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On the Nature of the Water−Hexafluorobenzene Interaction

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The interaction between water and hexafluorobenzene is discussed in light of an ab initio study. It is found that a dimer is formed with a binding energy of about −2 kcal/mol, with a geometry such that the oxygen of water is above the hexafluorobenzene molecule, with both hydrogen atoms pointing out of the ring, and the water C_2 axis is collinear with the main symmetry axis of the aromatic compound. In addition, the intermolecular potential surface (IPS) has been fully characterized. It comes out that the rotational motion of the water molecule around its C_2 axis is nearly "free", whereas the two other bending motions are found to be strongly hindered. These results are discussed in comparison with those reported in the literature for the water−benzene dimer, in which a weak e_π−H hydrogen bond interaction has been reported. We argue that in the water−hexafluorobenzene system the oxygen atom acts as a Lewis base and that the aromatic ring plays the role of a Lewis acid, owing to the withdrawing effect of the fluorine atoms on the π-electronic distribution of the cycle. These results have been used to rationalize the far-infrared experiments that we have previously reported on water diluted in organic solvents. We emphasize that the viewpoint of the isolated dimer provided by our ab initio study could be transposed to the liquid state if the observation time of the technique is shorter than the lifetime of the dimer. It turns out that mid-infrared spectroscopy is more adapted, than far-infrared absorption, to put in evidence the existence of very labile dimers in the liquid phase, taking into account its shorter time window of observation.

1. Introduction

The question of the existence and the nature of a specific interaction between the water and benzene molecules has stimulated a large number of investigations in the course of the past decade.[1−19] In this context, the experimental and theoretical study of Suzuki et al. has been a cornerstone.[1] Indeed, their spectroscopic measurements using a supersonic expansion molecular beam have been interpreted in light of ab initio calculations. The authors have established that benzene forms a weak hydrogen bond with water. More precisely, it was shown that the water is positioned above the benzene ring with both hydrogen atoms pointing toward the π-electron cloud. Since then, a number of theoretical investigations have been devoted to assess more deeply this weakly bounded complex.[3−6] The current knowledge about the dimer properties indicates that the center of mass separation of the two moieties is about 3.35 Å and that the binding energy D_0 is in the range 1.63−2.78 kcal/mol.[1] Moreover, it was emphasized that the contribution of the electron correlation in the binding energy is largely responsible for the strong interaction of the π-electrons of the ring with the hydrogen atoms of water. Finally, the lability of this complex is reflected in the large-amplitude motions of the water molecule above the aromatic ring. It was found that the rotational motions of water around its C_2 z-axis are nearly free whereas the motions around the perpendicular axes are more hindered. Indeed, the motion around the y-axis situated in the water molecular plane leads to a bending mode at about 260 cm^{-1}. The bending motion around the x-axis perpendicular to the molecular plane of water, the so-called "swapping motion"[4] is found at a frequency of about 47 cm^{-1}.

In the liquid state, the study of the interaction of water with organic solvents has been addressed for a long time by mid-infrared absorption spectroscopy.[22−26] In particular, it has been well established that the O−H stretching vibrational modes are shifted to lower frequencies ("red shift") as the strength of the hydrogen bonding interaction between the water and the solvent molecules increases. In this context, for water diluted in liquid benzene the frequencies of the symmetric ν_1 and antisymmetric ν_3 stretching modes are found respectively "red-shifted" by 62 and 72 cm^{-1} compared with their values for water in the gaseous phase.[23]

More recently, the studies of solitary water in liquid organic solvents have known a renewal of interest. In particular, the water−benzene solutions saturated in water (solubility of about 3.2×10^{-3} molar fraction at room temperature) have been investigated by vibrational and NMR spectroscopies.[9−13] In these investigations one of the issues that has been raised concerned the existence of such a weak complex in the liquid phase. Indeed, to be rationalized, these experimental findings needed to invoke a specific interaction that is reminiscent of the hydrogen bond signature observed under low-temperature conditions by matrix isolation and supersonic jet-cooled clusters spectroscopic studies.[1,7,8,15] Actually, three experimental investigations might be in favor of such interpretation. The first one is again provided by mid-infrared absorption spectroscopy. It was found that the O−H stretching mode of the monomeric HDO molecules diluted in liquid benzene and its methyl derivatives is shifted to lower wavenumbers as the ionization energies of the aromatic compounds decrease.[9] Thus, it was inferred that the interaction of water with aromatic compounds could be described as a π-hydrogen bond. The second argument in favor of this interpretation is provided by NMR T_1 relaxation

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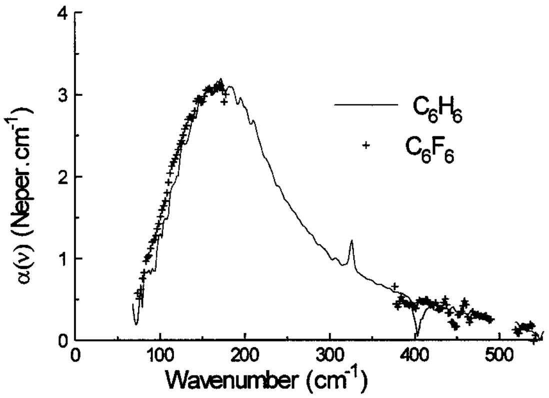

Figure 1. Far-infrared spectra of D_2O in benzene and hexafluorobenzene corrected from the contribution of the pure solvent. Note that the lack of experimental points in the spectrum of D_2O/hexafluorobenzene solution is due to the strong absorption of an internal mode of the solvent (see ref 14 for experimental details).

time measurements of D_2O molecules diluted in apolar solvents.[11−13] Indeed, from the evolution of the rotational correlation time τ_{2R} of D_2O as a function of the ratio η/T (where η is the solvent viscosity coefficient), it has been suggested that a specific solvent−solute interaction should be considered in liquid benzene. Finally, the third investigation has been performed on water diluted in a series of organic solvents using far-infrared (FIR) absorption spectroscopy.[14] It was found that the reorientational motion of the dipole moment of water, which involves the librations around the *x*- and *y*-axes, is quasi-free in liquid cyclohexane. In that case, the broad asymmetric FIR spectrum centered at 140 cm^{-1} has been interpreted as the profile calculated for a freely rotating single water molecule. In contrast, in liquid benzene, a broad spectrum with a different band shape is observed at about 230 cm^{-1}, hence indicating that the rotational motion of water is now more hindered. On the basis of Suzuki et al. calculations, it might be inferred that the contribution of the libration around the *y*-axis is dominant in this FIR profile. Again, the existence of a specific interaction between water and benzene might be appropriate for interpreting the results obtained so far in the liquid state. However, in our previous study, we have questioned this conclusion on the basis of the FIR spectrum of water diluted in liquid hexafluorobenzene. Indeed, for the C_6F_6 molecule, the strong electronegativity of the fluorine atoms leads to a π-electron distribution of the ring that is very different than the benzene one. This is for instance reflected in the values of their quadrupole moments Q_{zz}, which have the same order of magnitude but opposite sign.[27] Therefore, it is expected that the hydrogen bond interaction of the proton of water with the π-electron cloud of the cycle should be rather different for the C_6F_6 molecule compared to the C_6H_6 molecule. As a consequence, the far-IR spectra of water diluted in these two solvents should be distinguishable. This prediction has not been confirmed by the experiments, which show on the contrary that the FIR spectra are centered at about the same frequency and display very similar band shapes.[14] This result is illustrated in Figure 1 for perdeuterated water diluted in the two previous solvents.

It follows from this comparison that the FIR spectra can be understood by invoking similar packing of the solvent molecules around the water molecule. The steric effects on the water molecule are generated by the shape of the solvent molecule, which are roughly equivalent. Therefore, either the existence of a specific interaction like the π-hydrogen bond might be questioned or the results obtained in the liquid state cannot be simply interpreted along the lines of a “gas-state picture”.

The aim of the present paper is to provide a study of the $H_2O-C_6F_6$ isolated dimer on the basis of ab initio calculations. The structure of the complex and the interaction potential surface of the entity will be analyzed as a function of the intermolecular distance of the two moieties and also as a function of the angular orientations of water interacting with the aromatic ring. A comparison of the results obtained in this study with those previously reported on the $H_2O-C_6H_6$ dimer should provide a better insight into the intermolecular mechanisms involved in the genesis of the complex.

2. Methodology of the Calculation

In the present section, we will report the calculated properties of the isolated $C_6F_6-H_2O$ dimer in the electronic ground state using ab initio methods performed on an IBM RS6000 workstation and on CRAY C94 and C98 computers using the Gaussian 92 and 94 suites.[20] In the literature, it is well established that the 6-311G** basis set is well adapted to predict reliable structure, binding energy, and frequencies in weakly bound highly π-conjugated systems,[3] and therefore, this basis set was exclusively used in our computations. The full geometry optimizations were carried out at the restricted Hartree−Fock (RHF) and at the Moller−Plesset second-order perturbation theory (MP2) levels. Indeed, the electron correlation mechanism is known to play a significant role in the stabilization of the $H_2O-C_6F_6$ structure, and we aimed also in this current study to get some insight on such an effect on the structure and on the interaction energy of the $H_2O-C_6F_6$ complex. The computed interaction energies of the $H_2O-C_6F_6$ dimer were corrected for the basis set superposition error (BSSE) by the full counterpoise technique of Boys and Bernardi.[21]

3. Results

3.A. Dimer Structure. The geometry optimization of the $H_2O-C_6F_6$ dimer has been first performed at the RHF level.

The equilibrium structure is found to have the water molecule above the aromatic ring with the oxygen atom pointing toward the center of the hexafluorobenzene molecule, and the distance R_{int} between the oxygen atom and the center of mass of the ring is about 3.24 Å. The main symmetry axes of the two moieties are coincident and leads to an overall symmetry of the complex, which is C_{2v}. The interaction energy of the complex in its optimized geometry has been found equal to $\Delta E^{(\mathrm{uncor})} \approx -2.56$ kcal/mol, which leads to a value of $\Delta E^{(\mathrm{cor})} \approx -1.69$ kcal/mol after the BSSE energy correction. In the second step, we have carried out the same calculation including the full MP2 perturbation treatment. The same qualitative optimized structure was again obtained, but with a value of $R_{\mathrm{int}} \approx 2.96$ Å. The interaction energy is now $\Delta E^{(\mathrm{uncor})} \approx -3.79$ kcal/mol and $\Delta E^{(\mathrm{cor})} \approx -1.81$ kcal/mol, taking into account the BSSE energy contribution. This single geometry obtained from the two previous calculations for the $H_2O-C_6F_6$ dimer is shown in Figure 2. The values of the internal coordinates of the two interacting molecules of the complex are reported in Table 1. In the calculations for the dimer, the hexafluorobenzene molecule was constrained to be planar, with the intramolecular distances fixed to the values obtained from the geometry optimization of the isolated monomer.

3.B. Intermolecular Potential Surface. To better assess the intermolecular energy potential surface (IPS), we have first calculated the intermolecular energy of the dimer for both the RHF and MP2 levels as a function of R_{int} for the complex of C_{2v} symmetry. The details of the calculations are summarized in Table 2, where we have reported for the two treatments the

TABLE 1: Internal Coordinates Values of the Two Interacting Species Calculated in the Optimized Geometry at the RHF and MP2 Levels[a]

	intramolecular distances of C_6F_6	internal coordinates of H_2O
RHF/6-311G** ($R_{int} \approx 3.238$ Å)	$d_{CC} \approx 1.3765$ Å, $d_{CF} \approx 1.3094$ Å	$R_{OH} \approx 0.9414$ Å, $\delta r_{OH} \approx +0.0004$ Å $\alpha_{OH} \approx 105.5878°$, $\delta\alpha_{HOH} \approx +0.1264°$
MP_2/6−311 G** ($R_{int} \approx 2.959$ Å)	$d_{CC} \approx 1.3942$ Å, $d_{CF} \approx 1.3314$ Å	$R_{OH} \approx 0.9586$ Å, $\delta r_{OH} \approx +0.0008$ Å $\alpha_{OH} \approx 102.6989°$, $\delta\alpha_{HOH} \approx +0.2595°$

[a] δr_{OH} and $\delta\alpha_{HOH}$ are respectively the deviations of the OH bond distance and the HOH angle from their values calculated for monomeric water.

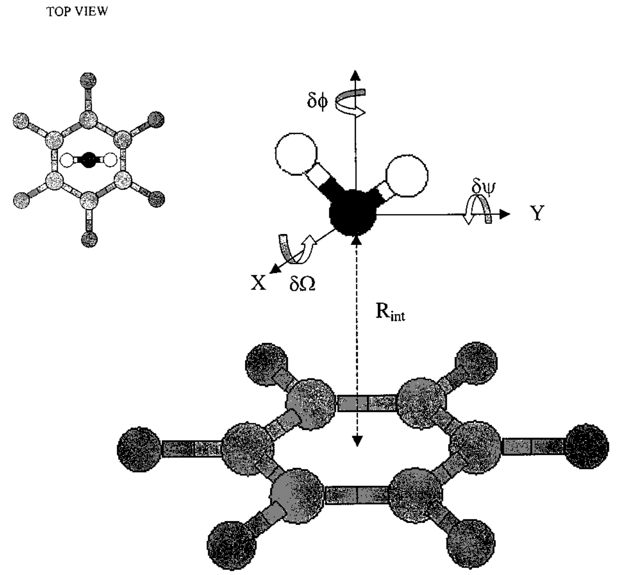

Figure 2. Representation of the optimized H_2O−hexafluorobenzene dimer structure. The axis and angles conventions are also reported (see text).

TABLE 2: Evolution of the Intermolecular Potential Energy $\Delta E_{Int}^{(cor)}$ (Corrected from the BSSE) and the Corresponding BSSE Contribution $\Delta E^{(BSSE)}$ as a Function of the Intermolecular Distance R_{int}[a]

	HF/6-311G** level		MP_2/6-311G** level	
R (Å)	$\Delta E_{int}^{(cor)}$	$\Delta E^{(BSSE)}$	$\Delta E_{int}^{(cor)}$	$\Delta E^{(BSSE)}$
2.0	+39.586	+3.348	+31.798	+7.618
2.25	+16.468	+2.351	+11.870	+5.324
2.5	+5.473	+1.761	+2.849	+3.713
2.75	+0.676	+1.369	−0.758	+2.616
2.959 (MP2)			−1.8115	+1.975
3.0	−1. 173	+1.075	−1.906	+1.869
3.238 (RHF)	−1.693	+0.864		
3.25	−1.726	+0.823	−2.054	+1.323
3.5	−1.766	+0.585	−1.866	+0.886
3.75	−1.631	+0.371	−1.604	+0.541
4.0	−1.449	+0.205	−1.357	+0.295
4.5	−1.097	+0.036	−0.963	+0.068
5.0	−0.819	+0.006	−0.688	+0.010
5.5	−0.615	∼0.0	−0.500	+0.002
6.0	−0.468	∼0.0	−0.372	∼0.0
6.5	−0.360	∼0.0	−0.282	∼0.0
7.0	−0.281	∼0.0	−0.280	∼0.0
8.0	−0.177	∼0.0	−0.217	∼0.0
9.0	−0.116	∼0.0	−0.087	∼0.0

[a] The energy values are given in kcal/mol. The intermolecular distance values labeled with the symbols (RHF) and (MP2) are those obtained from the geometry optimization calculation of the dimer performed at the RHF and MP2 levels, respectively.

corrected intermolecular energy and the BSSE energy contribution. Incidentally, we observe that the BSSE energy correction is significant up to intermolecular distances of about 5 Å. The corrected intermolecular energies are presented as a function of the intermolecular distance of the two moieties in Figure 3. Clearly, the IPS calculated at the RHF level presents a minimum at a value $\Delta E^{(cor)} \approx -1.77$ kcal/mol for an equilibrium separation distance $R°_{int} \approx 3.4$ Å. If the electron correlation is taken into account, the minimum is obtained at a lower distance of $R°_{int} \approx 3.2$ Å, and the predicted value of the binding energy (without the zero-point energy correction) D_e is about 2.08 kcal/mol. Finally, we note that the geometry of the water molecule interacting with the hexafluorobenzene molecule is slightly modified compared with the geometry of the isolated water molecule (Table 1).

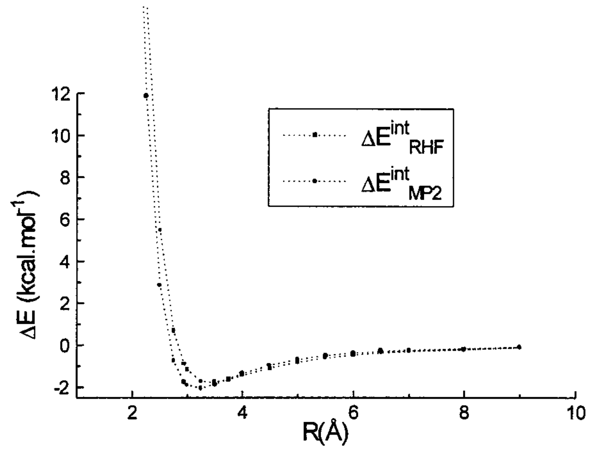

Figure 3. Variation of the intermolecular energy as a function of the distance R_{int} between the two moieties at the RHF and MP2 levels after BSSE correction.

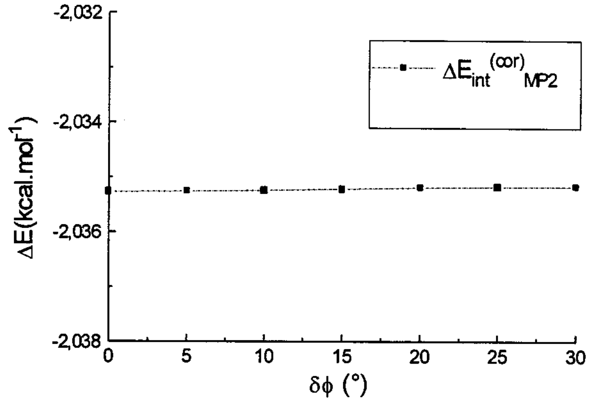

Figure 4. Variation of the intermolecular energy of the dimer as a function of the rotational angle $\delta\phi$ of water around its z axis ($R_{int} \approx$ 3.24 Å).

The aim of the second step has been to estimate the barrier associated with the rotational motion of water around its different axes. These calculations have been performed in the framework of the two previous treatments, and we shall only present here the post Hartree−Fock MP2 calculation. The rotational motion around the main symmetry axis (z) of water was found to be isotropic and nearly free, as indicated by the almost constant value of the calculated intermolecular energy as a function of the angular $\delta\Phi$ variable (Figure 4). Although the IPS is very flat, we emphasize that the C_{2v} geometry

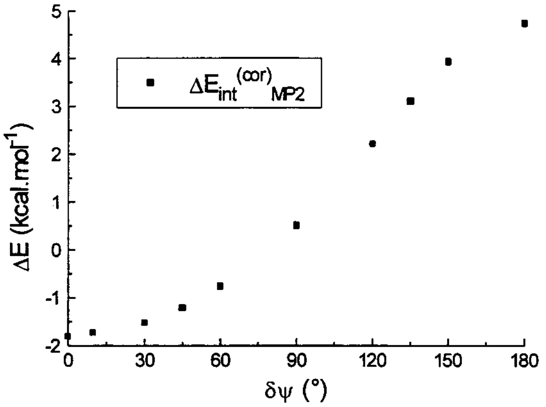

Figure 5. Variation of the intermolecular energy of the dimer as a function of the rotational angle $\delta\psi$ of water around its y axis at the MP2 level after BSSE correction ($R_{\mathrm{int}} \approx 2.959$ Å).

TABLE 3: Evolution of the Intermolecular Energy of the Dimer $\Delta E_{\mathrm{Int}}^{(\mathrm{cor})}$ (Corrected from the BSSE) and of the Corresponding BSSE Contribution $\Delta E^{(\mathrm{BSSE})}$ as a Function of the Rotational Angle $\Delta\Psi$ of Water around Its y Axis ($R_{\mathrm{int}} \approx$ 2.959 Å)

$\delta\Psi$ (deg)	$\Delta E^{(\mathrm{cor})}$ (kcal/mol)	$\Delta E^{(\mathrm{BSSE})}$ (kcal/mol)
0.0	−1.8115	+1.975
10.0	−1.742	+2. 033
30.0	−1.528	+2.185
45.0	−1.218	+2.410
60.0	−0.773	+2.737
90.0	+0.505	+3.587
120.0	+2.196	+4.245
135.0	+3.010	+4.387
150.0	+3.921	+4.441
180.0 (C_{2v})	+4.733	+4.459

corresponds to the minimum energy. In contrast, the rotational motion around the (y) molecular axis is strongly hindered. This is clearly shown in Figure 5 and Table 3, where the angular variation $\delta\psi$ of the angle ψ from its equilibrium value leads to an increase of the intermolecular interaction energy. It is noteworthy that for $\delta\psi = 180°$ the two hydrogen atoms of the water molecule are pointing toward the aromatic ring, leading also to a C_{2v} geometry of the dimer. However, this conformation at the equilibrium distance has the highest intermolecular energy. Let us point out that in this C_{2v} geometry the intermolecular energy calculated as a function of the intermolecular distance does not have any minimum, showing clearly that this conformation is found to be unstable. If we consider now the rotational motions around the (x) molecular axis, we find from the IPS that the reorientational motion of water is also hindered when the angle Ω departs from its equilibrium value. We note also that when one of the hydrogen atoms of the water molecule points toward the aromatic ring ($\delta\Omega \approx 128.6°$), the intermolecular energy is close to its maximum value (Figure 6 and Table 4). The exploration of the IPS in this C_s symmetry with the separation distance (not shown here) does not lead to any minimum of the intermolecular energy, and therefore, the dimer is also found to be unstable in this conformation.

4. Comparison with the $H_2O-C_6H_6$ Dimer

Clearly, the hexafluorobenzene and water molecules form a dimer, just as one has been found to exist between benzene and water in the gaseous phase. In particular, it is found that the binding energy of the $H_2O-C_6F_6$ dimer is only slightly greater than that of the $H_2O-C_6H_6$ dimer, as indicated by the values reported at the MP2 level, taking into account the BSSE correction, which are about 2.08 and 1.78 kcal/mol, respectively.[1] In contrast, a comparison between the structures of these two systems reveals significant differences. Indeed, the water molecule above the hexafluorobenzene molecule is found in an upside down relative orientation compared with the case of water interacting with benzene. This finding reveals that the water hexafluorobenzene dimer originates from the interaction of the electron lone pairs of the oxygen atom with the π-electron distribution of the carbon atoms of the ring weakened (compared to the benzene one) by the electron-withdrawing effect due to the presence of the fluorine atoms. In Lewis's acid−base concept, it follows that water plays the role of the acid with benzene and of the base with hexafluorobenzene. Finally, the difference existing in the nature of the interaction involved in these two dimers is also reflected through their respective IPS surfaces, which govern the water motions over the aromatic rings. Indeed, we have estimated from our previous results that the frequency of the intermolecular stretching vibration of the dimer is about 86 cm^{-1}, and those of the Ω and ψ water bends are 133 and 189 cm^{-1}, respectively. Let us remember that for the water−benzene system the corresponding frequencies were reported to be about 101, 47, and 260 cm^{-1}, respectively. It follows from a comparison of the frequencies associated with the bending motions of the water molecule that the reorientation around the x-axis is more constrained and that the Ω and ψ water bending motions are found in a narrower spectral range in the water−hexafluorobenzene system.

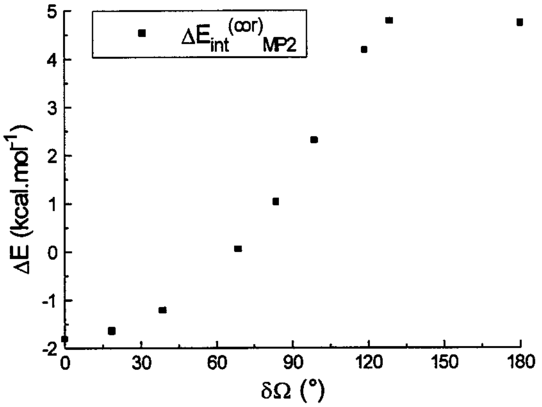

Figure 6. Variation of the intermolecular energy of the dimer as a function of the rotational angle $\delta\Omega$ of water around its x axis at the MP2 level after BSSE correction ($R_{\mathrm{int}} \approx 2.959$ Å).

TABLE 4: Values of the Intermolecular Energy of the Dimer $\Delta E_{\mathrm{int}}^{(\mathrm{cor})}$ (Corrected from the BSSE) and of the Corresponding BSSE Contribution $\Delta E^{(\mathrm{BSSE})}$ as a Function of the Rotational Angle $\Delta\Omega$ Of Water around Its x Axis ($R_{\mathrm{int}} \approx$ 2.959 Å)

$\delta\Omega$ (deg)	$\Delta E^{(\mathrm{cor})}$ (kcal/mol)	$\Delta E^{(\mathrm{BSSE})}$ (kcal/mol)
0.0 (*)	−1.8115	+1.975
18.6313	−1.643	+2.068
38.6313	−1.220	+2.212
68.6313	+0.052	+2.542
83.6313	+1.024	+2.810
98.6313	+2.310	+3.206
118.6313	+4.177	+3.874
128.6313 (C_s)	+4.767	+4.186
180.0 (C_{2v})	+4.733	+4.459

5. Conclusion

The first conclusion that comes from this study is that water forms dimers with either benzene or hexafluorobenzene. However, as we have emphasized before, neither the geometry of the complex nor the bending motions of water on the IPS are identical. It results from these findings that the Ω and ψ water bending motions in the isolated complex, which give rise to the far-infrared spectra, should be different. Indeed, even if in both systems the librational motion around the *y*-axis is the more constrained, their frequency values are nevertheless distinct and separated by about 70 cm^{-1}. If we assume that the "gas-phase picture" obtained so far is still valid in the liquid state, we should expect that the FIR spectra associated with the water molecule diluted in liquid benzene and hexafluorobenzene should be different. Actually, we do know that this prediction is not supported by our experimental study (Figure 1).[14] This situation is not unexpected if we consider that in the liquid state the existence of an isolated pair of molecules is an oversimplified and nonrealistic picture. Indeed, even if a dimer exists, it is expected that the librational motions of water are perturbed by the mean intermolecular potential due to the neighboring molecules constituting the solvent cage. Therefore, the experimental results lead us to conclude that the mean intermolecular potential affects the librational motions of water in such a way that only steric effects acting on the water molecule, due the similar shape of the solvent molecules, are relevant.[14] However, this conclusion is not in contradiction with the existence of a "complex", as it might appear at a first glance. The clue is contained upon the recognition that the observation time of the spectroscopic techniques should be much shorter than the lifetime of the complex. This is the so-called "time window of opportunity" that we have discussed in a number of studies concerning the spectroscopy of very weak complexes in the liquid state.[28,29] Indeed, in mid-infrared spectroscopy at the typical frequency values of the stretching vibrations of monomeric water (3700 cm^{-1}), the observation time is about 10^{-14} s. In contrast, at the bending mode frequencies (typically 100 cm^{-1}), the observation time is in the picosecond range in far-infrared absorption region. Clearly, very short-lived transient associations of pairs of molecules should be much better put in evidence from mid-infrared spectroscopy. These statements are supported by the red shifts of stretching vibrations of water diluted in benzene, which have been reported and which are expected on the grounds of a hydrogen bond type of interaction. Upon these considerations, we can infer that in the water−hexafluorobenzene system the stretching vibrations of water should be also affected by dimer formation, but the frequency shifts and the intensity variations should be different from those observed in the benzene−water dimer. Actually, we do know that these predictions are indeed correct on the basis of an experimental study and theoretical study, which will be presented in forthcoming papers.[30]

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