monomer solutions, recorded at similar concentrations and at the same temperatures, were subtracted. Rescaling factors were varied until the monomer absorptions were optimally removed. The rescaled monomer spectra, traces *b* and *c*, and the result of the subtraction, traces *d*, are shown for an experiment at 135 K, in Figure 2, parts A and B. It can be seen that also in the single-species spectra in the $\nu_2^{HCCl_3}$ region overlapping bands are present: no attempts were made to resolve these, and the combined areas were numerically integrated, which has the added advantage of decreasing the relative errors on the obtained areas. The Van't Hoff plots obtained for the various complexes are shown in Figure 3. The complexation enthalpies derived from them, ΔH°_{exp}(LKr) and ΔH°_{exp}(LAr), are given in Table 1. The uncertainties quoted on them are 2σ values.

For the $HCClF_2$ and $HCCl_2F$ complexes of DME the complexation enthalpies were determined in both solvents. The uncertainty ranges for both solvents overlap, showing that the complexation enthalpy of a complex does not vary greatly from solvent to solvent.

The ΔH°_{exp}(LAr) in the series $HCCl_nF_{3-n}$ ($n = 0-2$) for the same Lewis base are nearly identical; the ΔH°_{exp}(LKr) of the $HCClF_2$ and $HCCl_2F$ complexes are also very close, with the enthalpy for the $HCCl_3$ complex but slightly less. The ΔH°_{exp}(LKr) for the OX complexes fall within a narrow range, the largest difference being a mere 1.2 kJ mol^{-1}. It can also be seen that the evolution over the series is irregular: the first three complexes have very similar complexation enthalpies, while the $HCCl_3$ complex is slightly less stable. Thus, the behavior of the OX complexes is similar to that of the DME complexes. Only for the AC complexes does a consistent evolution

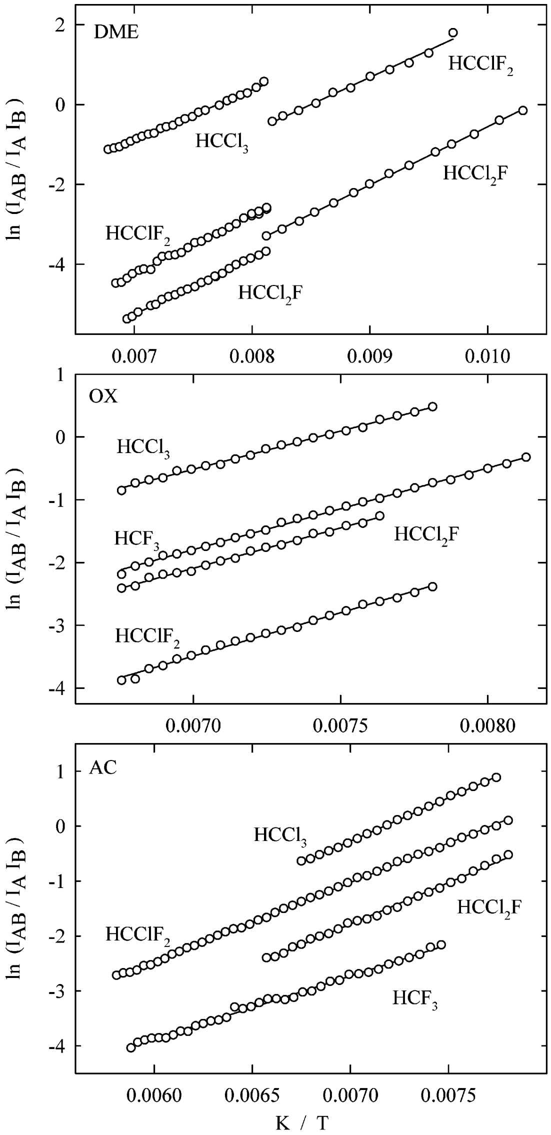

Figure 3. Van't Hoff plots obtained for the CH···O bonded complex between dimethyl ether and chloroform observed in liquid krypton.

emerge: the complexes become more stable from fluoro- to chloroform, albeit it that the total change is limited to some 25% of the $\Delta H^\circ_{\text{exp}}$(LKr) for the weakest complex.

Some insight into the above experimental results was gained by deriving theoretical values for the complexation enthalpies, starting from ab initio complexation energies. To this end, the structures of monomers and complexes were systematically optimized at the MP2=FULL/6-31++G(d,p) level. The resulting complexes are shown in Figures 4−6. For the OX/fluoroform complex our result agrees with the ab initio structure reported recently.[6] For all complexes, the main interaction occurs between the haloform hydrogen atom and the oxygen atom of the Lewis base. In all cases, the hydrogen bond is nonlinear, the O···H−C angle varying in the intervals 156.2−171.1, 124.2−148.7, and 155.3−163.2° for the complexes with DME, OX, and AC, respectively. This nonlinearity is the consequence of secondary interaction of some of the halogen atoms of the haloform with some of the hydrogen atoms of the base. For the haloforms containing two different halogens, two different secondary interactions can occur, giving rise, in a number of cases, to two stable conformers of the complex. The exceptions are the complexes of HCCl$_2$F with DME and AC, for which only one stable conformer was calculated.

Complexation energies of the optimized structures are given in Table 1. The influence of basis set saturation on the energies was investigated by performing, at the optimized geometries, single point energy calculations with the MP2=FULL/aug-cc-pVTZ basis set. These energies are also given in Table 1. It can be seen that the complexation energy for the expanded basis set is always higher than for the 6-31++G(d,p) basis. For the fluoroform complexes the correction varies between 3 and 8% of the lower value, and the increase tends to become more important in the series of the haloforms, the corrections falling between 12 and 22% for the chloroform complexes. This can be interpreted to mean that for the fluoroform complexes the ΔE is close to convergence already for the smaller basis set, but becomes increasingly less converged toward the chloroform complexes. This imposes the conclusion that the complexation energies for the expanded basis set are somewhat underestimated, by an amount increasing from fluoroform to chloroform.

For each of the Lewis bases, both sets of energies show an increasing complexation energy, by approximately 20% for the expanded basis set, from fluoroform to chloroform. Despite differences in the secondary interactions between the complexes in each series, the trend is quite regular. For instance, it can be seen that when two conformers are found, their energies both are between the values for the preceding and the following complex of the same series. This shows that the secondary interactions play a minor role in the determination of the stability.

In a first step toward a comparison with the experimental data, the complexation energies were transformed into vapor phase enthalpies by correcting for zero point and thermal influences using rotational constants and harmonic vibrational frequencies obtained from the ab initio calculations. The corrections were calculated at the temperatures at which the complexation enthalpy was determined experimentally, i.e., at 110 K for the LAr solutions and at 135 K for the LKr solutions. The resulting vapor phase complexation enthalpies, ΔH°(g), and entropies, ΔS°(g), are also given in Table 1. It can be seen that this transformation largely leaves the stability trend intact.

In the next step, the standard solvation enthalpies, $\Delta_{\text{sol}}H^{\text{o}}$, and entropies, $\Delta_{\text{sol}}S^{\text{o}}$, were calculated. Their detailed values are given in Table 2. The data make clear that the solvation enthalpy for some species can be relatively important, up to −53.3(2) kJ mol^{-1} for the complex of AC with HCCl$_3$. The same data also show that in the calculation of the solvation effect on the complexation enthalpy the contribution of the complex is nearly canceled by those of the monomers. Hence, the uncertainty on that sum is relatively more important than for the individual species. The uncertainties quoted in Table 2 are very small, and they propagate, despite the magnifying effect, into an uncertainty on the sum which is still quite acceptable. A point which must be considered here is that the uncertainties in Table 2 are based on the analysis of the Monte Carlo simulations and do not account for the shortcomings of the model. In the latter, the binary collision approximation was assumed, a relatively simple intermolecular interaction potential was adopted, and the species are introduced into the solvent as rigid structures. At first sight, accounting for all this evidently would dramatically increase the uncertainty for the solvent effect on the complexation enthalpy. However, it must be realized that the shortcomings of the model will cause errors in the same direction for all species involved in a complexation reaction. Therefore, it may be expected that these errors will, for an important fraction, cancel when the correction for ΔH(g) is calculated. All in all, it must be taken into account that a realistic uncertainty for the solvent effect on a complexation enthalpy will certainly be larger

TABLE 1: Complexation Energies and Enthalpies of the Complexes in Gas, Liquid Argon, and Liquid Krypton

	ab initio		$T = 110$ K				$T = 135$ K			
			calculated		experimental		calculated		experimental	
	ΔE^{a}	ΔE^{b}	$\Delta H°$(g)	$\Delta H°$(LAr)	$\Delta H^{\circ}_{\mathrm{exp}}$(LAr)	$\Delta\nu_1{}^{c}$	$\Delta H°$(g)	$\Delta H°$(LKr)	$\Delta H^{\circ}_{\mathrm{exp}}$(LKr)	$\Delta\nu_1{}^{c}$
DME										
HCF_3	−17.3	−17.9	−15.7	−11.2(4)	−12.5(2)	17.7				
$HCClF_2$	−17.5	−18.9	−16.7	−11.9(6)	−12.6(1)	14.0	−16.5	−11.1(3)	−12.5(1)	14.0
$HCClF_2$	−17.5	−18.5		−11.5(6)			−16.1	−10.7(3)		
$HCCl_2F$	−18.1	−20.0	−16.3	−10.4(5)	−12.9(6)	4.8	−17.4	−9.2(4)	−12.2(2)	4.8
$HCCl_3$	−19.0	−21.2	−17.7				−18.5	−8.5(4)	−11.3(1)	−8.3
acteone										
HCF_3	−17.2	−18.6					−16.0	−10.8(2)	−10.9(3)	24.1
$HCClF_2$	−17.1	−19.6					−17.0	−10.5(2)	−12.5(1)	20.7
$HCClF_2$	−17.3	−19.4					−17.8	−11.5(2)		
$HCCl_2F$	−17.9	−20.4					−17.7	−9.6(2)	−12.9(1)	14.2
$HCCl_3$	−18.6	−22.6					−19.8	−10.8(3)	−13.7(1)	1.3
oxirane										
HCF_3	−16.9	−18.2					−16.0	−10.0(2)	−11.6(2)	26.7
$HCClF_2$	−17.1	−19.6					−17.3	−11.0(1)	−12.0(4)	24.1
$HCClF_2$	−17.3	−19.5					−17.7	−10.8(1)		
$HCCl_2F$	−17.6	−20.4					−18.0	−9.7(1)	−11.8(3)	15.5
$HCCl_2F$	−17.9	−21.0					−18.9	−10.9(2)		
$HCCl_3$	−18.5	−21.4					−18.8	−9.4(2)	−10.8(3)	0.6

[a] CP-corrected, MP2=FULL/6-31++G(d,p). [b] CP-corrected, MP2=FULL/aug-cc-pVTZ. [c] Observed complexation shift of haloform ν_1.

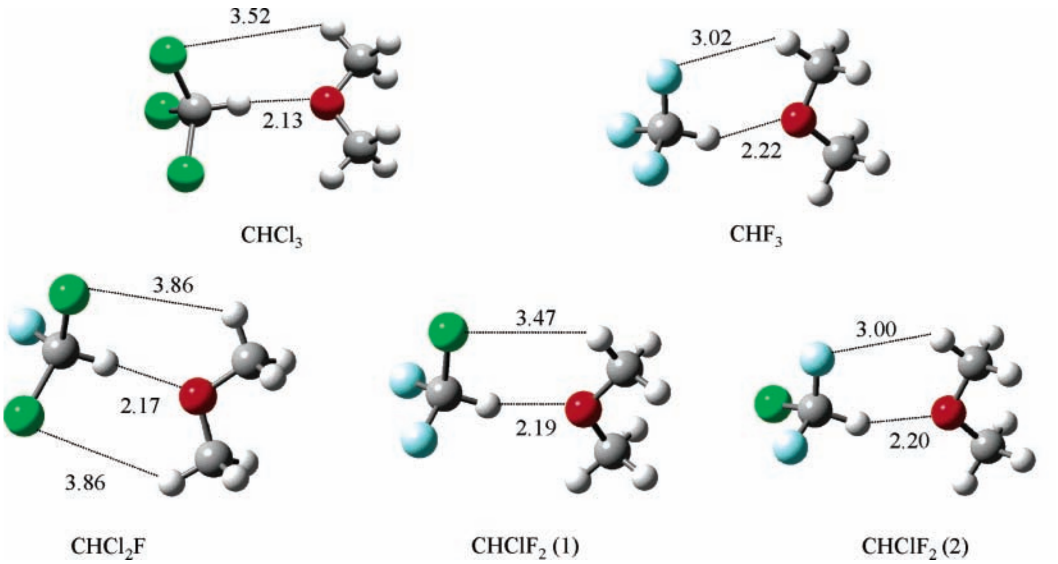

Figure 4. Perspective view of the ab intio structures of the stable conformers of the complexes of dimethyl ether with the haloforms $HCCl_nF_{3-n}$. Distances indicated are in ångstrom.

than that calculated from the data in Table 2. Sufficient experimental data on solvation enthalpies of individual species in liquid krypton is lacking, which prevents that such more realistic errors can be estimated. Therefore, in what follows we will tabulate uncertainties on complexation enthalpies that are based on the data in Table 2.

In line with expectations, the solvation characteristics of OX and its complexes are rather similar to the corresponding values for the DME complexes. In the series of the monomer haloforms the solvation enthalpy increases from fluoroform to chloroform, i.e., increases with the bulk and polarizability of the compounds in the series. A similar behavior is observed for the different haloform complexes of each of the bases. It can also be seen that the solvation enthalpy for each complex is smaller than the sum of the corresponding monomer enthalpies. This difference is readily explained by the loss of solvation when two monomers form a complex, and it implies that the complexes are destabilized by solvation.

Correcting the vapor phase complexation enthalpies for solvation using the $\Delta_{\mathrm{sol}}H^{\mathrm{o}}$ from Table 2 results in complexation enthalpies for the liquid rare gas solutions. These data are also given in Table 1.

A first comparison of experimental with theoretical solution enthalpies in Table 1 shows that there is a satisfactory order-of-magnitude agreement. For instance, for the OX complexes the complexation energies are in the −18.2 to −21.4 kJ mol^{-1} range, which reduce to $\Delta H°$(LKr) between −9.1(2) and −11.4(2) kJ mol^{-1}, with their experimental counterparts falling between −10.8(3) and −12.0(4) kJ mol^{-1}. Similar comparisons hold for the DME and AC complexes.

One of the reasons why this study was set up was to see if in the haloform series of complexes a systematice stability trend could be detected. A more detailed analysis of the data in Table 1 from that point of view reveals the results are somewhat disappointing. For the OX and AC complexes, the experimental complexation enthalpies have consistently been obtained in the same solvent, and therefore, these series lend themselves best for a comparison with calculations.

In the series of haloforms the transformation from ab initio energies to vapor phase enthalpies maintains the stability order,

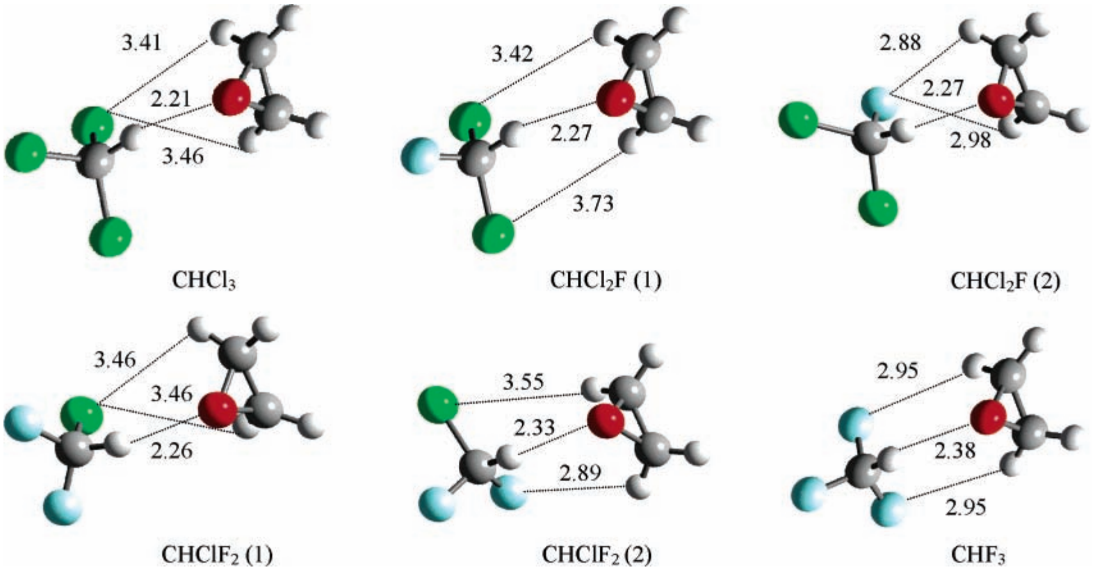

Figure 5. Perspective view of the ab intio structures of the stable conformers of the complexes of oxirane with the haloforms $HCCl_nF_{3-n}$. Distances indicated are in ångstrom.

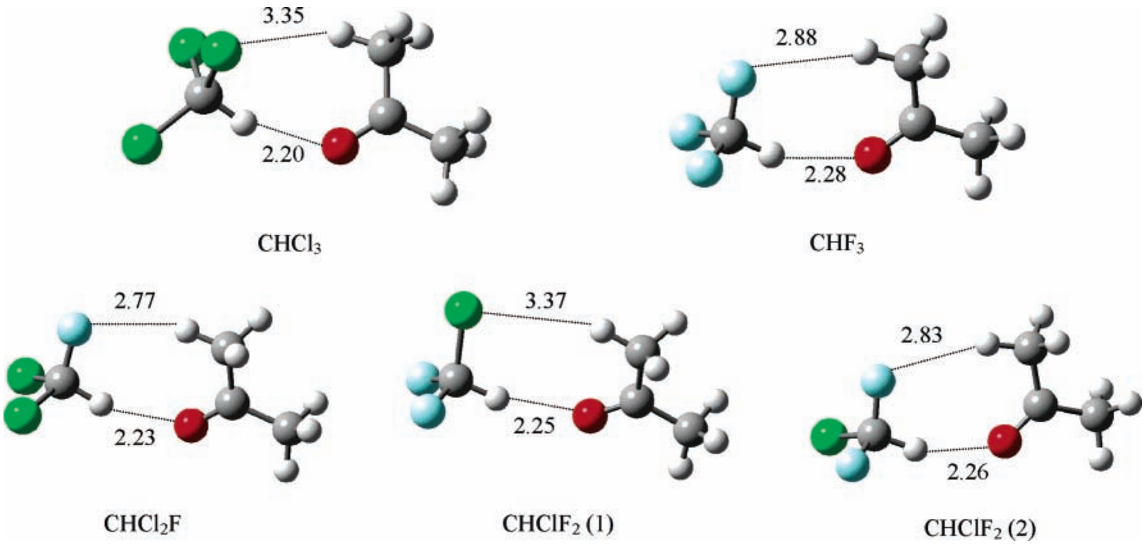

Figure 6. Perspective view of the ab intio structures of the stable conformers of the complexes of acetone with the haloforms $HCCl_nF_{3-n}$. Distances indicated are in ångstrom.

although the total range of values is decreased, by more than 10% for the OX complexes, and by 5% for the AC complexes. The situation changes, however, when the vapor phase values are transformed into solution values. For the discussion below it will be assumed that when two stable conformers of a same complex have been predicted, the one with the largest complexation enthalpy corresponds to the one observed experimentally. Hence, our discussion will consider only these more stable conformers.

For the OX complexes the calculations predict a (weak) increase in the complexation enthalpy, from $-10.0(2)$ to $-11.4(2)$ kJ mol^{-1}, which is not confirmed by experiment, the $\Delta H^{\circ}_{\text{exp}}$(LKr) for these complexes showing only statistically insignificant differences. In agreement with predictions, the chloroform complex is found to be less stable, albeit that the observed decrease to $-10.8(3)$ kJ mol^{-1} is less than that calculated, to $-9.1(2)$ kJ mol^{-1}.

For the AC complexes the calculations predict a somewhat irregular evolution of the complexation enthalpies that vary by not more than 0.6 kJ mol^{-1}. This result, again, is not consistent with the experimental results, which show a systematic increase, from $-10.9(3)$ to $-13.7(1)$ kJ mol^{-1}.

From the above is clear that despite the order-of-magnitude agreement, the calculations fail to reproduce the finer details of the experimental results. There may be several reasons for this, including the lack of more realistic errors for the calculated complexation enthalpies, but it appears as if the incomplete convergence of the ab initio complexation energies plays an dominant role. It was pointed out above that from fluoroform to chloroform these energies, given in Table 1, are increasingly further away from the true values. This accounts for the fact that in most cases, including the DME complexes, the calculated enthalpy is smaller than the experimental value, with often the difference being more important for the haloform with a higher number of chlorine subtituents, and it also accounts for the lack of a clear increase, which is observed experimentally, in the ΔH°(LKr) for the acetone complexes.

We have previously discussed the complexation shift of the haloform C−H stretch in the same series of complexes, under identical circumstances, i.e., in solution in LAr and LKr.[21,22,42]

TABLE 2: Standard Enthalpies of Solvation $\Delta_{sol}H°$, in kJ mol^{-1}, and Standard Entropies of Solvation $\Delta_{sol}S°$, in J K^{-1} mol^{-1}, Calculated Using the Free Energy Perturbation Theory

	liquid krypton		liquid argon	
	$\Delta_{sol}H°$	$\Delta_{sol}S°$	$\Delta_{sol}H°$	$\Delta_{sol}S°$
DME	−23.7(1)	−66.1(6)	−23.4(3)	−80.8(24)
OX	−23.3(1)	−65.7(4)		
AC	−30.9(1)	−86.2(8)		
HCF_3	−12.2(1)	−34.1(6)	−12.6(2)	−43.5(14)
$HCClF_2$	−18.9(2)	−52.0(13)	−19.9(5)	−74.0(5)
$HCCl_2F$	−25.0(1)	−67.1(7)	−26.7(1)	−100.0(13)
$HCCl_3$	−31.6(1)	−87.0(9)		
DME·HCF_3			−31.5(3)	−107.4(24)
DME·$HCClF_2$	−37.2(3)[a]	−106.5(17)	−38.5(5)	−144.5(43)
	−37.2(4)[a]	−107.5(24)	−38.5(4)	−145.1(38)
DME·$HCCl_2F$	−40.5(3)	−112.1(2)	−42.8(3)	−158.3(27)
DME·$HCCl_3$	−45.3(1)	−123.9(9)		
OX·HCF_3	−29.5(1)	−80.0(10)		
OX·$HCClF_2$	−36.0(1)	−98.5(8)		
	−35.4(1)	−95.6(7)		
OX·$HCCl_2F$	−40.5(9)	−108.6(6)		
	−40.8(1)	−110.5(8)		
OX·$HCCl_3$	−45.2(1)	−120.8(8)		
AC·HCF_3	−38.0(1)	−104.5(6)		
AC·$HCClF_2$	−43.5(2)	−119.1(11)		
	−43.8(1)	−119.2(7)		
AC·$HCCl_2F$	−48.4(1)	−132.1(10)		
AC·$HCCl_3$	−53.3(2)	−145.8(15)		

[a] In cases where two values are given, they refer to the two different stable conformers of the complex.

These shifts have been collected in Table 1. It can be seen that for each Lewis base the shift varies systematically from a pronounced blue shift for the fluoroform complex to a small blue shift, or even a small red shift. For each of the Lewis bases the systematic decrease of the $\Delta\nu_1^{haloform}$ from fluoroform to chloroform correlates with the systematic increase in the ab initio complexation energy. As is clear from Table 1, however, the behavior of the $\Delta H°$(LKr) and the $\Delta H°_{exp}$(LKr) is somewhat inconsistent and, therefore, their correlation with the $\Delta\nu_1^{haloform}$ is weak. These conclusions are in line with the fact that the energies more directly reflect the characteristics of the hydrogen bond in the complex, while the enthalpies depend in a complicated way on the interactions of the complete species with the solvent.

Attempts to rationalize the systematic trends in the complexation energies of the haloform series were made via a SAPT analysis. The results, in terms of the contributions discussed above, are given in Table 3. The rightmost column contains the net evolution Δ from fluoroform to chloroform complex for each contribution. The evolution of the individual terms in the series from fluoroform to chloroform can be rationalized from the increase in polarizability of the haloform and from the observation that, as shown in Figures 4−6, the intermolecular distance R decreases. The increase in electrostatic attraction E_{el} from HCF_3 to $HCCl_3$ complexes is a consequence of the decreasing value of R, the effect being modulated by the variations in the haloform multipole moments. The increase in haloform polarizability causes the increase in induction, E_{in}, and dispersion, E_{di}, attractions, while the increase of the exchange repulsion, E_{ex}, finds it cause in the decrease of R. The sum of the individual terms can be seen in Table 3 to lead to a small increase of the complexation energy for each Lewis base. The data in Table 3 show that the increases in the attractive terms are more or less evenly distributed over electrostatic, induction and dispersion interactions for the DME and for the OX complexes. Only for the AC complexes is the electrostatic value of Δ significantly smaller that those of the other two attractive terms. Combined with the evolution in exchange repulsion, it follows that the increased stability of the complexes is a phenomenon which cannot be explained in terms of a single contribution.

TABLE 3: Contributions, in kJ mol^{-1}, to the SAPT Interaction Energy for the Complexes of Dimethyl Ether, Acetone, and Oxirane with Haloforms $HCCl_nF_{3-n}$ (n = 0−3)[a]

	dimethyl ether				
	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$	Δ
E_{el}	−23.61	−23.61	−24.62	−25.87	−2.26
E_{in}	−6.82	−7.40	−8.43	−9.55	−2.73
E_{di}	−7.89	−8.78	−9.97	−11.04	−3.15
E_{ex}	22.36	23.99	27.0	30.14	+7.78
δ	−1.86	−2.13	−2.41	−2.95	−1.09
E_{int}	−17.82	−17.93	−18.43	−19.27	−1.45

	Oxirane						
	HCF_3	$HCClF_2$[b]	$HCClF_2$[c]	$HCCl_2F$[b]	$HCCl_2F$[c]	$HCCl_3$	Δ
E_{el}	−23.16	−23.36	−23.56	−24.33	−23.50	−25.70	−2.54
E_{in}	−5.99	−7.72	−7.96	−8.44	−8.44	−10.11	−4.12
E_{di}	−9.05	−10.33	−9.92	−11.23	−11.54	−11.97	−2.92
E_{ex}	22.34	24.44	24.98	27.15	26.50	31.83	+9.49
δ	−1.25	−1.51	−1.86	−1.95	−1.85	−2.89	−1.64
E_{int}	−17.11	−18.48	−18.32	−18.81	−18.62	−18.84	−1.73

	acetone					
	HCF_3	$HCClF_2$[b]	$HCClF_2$[c]	$HCCl_2F$	$HCCl_3$	Δ
E_{el}	−24.33	−23.37	−24.29	−25.14	−24.95	−0.62
E_{in}	−6.93	−7.12	−7.57	−8.62	−9.55	−2.62
E_{di}	−7.64	−8.44	−8.69	−9.90	−11.72	−4.08
E_{ex}	21.12	21.69	23.09	26.30	28.97	+7.85
δ	−1.63	−1.85	−1.87	−2.28	−2.50	−0.87
E_{int}	−19.42	−19.09	−19.33	−19.64	−19.75	−0.33

[a] All SAPT calculations were carried out using the 6-31++G(d,p) basis set and using the MP2=FULL-6-31++G(d,p) equilibrium geometry derived from the CP-corrected PES. [b,c] Different stable conformers of the same complex.

For the AC/chloroform complex, the complexation enthalpy has previously been derived, a considerable number of years ago, from a study of the infrared spectra at temperatures in the 180−300 K range, of solutions of both compounds in *n*-hexane.[23] In that study, no separate bands due to a 1:1 complex were observed, but information on relative populations of monomers and complex was derived from an analysis of the infrared intensities of the chloroform ν_1, which changes its absorption by a factor 20 from monomer to complex.[23] The complexation enthalpy derived was −14.6(8) kJ mol^{-1}. This value is somewhat higher than the present result in liquid krypton, −10.8(3) kJ mol^{-1}. However, taking into account the difference in temperature range, and the difference in environment, certainly in view of the above discussion of the importance of solvation, the agreement may be termed satisfactory.

The stability of the OX/fluoroform complex has recently been estimated using data from the vapor phase microwave study of the complex.[6] Using a well-known theory[43,44] that links the stretching force constant of the complex, which is treated as if consisting of two rigid monomers, to the first-order centrifugal distortion constant D_J, and by subsequently relating that force constant to the well depth of a Lennard-Jones potential, the authors derive a dissociation energy of −6.7 kJ mol^{-1}. This value differs by more than a factor two from their BSSE corrected ab initio value of −15.7 kJ mol^{-1}, calculated at the MP2/6-311++G(2df,p) level. The authors expressed the believe that their experimentally related value of −6.7 kJ mol^{-1} is more reliable than the theoretical value. From the discussion in the previous paragraphs we think there is reason to question this believe. To expand the discussion to several complexes studied here, we have applied the same model to the fluoroform complexes of the present Lewis bases, starting from the ab inito value of the centrifugal distortion constant to derive the dissociation energy, E_D. The values found are −5.9, −11.5, and −9.1 kJ mol^{-1} for the OX, DME, and AC complexes, respectively. The value for the OX complex is slightly less than that derived by Alonso et al.,[6] which must be due to the use in our calculation of an ab initio value for D_J. The difference being small, it can be assumed that for the other complexes the ab initio D_J are similarly close to the experimental values, which hitherto have not been measured experimentally.

It was discussed above that the comparison with the experimental complexation enthalpies suggests that the expanded basis set ab initio energies in Table 1 most likely are somewhat smaller than the true dissociation energies. The above E_D values, however, are significantly smaller than the tabulated ab initio values, Hence, it follows that the applied model does not predict reliable dissociation energies. Several reasons can be given for the failure of the model. One possibility would be that the equations derived assume that the principal inertial axis *a* is parallel to the “bond” connecting the two monomers, which in this case is the line connecting the centers of mass of the monomers involved. This assumption, however, appears rather plausible, as the angles between the “bond” and the *a* axis are small, being 7.1, 0.4, and 1.2° for the OX, DME, and AC complexes, respectively. A more likely cause lies in the centrifugal distortion constants used. It has been pointed out in the literature that the model works only when all distortions other than that due to the stretching of the complex can be neglected.[43] For the present complexes, all ab initio van der Waals frequencies are very small, suggesting important intermonomer angular flexibility of the complexes. Therefore, the van der Waals bending modes must have significant contributions to the experimentally observed D_J, used by Alonso et al.,[6] as well as to the ab initio values used in our calculations. Because D_J is inversily related to the stretching force constant of the complex, and, subsequently, to E_D, this must lead to an underestimation of the dissociation energy, which is the case here.

A final note on the centrifugal distortion model is that its weak perfomance appears not to be restricted to the present class of compounds: for the complexes of HCl with ethene and with cyclopropane, the model derives well depths of 575 and 855 cm^{-1},[44] respectively, while the dissociation energies derived from complexation enthalpies in liquid argon are 1062(42) and 1212(50) cm^{-1}, respectively.[45,46]

Conclusions

In this study, we have reported on the ab initio complexation energies and on the complexation enthalpies in liquid rare gases of the complexes of the haloforms $HCCl_nF_{3-n}$ ($n = 0-3$) with DME, OX and chloroform. It was found that for each of the Lewis bases the ab initio complexation energies increases slightly from the fluoroform to the chloroform complex. An SAPT analysis of these energies shows that this increase is a balance between increased attractive and repulsive contributions, the former sligthly more important than the latter. This analysis also shows that each of the attractive terms contributes significantly to the increased stability, so that it is not straightforward to pinpoint the causes of the trend.

The experimental complexation enthalpies measured in liquid krypton and liquid argon vary less regularly in the same series. Monte Carlo perturbation calculations of the solvation of the species involved shows that the irregularities reflect the behavior of the solvation enthalpies and not of the complexation energies.

Finally, the less regular evolution of the complexation enthalpies contrasts with the regular evolution of the complexation shifts of the haloform C−H stretch, showing that the correlation between the two properties must be weak.

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