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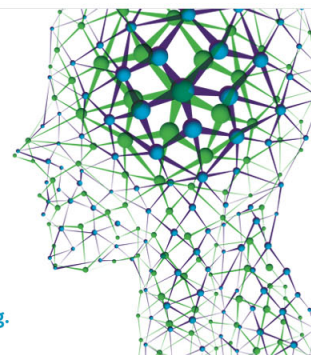
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NOTES

On the microscopic interaction of para-chlorofluorobenzene with water

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The spectroscopic investigation of microsolvated molecules provides important structural information for the understanding of solvation phenomena on a microscopic level.¹ We report on an IR/R2PI (Infrared/Resonant Two-Photon Ionization) depletion experiment^{2–4} of the system para-chlorofluorobenzene with water (pClFB/H₂O), which supplements recently reported results on pClFB/CH₃OH.⁵ In addition, the corresponding spectra of chlorobenzene (ClB)/H₂O have been measured. We observed two cluster isomers for the pClFB/H₂O (1:1) complex and report their structural characterization, which is compared with *ab initio* results of the IR frequency shifts. This assignment is supported by the experimental results on monosubstituted halobenzene/H₂O clusters.⁶

The experimental setup for the R2PI and IR/R2PI spectroscopy experiments has been described in detail in previous contributions.^{5,6} The mass-selective UV spectra (R2PI spectra) of the (1:1) clusters of pClFB/H₂O and ClB/H₂O exhibit blueshifted bands ($\Delta\nu_{UV}$), corresponding to the 0_0^0 electronic transitions of the bare chromophores. These band positions are listed in Table I together with a tentative assignment, based on the IR spectroscopic data. The IR spectra for pClFB/H₂O obtained by means of IR/R2PI depletion spectroscopy, corresponding to vibrational spectra in the OH-stretch region of water, are depicted in Figs. 1(b)–1(d) together with the spectra of fluorobenzene (FB)/H₂O [Fig. 1(a)]⁶ and ClB/H₂O [Fig. 1(e)]. It can be seen that the pClFB/H₂O results can be related to two isomers, I and II, respectively. Isomer I, with $\Delta\nu_{UV}$: 145 cm⁻¹, is weakly redshifted [Fig. 1(b)] compared to free water, whereas isomer II, with $\Delta\nu_{UV}$: 195 and 268 cm⁻¹, is strongly redshifted [Figs. 1(c) and 1(d)]. The relevant IR spectroscopic data are summarized in Table I.

A detailed description of the computational methodology has been given in previous accounts.^{7,8} The *ab initio* calculations were typically carried out at the MP2/6-31+G(d) level with a 50% BSSE correction, which has proved useful

for a large number of complexes containing π systems.⁸ From the calculations, three energy minimum structures are found for the pClFB/H₂O complex. They correspond to isomers of σ_F -, σ_{Cl} -, and π -type. In Table I the calculated zero-point vibrational energy corrected binding energies (ΔE_0) and the IR frequency shifts of the OH stretching frequencies are tabulated. In the σ_x isomers, water is coordinated in the aromatic plane with the O–H bond nearly parallel to the CH–CX bond (X=F, Cl), so that a six-membered ring is formed. The sandwich structure of the π complex is similar to that of benzene/H₂O.³ The intermolecular distance is slightly larger, consistent with the smaller binding energy presumably due to the reduced charge in the aromatic ring.

The σ_F isomer is the most strongly bound, with a binding energy similar to that of the (1:1) cluster of FB/H₂O. Compared to the aggregates with methanol, the binding energy is lower by 0.6–1.4 kcal/mol for the complexes with water. The binding energies of the π and σ_{Cl} isomers are 1–1.7 kcal/mol lower than that of the σ_F . The π isomer is the least stable one.

Contrary to the order in binding energy, the redshift of both the antisymmetric ν_3 as well as symmetric ν_1 OH stretch of the complexed water is the largest for σ_{Cl} isomer. For the π complex, a larger shift of both modes and also a stronger redshift of the ν_3 versus the ν_1 is found.

The results of *ab initio* calculations for the complexes ClB/H₂O and FB/H₂O (Ref. 7) are given in Table I. For both systems, π and σ complexes were located. For FB/H₂O the binding energy of the π isomer is significantly lower than that of the σ isomer, but the opposite is true for ClB/H₂O. The anomaly is due to the presence of chlorine. Earlier calculations on the complexes of benzene with HF and HCl indicated that the experimental binding energy with HCl could only be reproduced by calculations at the MP2/6-311++G(3df,2p) level, while those at the MP2/6-31+G* and MP2/6-311++G** levels underestimate this binding energy.⁹ Similar calculations on the present systems cannot

TABLE I. Data from IR/R2PI depletion and R2PI spectroscopy and *ab initio* calculations. UV shifts ($\Delta\nu_{UV}$) are given relative to the 0_0^0 -transition of the corresponding aromatic chromophore. OH stretching frequencies are given relative to free water. Calculated frequencies in parentheses are relative to calculated free water. All frequencies are given in cm^{-1} ; energies in kcal/mol.

	pClFB σ_F (isomer I)	pClFB σ_{Cl} (isomer II)	pClFB π	CIB σ_{Cl}	CIB π	FB ^a σ_F	FB ^a π
$\Delta\nu_{UV}$	145	195,268	not observed	131	not observed	118	not observed
OH stretch							
$\Delta\nu_3$	-12 (-13)	-17 (-16)	(-16)	-19 (-16)	(-24)	-14 (-12)	(-23)
$\Delta\nu_1$	-12 (-12)	-21 (-18)	(-11)	-25 (-11)	(-15)	-15 (-12)	(-16)
$\nu_3 - \nu_1$	99 (145)	103 (147)	(140)	105 (148)	(137)	100 (146)	(139)
$-\Delta E_0$	2.79	1.75	1.04	1.68	2.23	2.68	1.86

^aReference 6.

be envisaged with the current computational resources. The relative IR shifts, however, seem to be less dependent on the basis set size.⁷

From the experimental results the following conclusions can be drawn. Both isomer I and II, exhibit two strong IR bands moderately redshifted relative to the frequencies of free water. If these results are compared quantitatively with that of monohalogenated benzenes, it can be deduced that the structure of isomer I is similar to that of FB/H₂O, which has been identified as σ_F type,⁷ while for isomer II a structure

like that of CIB/H₂O (σ_{Cl}) can be assumed. This assignment is further corroborated by the UV spectral shifts. The fluorine coordinated complexes exhibit the smaller UV shifts, while the chlorine coordinated complexes the larger UV shift. A presumable π isomer could not be found. It should have a smaller UV shift ($<100 \text{ cm}^{-1}$). In this spectral region no UV bands of appreciable intensity appear.

From the computations of the IR bands, it was found that the σ_F complex shows a redshift of around -12 cm^{-1} for ν_3 and ν_1 . For the σ_{Cl} complex larger shifts (-16 to -18 cm^{-1}) were found. The π complex displayed a strongly redshifted ν_3 and a slightly redshifted ν_1 . The binding energy of the π complex however is the smallest of all isomers, so that its abundance should be very small at low temperature. The trend of the difference in frequencies ($\nu_3 - \nu_1$) is reproduced computationally only if the experimental spectrum of the CIB/H₂O complex is attributed to a σ_{Cl} isomer (highest value). On the contrary, if the π isomer of the CIB/H₂O complex is assumed to account for the experimental spectra, the calculated difference frequency (lowest value) is in contrast to what is observed in the experiments. Thus, it is concluded that the in-plane intermolecular structures for the σ_F and σ_{Cl} isomer represent adequately the experimental complexes of isomer I and II, respectively.

In summary, we have experimentally observed two in-plane coordinated isomers (σ_F and σ_{Cl}) of pClFB/H₂O, which are also predicted from *ab initio* calculations. A π isomer suggested by theory was, however, not observed in experiments. The corresponding R2PI spectrum was assigned by comparison of the IR and UV spectral shifts with those of the monohalobenzene complexes. The experimental findings are substantiated by *ab initio* calculations of the IR redshifts and binding energies. Interestingly the IR redshifts do not correlate with the calculated binding energies. The comparison between water and methanol as solvent molecule for halobenzenes revealed that π complexes are not formed in water, whereas they have been observed for methanol.⁵ Moreover, the binding energies for H-bonded complexes with water are systematically smaller than those with methanol.

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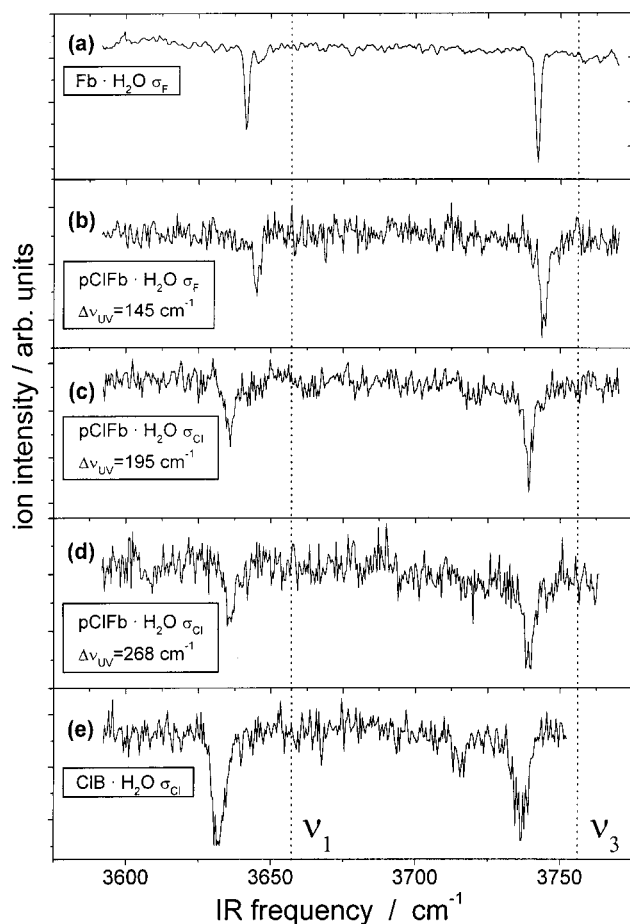


FIG. 1. IR/R2PI spectra of the (1:1) aggregates of pClFB/H₂O, CIB/H₂O, and FB/H₂O. The free H₂O stretch frequencies (ν_3, ν_1) are indicated as dotted lines. (a) fluorobenzene (FB)/H₂O, (b) pClFB/H₂O isomer I ($\Delta\nu_{UV} = 145 \text{ cm}^{-1}$), (c) pClFB/H₂O isomer II ($\Delta\nu_{UV} = 195 \text{ cm}^{-1}$), (d) pClFB/H₂O isomer II ($\Delta\nu_{UV} = 268 \text{ cm}^{-1}$), (e) CIB/H₂O.

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