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Blue Shifting Hydrogen Bonding in the Complexes of Chlorofluoro Haloforms with Acetone-d_6 and Oxirane-d_4

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The nature of the C−H···O hydrogen bond has caught the attention of theoreticians and experimentalists alike.[1] Ab initio calculations on the weaker systems of this type have been consistent in predicting a shortening of the C−H bond length, accompanied by a blue shift of the CH stretch fundamental, and a decrease of the infrared intensity of that mode. From the latter properties, the blue shifting hydrogen bond derives its name. As compared to the vast amount of vibrational data on classical, red shifting hydrogen bonds, extremely few experimental vibrational data on the blue shifting variety are available. A systematic series in which the phenomenon was recently observed is the one of the hydrogen bonded complexes of the haloforms $HCCl_nF_{3-n}$ ($n = 0-3$) with dimethyl ether.[2] These complexes were studied in cryosolutions in liquid krypton, using infrared spectroscopy. It was found that from fluoroform to chloroform the haloform CH stretch changes in a systematic way from blue shifting to red shifting, with its infrared intensity changing from a decrease to an increase in comparison with that of the monomer haloform.

The present study of the infrared spectra of the complexes of the same haloforms with two further oxygen donors, acetone and oxirane, serves to show that this type of hydrogen bonding is more common than usually assumed. The complexes were investigated in liquid krypton, under the same experimental conditions as used for the dimethyl ether complexes.[2] Normal acetone and oxirane give rise to several infrared active modes in the C−H stretching region. To simplify the detection of the haloform ν_{CH}, therefore, the fully deuterated versions of these electron donors were used.

The complexation shifts $\Delta\nu_{CH} = \nu_{complex} - \nu_{monomer}$ of the haloform CH stretch have been summarized in Table 1. It can be seen that in all cases a blue shift is observed, which increases, for either Lewis base, with the number of fluorine atoms in the haloform. This is similar to the behavior of the dimethyl ether complexes, with the exception that for the present bases also the chloroform complexes give a blue shift. The ratio of the infrared intensities of the ν_{CH} in complex and monomer, $\epsilon_{complex}/\epsilon_{monomer}$, has also been measured, in the same way as before.[2] The results are also given in Table 1. For the tri- and dichloro haloforms, the intensity increases upon complexation, while for the other two, a decrease is found, which is the more pronounced for the fluoroform complexes. These results confirm that there is no strict coupling between the blue shift and the intensity decrease.[2]

For the complexes described here, frozen core ab initio calculations at the MP2/6-31G(d) level have been made. The predicted complexation shifts and intensity ratios for the relevant ν_{CH} have been collected in Table 1, together with the calculated complexation energies ΔE. It is clear that for all but one complex that a blue shift is predicted. The shifts reproduce the experimental trend with increasing fluorination, albeit that the quantitative agreement leaves to be desired. For the exception, chloroform/oxirane, a small blue shift of 1.3 cm^{-1} has been observed, while a much more significant red shift of −8.5 cm^{-1} is predicted. In terms of absolute values of the shifts, this situation is analogous to the chloroform/acetone case, where the calculated shift overshadows the experimental one by an order of magnitude. This appears to indicate that with calculations at the present level, the more subtle intricacies of hydrogen bonding are not accurately predicted. It is felt that the experimental data reported in this communication may serve as benchmarks, not only for more sophisticated ab initio calculations, but also for other theoretical models attempting to rationalize the blue shifting phenomenon.

Table 1. Complexation Shifts $\Delta\nu_{CH}$, in cm^{-1}, Infrared Intensity Ratios $\epsilon_{complex}/\epsilon_{monomer}$, and Complexation Energies ΔE, in kJ mol^{-1}, for the Complexes of Acetone and Oxirane with HCF_3, $HCClF_2$, $HCCl_2F$, and $HCCl_3$

	experiment[a]		ab initio [b]		
complex	$\Delta\nu_{CH}$	ϵ_c/ϵ_m	$\Delta\nu_{CH}$	ϵ_c/ϵ_m	ΔE
$CD_3COCD_3{\cdot}HCCl_3$[c]	0.6	58 (4)	7.2	2738.3	17.9
$CD_3COCD_3{\cdot}HCCl_2F$	15.5	3.8 (2)	19.2	6.35	16.3
$CD_3COCD_3{\cdot}HCClF_2$	24.1	0.61 (4)	21.9	0.285	15.0
$CD_3COCD_3{\cdot}HCF_3$	26.7	0.08 (1)	38.9	0.080	13.9
$C_2D_4O{\cdot}HCCl_3$	1.3	69 (7)	−8.5	2522.7	18.0
$C_2D_4O{\cdot}HCCl_2F$	14.2	4.5 (2)	14.9	21.44	16.8
$C_2D_4O{\cdot}HCClF_2$	20.7	0.48 (2)	23.1	0.204	15.8
$C_2D_4O{\cdot}HCF_3$	24.1	0.13 (1)	49.3	0.316	13.5

[a] Solutions in LKr, at 135 K. [b] CP-corrected calculations performed using Gaussian 98.[4] [c] Previous results obtained for the complex between acetone and $HCCl_3$ have been reviewed by Fell et al.[3] The results reported here and the results described in ref 3 agree well with each other.

The ab initio calculations on the acetone complexes converge on structures in which a C−halogen bond of the haloform is eclipsed with a C−H bond of acetone, while for the oxirane complexes, the converged structure has a C−halogen bond that is staggered between two adjacent C−H bonds of oxirane. These structures suggest that secondary halogen/hydrogen interactions influence the stability of the complexes. However, the barriers hindering internal rotation of the haloform around its C−H bond in the complex are on the order of 0.1−0.3 kJ mol^{-1}, so that, at least for the present complexes, the contributions of the secondary interactions to the ΔE are small; that is, the stabilities of the complexes are largely characteristic for the strength of the C−H···O hydrogen bond. The data in Table 1 indicate that for each Lewis base, the blue shift increases with decreasing stability of the complex. This is remarkable, because straightforward extrapolation to complexes that are weaker than the present ones leads to the contradiction that the larger shift should be observed for a complex with zero strength, that is, for the monomer. The reason for the remarkable correlation between shift and stability in Table 1 reflects the fact that the

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observed shift is the result of a subtle interplay between contributions due to the attractive and the repulsive terms in the interaction potential between Lewis acid and base, which has recently been shown to be the case.[1a,d] The above contradiction makes clear that for the very weak complexes, the blue shifting trend must be reversed. Ab initio calculations on the complexes of fluorinated methanes with water appear to corroborate this.[1k] That series starts with the haloform which gives rise to the weakest complex in our series, and the stability decreases with decreasing fluorination of the methane. Apart from the global minima of the potential hypersurface, the authors also explicitly consider conformers of the complex with linear hydrogen bonds, in which secondary fluorine/hydrogen interactions are impossible. For these conformers, the authors predict that the interaction energy decreases from fluoroform to methane, while the ν_{CH} blue shift increases from HCF_3 to $HCDF_2$, but then systematically decreases for HCD_2F and HCD_3. Our understanding of the blue shifting phenomenon would undoubtedly benefit from an experimental verification of such a reversal.

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