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Conformational Stability of Lactonitrile−Water Complexes: An ab Initio Study

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The conformational stabilities of three possible hydrogen bonded complexes of lactonitrile rotamers (**A**, **B**, and **C**) and water have been studied using high-level ab initio calculations. After full geometry optimizations at the second-order Møller−Plesset level of theory (MP2), the bimolecular complexes **A**−OH···OH_2, **B**−OH···OH_2, and **C**−OH···OH_2 are found to be true energy minima. It is found that rotamers **A** and **B** form strongly bonded hydrated complexes with their binding energies calculated between ca. 8.0−9.0 kcal mol^{-1}, after correcting for BSSE. This is ∼2.0 kcal mol^{-1} higher than the calculated binding energy for the complex **C**−OH···OH_2. The geometrical parameters and vibrational spectra of the three complexes are determined and compared with their corresponding isolated moieties. In the three species investigated here there exist a good correlation between the red shift of the OH vibrational stretching mode involved in the hydrogen bonds and the binding energies of the complexes.

Introduction

The degradation process of lactonitrile ($CH_3CHOHCN$) is of great importance for environmental impact studies.[1] As it is known, $CH_3CHOHCN$ reacts in aqueous solutions[2] at high pHs to form HCN and CH_3CHO. In pure water the dissociation of lactonitrile is very difficult to occur. However, because this molecule is miscible in water, physical removal from air by wet deposition is likely to occur. The $CH_3CHOHCN$ molecule has potentially three sites amenable to form hydrogen bonds with water, i.e., the OH, CN, and CH groups. Especially important is the OH···O bond formed between the OH group of lactonitrile and water, which seems to yield a possible route for the dissociation of lactonitrile in dilute aqueous solutions.[2] The two other groups, CN and CH, can also bind to the water molecule, each one forming a weak hydrogen bond.[3−6] In the first case (CN···H) the water molecule acts as a proton donor, whereas in the second case (CH···O) it acts as a proton acceptor. All these possibilities turn the hydration of lactonitrile into an interesting subject to be investigated in microscopic detail.

The isolated molecule of lactonitrile has already been studied by microwave spectroscopy,[7,8] in which two sets of rotational constants are found. These are assigned to the two gauche conformers relative to the CN group, as shown in Figure 1a,b. In fact, rotating the OH group there are three stable conformers of lactonitrile (Figure 1). The potential energy profile for the OH torsion and CH_3 rotation in the isolated molecule has been previously investigated at the ab initio SCF level only.[9] An important step in this direction is to consider higher level calculations including electron correlation effects. In fact, our interest here goes beyond and we investigate the stability of these rotamers in the presence of water, in particular when the water molecule acts as a proton acceptor of the OH group in lactonitrile. The interaction with water is expected to affect the conformational stability of lactonitrile, and the characterization of the complexes seems to be an important step for understanding the mechanism of dissociation of lactonitrile releasing cyanide.[2] Thus, performing accurate ab initio calculations for the lactonitrile−water complexes allows obtaining valuable information on the properties of the OH···O hydrogen bonds. Also, low-temperature environment in the jet-cooled rotational

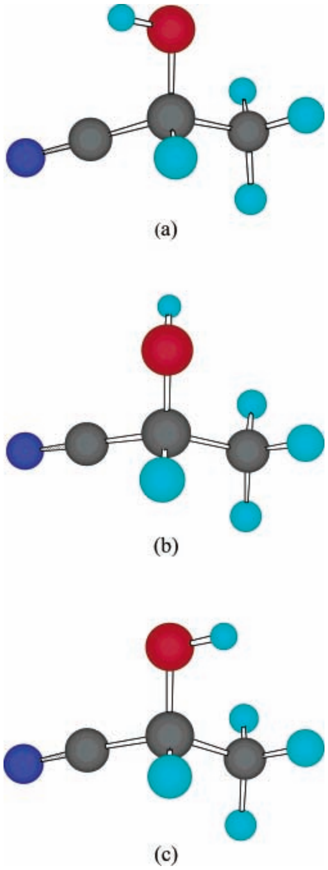

Figure 1. Rotamers of lactonitrile: (a) gauche 1 (rotamer **A**); (b) gauche 2 (rotamer **B**); (c) trans (rotamer **C**). The dihedral angle that determines the rotamers is chosen to be zero for the eclipsed conformation of the O−H and C−CN bonds.

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TABLE 1: Comparison of the Calculated Properties of the Isolated Rotamer of Lactonitrile (A) and Its Water Complex at the MP2 Level of Theory

	rotamer **A**			**A**−OH···OH$_2$	
	6-311++G(d,p)	6-311++G(2df,2p)	exp[8]	6-311++G(d,p)	6-311++G(2df,2p)
A (MHz)	8807.47	8870.80	8790.22	4409.82	4498.42
B (MHz)	3969.10	4005.90	4005.86	2319.94	2333.12
C (MHz)	2962.76	2990.11	2975.80	1603.77	1619.79
μ (D)	2.876	2.982	1.538	1.712	1.382
O−H (Å)	0.963	0.962	0.96[a]	0.971	0.971
C−O−H (deg)	108.2	109.0	107.5[a]	106.8	107.6
O···O (Å)				2.842	2.839
O−H···O (deg)				158.5	157.7
H−O−C−CN (deg)	56.6	57.5		51.7	50.9

[a] Average parameters between rotamers **A** and **B**.

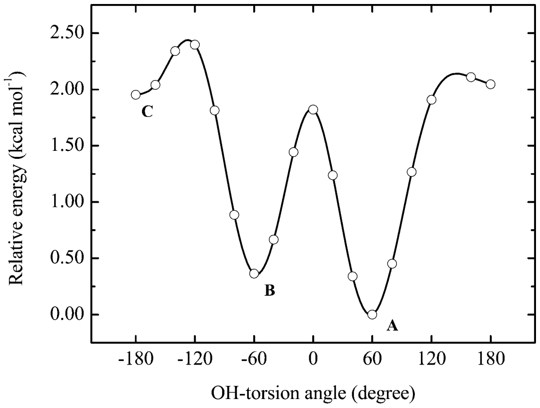

Figure 2. Potential energy profile for the OH group torsion in lactonitrile calculated at the MP2/6-311++G(d,p) level of theory. The points have been obtained by completely optimizing all other geometrical parameters, except the dihedral angle H−O−C−CN.

experiment has been successfully used to probe the conformational behavior of other hydrogen bonded complexes[10,11] and perhaps could be used in the lactonitrile-water case.

In this study we analyze the conformational stability of three 1:1 hydrogen bonded complexes formed between lactonitrile rotamers (**A**, **B**, and **C**) and water, as obtained from high-level ab initio calculations. The structures, vibrational frequencies, rotational constants, dipole moments, and interactions of these hydrated systems are reported and compared with the isolated rotamers of lactonitrile. As far as we are aware, the lactonitrile−water complexes have never been observed in spectroscopic experiments or previously considered in theoretical studies. Hence, to assist in identifying a possible structure we also calculate and report the infrared spectra of the three stable hydrated complexes, assigning both the transitions and intensities and comparing them with the separate moieties.

Methods and Calculations

All molecular structures considered in this study have been fully optimized at the second-order Møller−Plesset perturbation theory (MP2) with the frozen core approximation. The calculations are carried out using two basis sets of diffuse-polarized functions with triple-ζ split-valence quality,[12] i.e., 6-311++G(d,p) and 6-311++G(2df,2p). Thus, the vibrational spectra for the complexes and their isolated species are obtained at the MP2/6-311++G(d,p) and MP2/6-311++G(2df,2p) levels. Calculations using the MP2 method with sufficiently large basis sets have been successful in obtaining structures and properties of different hydrogen bonded systems.[13−15] The binding energies are calculated as the difference of total energy between the complex and the isolated moieties at infinite distance. In this sense, they are corrected for the basis set superposition error (BSSE) via the usual counterpoise method.[16] Also, these binding energies are reported considering the differences in zero-point vibrational energy (ZPVE), estimated from the harmonic frequencies. Hence we report both D_e and D_0 binding energies. The computational calculations have been performed with the Gaussian 98 program.[17]

Results and Discussion

Conformational Properties. The three conformers of lactonitrile are shown in Figure 1. There are no significant changes in the bond lengths and bond angles in these rotamers. The optimized OH distance varies by only ±0.001 Å whereas the optimized COH angle changes by ±1° along the internal torsion. For the isolated case the conformational stability[9] is obtained in decreasing order from rotamers **A** to **C**. In Figure 2 we show the potential energy profile as a function of the OH-torsion angle of lactonitrile, which is chosen to be zero for the eclipsed conformation of the O−H and C−CN bonds. The curve is obtained using the MP2/6-311++G(d,p) method, where all the geometry parameters are completely relaxed. The fully optimized dihedral angle H−O−C−CN is given in Tables 1−3 for the three stable rotamers. At the MP2 level of theory we find that rotamer **A** is 0.36 kcal mol^{-1} more stable than rotamer **B**, using the 6-311++G(d,p) or 6-311++G(2df,2p) basis sets. These gas-phase values are in very good agreement with the experimental result of 0.34 kcal mol^{-1} obtained from microwave spectroscopy.[8] Rotamer **C** is less stable than rotamer **A** by 1.95 kcal mol^{-1} calculated with 6-311++G(d,p), and 1.85 kcal mol^{-1} calculated with 6-311++G(2df,2p). This calculated energy stability order is also in agreement with previous SCF ab initio calculations.[9]

The structures of three possible lactonitrile−water complexes corresponding to the stable rotamers **A**, **B**, and **C** of the isolated molecule are given in Figure 3. These have been obtained by completely optimizing the geometries at the two levels of calculations reported above. As in the case of the isolated lactonitrile molecule, **A**−OH···OH$_2$ is found to be the most stable hydrogen bonded conformer, followed by **B**−OH···OH$_2$ and **C**−OH···OH$_2$. However, the complexation with water decreases the difference in energy between the two most stable species to only 0.1 kcal mol^{-1} and increases the difference between **A**−OH···OH$_2$ and **C**−OH···OH$_2$ to 3.6 kcal mol^{-1}. The relative energies for the complexes obtained with MP2 are given in the diagram of Figure 4. Tables 1−3 summarize some important properties calculated for these hydrated complexes in comparison with their corresponding isolated rotamers. These are rotational constants, dipole moments, and the geometric

TABLE 2: Comparison of the Calculated Properties of the Isolated Rotamer of Lactonitrile (B) and Its Water Complex at the MP2 Level of Theory

	rotamer **B**			**B**−OH···OH$_2$	
	6-311++G(d,p)	6-311++G(2df,2p)	exp[8]	6-311++G(d,p)	6-311++G(2df,2p)
A (MHz)	8594.53	8640.82	8584.20	3311.57	3355.52
B (MHz)	3987.29	4025.40	4028.72	2746.61	2757.23
C (MHz)	2970.53	2995.51	2987.85	2029.74	2045.12
μ (D)	3.193	3.274	1.687	1.831	1.788
O−H (Å)	0.963	0.963	0.96[a]	0.971	0.971
C−O−H (deg)	107.5	108.3	107.5[a]	106.2	107.0
O···O (Å)				2.853	2.849
O−H···O (deg)				157.6	156.6
H−O−C−CN (deg)	−61.3	−61.9		−53.7	−52.0

[a] Average parameters between rotamers **A** and **B**.

TABLE 3: Comparison of the Calculated Properties of the Isolated Rotamer of Lactonitrile (C) and Its Water Complex at the MP2 Level of Theory

	rotamer **C**		**C**−OH···OH$_2$	
	6-311++G(d,p)	6-311++G(2df,2p)	6-311++G(d,p)	6-311++G(2df,2p)
A (MHz)	8736.17	8771.00	7200.91	7682.03
B (MHz)	4009.14	4050.05	1431.42	1419.04
C (MHz)	2972.35	2996.23	1265.52	1253.31
μ (D)	4.973	4.960	7.347	7.124
O−H (Å)	0.963	0.962	0.969	0.970
C−O−H (deg)	106.7	107.6	106.1	107.1
O···O (Å)			2.853	2.852
O−H···O (deg)			174.1	177.4
H−O−C−CN (deg)	−176.6	−180.0	−167.3	−175.3

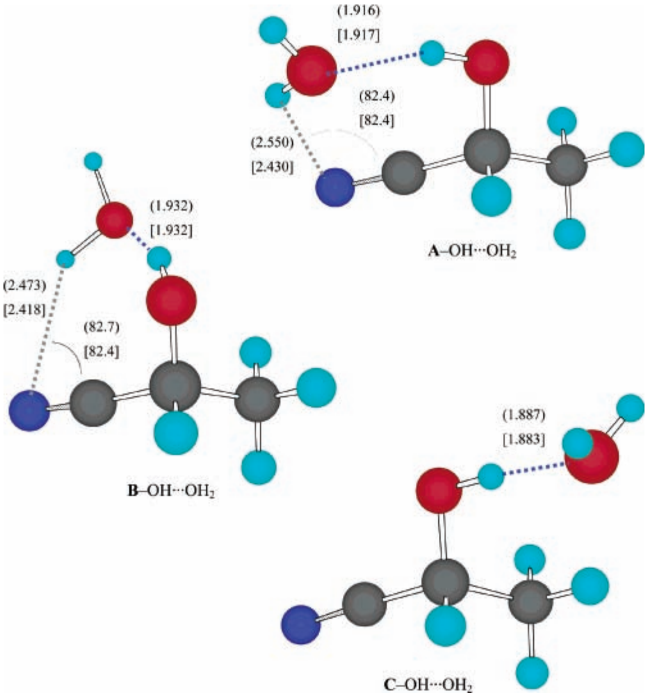

Figure 3. Optimized structures of the complexes type **X**−OH···OH$_2$ of lactonitrile and water, where **X** corresponds to rotamers **A**, **B**, and **C**. Values are calculated at the MP2 level using (in parentheses) the 6-311++G(d,p) and (in brackets) using the 6-311++G(2df,2p) basis sets.

parameters: O−H bond distances, C−O−H bond angles, intermolecular O···O distances, O−H···O hydrogen bond angles, and H−O−C−CN dihedral angle. In general, a reasonable agreement between the calculated and experimental properties is noted for the isolated rotamers. For instance, our rotational constants are reported to accuracy better than 1% compared to the experimental measurements.[8] The calculated dipole moments for rotamers **A** and **B** are surprisingly higher than the available experimental[8] ones. Our theoretical result is, however, in very good accord with previous and recent calculations using density functional theory (DFT).[18] As given in Tables 1 and 2, we have obtained 2.982 and 3.274 D for rotamers **A** and **B**, respectively, whereas the corresponding values obtained using DFT, using the experimental geometries are 2.982 and 3.139 D. As it is normally expected the MP2/6-311++G(d,p) and MP2/6-311++G(2df,2p) models produce excellent dipole moments for different systems.[13,15] It is not unlikely that the experimental results reported for the dipole moments[8] do not refer to the isolated rotamers **A** and **B**.

Comparing the structures of the **X**−OH···OH$_2$ complex series (**X** = **A**, **B**, or **C**), we can see that the intermolecular O···O distance increases approximately by 0.01 Å in going from **X** = **A** to **B**, using both basis sets, and only 0.003 Å from **X** = **B** to **C** with 6-311++G(2df,2p). The addition of more polarization functions to the basis set produces no meaningful change in this intermolecular distance. Even the O−H bond distance changes a small amount, varying between 0.006 and 0.009 Å, for the three complexes. This also seems to be not dependent on the basis sets used. It is interesting to notice a small decrease in the dipole moments when we perform the calculations using the 6-311++G(2df,2p) basis set. This decrease is 0.3 D for **A**−OH···OH$_2$, 0.04 D for **B**−OH···OH$_2$, and 0.2 D for **C**−OH···OH$_2$. In this series, the less stable complex has the largest dipole moment. At the MP2/6-311++G(2df,2p) level this is calculated to be 7.12 D, which is only about 0.2 D larger than the vector sum between the dipole moments of the separated molecules of water and lactonitrile **C**. As can be seen in Tables 1 and 2, the two most stable complexes **A**−OH···OH$_2$ and **B**−OH···OH$_2$ have dipole moments of 1.38 and 1.79 D, respectively, with the 6-311++G(2df,2p) basis set.

Binding Energies. The calculated binding energies at the MP2 level, carried out with the two reported basis sets, for the **X**−OH···OH$_2$ complex series, are given in Table 4. All values are counterpoise-corrected for BSSE. This effect reduces the

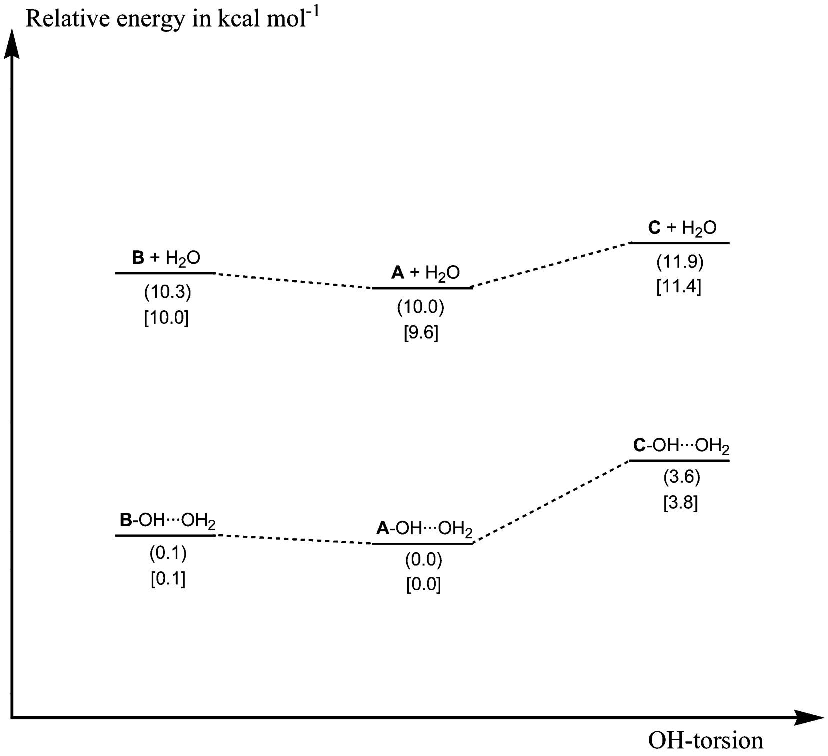

Figure 4. Relative energies for the three hydrogen bonded complexes of lactonitrile and water. Values are differences in energies with respect to complex (**A**−OH···OH$_2$) calculated at the MP2 level using (in parentheses) the 6-311++G(d,p) and (in brackets) the 6-311++G(2df,2p) basis sets. The difference between **X**−OH···OH$_2$ and **X** + H$_2$O corresponds to the binding energy without BSSE correction.

TABLE 4: Binding Energies (kcal mol^{-1}) for the Complexes of the Lactonitrile Rotamers

	A−OH···OH$_2$		B−OH···OH$_2$		C−OH···OH$_2$	
method	D_e	D_0	D_e	D_0	D_e	D_0
MP2/6-311++G(d,p)	7.87	5.81	7.96	5.76	6.34	4.44
MP2/6-311++G(2df,2p)	8.56	6.52	8.79	6.68	6.57	5.85

All values are corrected for BSSE. The symbols D_e and D_0 refer respectively to the binding energies without and with ZPVE correction.

calculated binding energies by about 2.0 kcal mol^{-1} using the 6-311++G(d,p) and 1.0 kcal mol^{-1} using the 6-311++G(2df,2p) basis sets. Also, the corresponding binding energies corrected for ZPVE are given in Table 4. As can be seen, the complexes **A**−OH···OH$_2$ and **B**−OH···OH$_2$ have a fairly similar binding energy (D_e about 8.0−9.0 kcal mol^{-1} or D_0 about 6.0−7.0 kcal mol^{-1}). These two complexes are more strongly bound than **C**−OH···OH$_2$ by almost 2 kcal mol^{-1}, although the calculated binding energies for the three species indicate relatively strong hydrogen bonded systems,[3] i.e., with binding energies in the range 4−8 kcal mol^{-1}. The strength of the hydrogen bonds in the complexes **A**−OH···OH$_2$ and **B**−OH···OH$_2$ is increased compared to that in **C**−OH···OH$_2$ because of the additional interaction between one hydrogen atom of water and the nitrogen in lactonitrile, forming a bent N···H hydrogen bond (Figure 3). The angle H···N≡C is about 82° in both cases with the dihedral angle N···H−O···H varying between ca. 20 and 26°. This type of bent hydrogen bond has been noted before[4] for the $(CH_3)_3C-C\equiv N\cdots H_2O$ complex. In the case of **C**−OH···OH$_2$ the hydrogen bond is very similar to that occurring in the water dimer and in alcohol−water complexes.[19] Thus, considering the energetic aspects of lactonitrile−water aggregates, there is a preference for rotamers **A** and **B** of lactonitrile. This preference amounts to only ca. 2 kcal mol^{-1} and may be traced to the additional N···H interaction.

Figure 4 shows the relative stability of these hydrated complexes compared to their isolated moieties. As indicated in the diagram, complex **A**−OH···OH$_2$ is only 0.1 kcal mol^{-1} more stable than complex **B**−OH···OH$_2$, at the MP2/6-311++G(d,p) or MP2/6-311++G(2df,2p) levels. This difference in energy from **A**−OH···OH$_2$ increases to 3.6 kcal mol^{-1}, calculated with 6-311++G(d,p), or 3.8 kcal mol^{-1}, calculated with 6-311++G(2df,2p), as compared to the total energy of **C**−OH···OH$_2$. At the MP2/6-311++G(2df,2p) level, **B**−OH···OH$_2$ is slightly more bound than **A**−OH···OH$_2$ by 0.2 kcal mol^{-1}. However, as we have noticed before, this small amount of energy difference is not accompanied by a shortening of the intermolecular O···O distance, which is instead increased by 0.01 Å. Indeed, an expected shortening of 0.02 Å occurs for the intermolecular N···H distance in going from **A**−OH···OH$_2$ to **B**−OH···OH$_2$. As we shall see in the forthcoming section, this unusual fact is also observed for the frequency shifts of the donor OH stretching in lactonitrile (see Tables 5 and 6). At both levels of calculations the complex **A**−OH···OH$_2$ undergoes a red shift larger than **B**−OH···OH$_2$, although a consistent red shift appears for the CN stretching in these complexes. In the case of **C**−OH···OH$_2$, which is the less stable complex in this series, the O···O distance increases a little, i.e., by 0.013 Å, compared with **A**−OH···OH$_2$, considering the MP2/6-311++G(2df,2p) method. The calculated red shift for the donor OH stretching frequency is also consistent with the lower binding energy of **C**−OH···OH$_2$.

Vibrational Analysis. We have computed the harmonic vibrational frequencies and the corresponding infrared intensities for the three stable hydrated complexes of lactonitrile and their corresponding moieties as well, at the MP2 level using the 6-311++G(d,p) and 6-311++G(2df,2p) basis sets. The predicted infrared spectra of the complexes may be useful for a possible experimental detection of the complexes. Thus, we present these spectra in Tables 5−7. The three species,

TABLE 5: Calculated Vibrational Spectrum of the A−OH···OH$_2$ Complex of Lactonitrile

	MP2/6-311++G(d,p)				MP2/6-311++G(2df,2p)			
assgnt	ω (cm^{-1})	$\Delta\omega$ (cm^{-1})	I(km mol^{-1})	I_{ratio}	ω (cm^{-1})	$\Delta\omega$ (cm^{-1})	I(km mol^{-1})	I_{ratio}
$\nu_{OH(H_2O)}$	3974	−28	107.2	1.7	3944	−39	128.0	1.7
$\nu_{OH(H_2O)}$	3849	−35	24.5	1.9	3807	−52	43.6	4.0
ν_{OH}	3727	−141	369.6	7.5	3682	−166	379.5	6.8
$\nu_{CH(CH_3)}$	3193	−2	9.1	1.2	3203	−1	6.3	1.1
$\nu_{CH(CH_3)}$	3187	−3	9.8	1.2	3198	−3	7.3	1.2
$\nu_{CH(CH_3)}$	3089	−2	8.7	1.4	3099	−2	6.8	1.4
ν_{CH}	3062	−11	20.1	1.1	3064	−13	15.9	1.1
ν_{CN}	2173	−5	1.9	0.3	2184	−7	1.0	0.2
δ_{HOH}	1640	10	94.5	1.7	1646	−3	96.0	1.4
$\delta_{CH(CH_3)}$	1517	1	1.5	0.6	1517	1	1.7	0.7
$\delta_{CH(CH_3)}$	1502	0	6.5	1.2	1502	0	7.0	1.2
$\delta_{CH/OH}$	1472	37	39.2	3.6	1470	42	48.8	4.1
$\delta_{CH(CH_3)}$	1419	16	11.4	13.4	1416	17	9.7	0.7
δ_{CH}	1386	2	25.1	0.7	1376	−3	11.7	0.7
$\delta_{CH/OH}$	1338	37	22.6	0.5	1328	37	24.5	0.5
ν_{CO}	1172	8	53.6	1.1	1168	7	52.5	1.1
$\delta_{CH/OH}$	1122	18	19.3	1.6	1116	19	18.0	1.9
$\delta_{CH/CH}$	1085	12	27.0	0.5	1083	13	26.4	0.5
δ_{CCH}	957	0	14.7	0.8	955	−1	13.6	0.8
δ_{CCH}	813	−6	6.3	1.1	814	−7	3.6	0.9
OH tors	684		152.4		669		127.9	
δ_{CCN}	598	6	0.4	0.1	603	10	0.2	0.1
δ_{CCN}	559	4	5.7	1.0	564	5	4.2	1.4
δ_{OCC}	409	9	9.4	1.0	407	10	13.9	1.6
OH tors	352	14	75.6	0.6	387	63	84.8	0.7
intermol	296		158.0		300		115.2	
CH$_3$ tors	278	3	4.2	0.5	277	3	6.5	0.4
CH$_3$ tors	226	2	1.2	0.9	228	3	0.7	0.5
skeleton	194	14	2.3	0.3	200	17	14.0	1.5
intermol	176		52.4		185		43.5	
intermol	168		40.1		168		53.7	
intermol	105		9.2		110		6.7	
intermol	51		17.7		47		17.1	

TABLE 6: Calculated Vibrational Spectrum of the B−OH···OH$_2$ Complex of Lactonitrile

	MP2/6-311++G(d,p)				MP2/6-311++G(2df,2p)			
assgnt	ω (cm^{-1})	$\Delta\omega$ (cm^{-1})	I(km mol^{-1})	I_{ratio}	ω (cm^{-1})	$\Delta\omega$ (cm^{-1})	I(km mol^{-1})	I_{ratio}
$\nu_{OH(H_2O)}$	3967	−35	109.0	1.7	3940	−42	124.1	1.6
$\nu_{OH(H_2O)}$	3842	−42	30.5	2.3	3802	−57	42.6	3.9
ν_{OH}	3723	−137	302.3	7.2	3686	−154	310.4	6.5
$\nu_{CH(CH_3)}$	3187	−1	9.1	1.1	3198	−0	6.2	1.0
$\nu_{CH(CH_3)}$	3178	3	12.3	0.8	3186	3	9.3	0.9
$\nu_{CH(CH_3)}$	3128	−9	8.2	3.4	3129	−8	6.4	3.4
ν_{CH}	3080	1	8.1	1.3	3090	1	6.6	1.4
ν_{CN}	2172	−8	1.9	0.3	2184	−9	1.0	0.2
δ_{HOH}	1646	17	86.6	1.5	1647	−3	95.2	1.4
$\delta_{CH(CH_3)}$	1516	7	18.2	2.8	1515	5	1.9	0.6
$\delta_{CH(CH_3)}$	1515	6	4.1	0.9	1512	4	13.0	1.6
$\delta_{CH/OH}$	1484	50	37.7	0.9	1475	51	44.0	1.2
$\delta_{CH(CH_3)}$	1421	−4	10.3	1.2	1415	−4	10.3	1.2
δ_{CH}	1353	−1	5.7	0.7	1352	−3	5.7	0.9
$\delta_{CH/OH}$	1336	40	3.5	0.6	1331	35	2.5	0.4
ν_{CO}	1159	5	97.0	1.1	1155	4	91.7	1.0
$\delta_{CH/OH}$	1134	8	11.9	0.8	1130	6	11.1	0.8
$\delta_{CH/CH}$	1077	14	32.3	0.7	1072	16	33.6	0.6
δ_{CCH}	943	−3	9.6	0.9	942	−4	8.3	0.9
δ_{CCH}	808	0	4.3	0.5	809	0	3.3	0.5
OH tors	688		156.6		657		131.9	
δ_{CCN}	600	18	2.9	0.8	605	17	1.1	0.6
δ_{CCN}	563	−2	1.1	0.1	566	2	1.4	0.2
δ_{OCC}	404	−6	4.4	0.1	400	−1	5.9	0.3
OH tors	378	48	88.1	1.0	390	74	80.0	0.9
intermol	317		154.3		302		119.3	
CH3 tors	291	8	0.8	0.1	292	12	1.6	0.1
CH3 tors	233	14	2.1	0.2	239	18	1.9	0.1
skeleton	200	16	2.0	0.5	200	14	2.9	0.8
intermol	179		43.9		190		86.9	
intermol	173		47.7		176		21.4	
intermol	113		4.1		114		6.5	
intermol	61		14.8		62		12.3	

A−OH···OH$_2$, **B**−OH···OH$_2$, and **C**−OH···OH$_2$, as shown in Figure 3, are found to be true minima with the two theoretical models. Because the asymmetry of lactonitrile most of the vibrational modes are combinations of more than two stretching or bending modes. In general, these change to a lesser extent, but for some CH/OH combining modes we observe blue shifts in the range of about 1−50 cm^{-1} upon complexation. It is worthwhile to mention some typical observations occurring for

TABLE 7: Calculated Vibrational Spectrum of the C−OH···OH$_2$ Complex of Lactonitrile

	MP2/6-311++G(d,p)				MP2/6-311++G(2df,2p)			
assgnt	ω (cm^{-1})	$\Delta\omega$ (cm^{-1})	I(km mol^{-1})	I_{ratio}	ω (cm^{-1})	$\Delta\omega$ (cm^{-1})	I(km mol^{-1})	I_{ratio}
$\nu_{OH(H_2O)}$	3982	−20	99.5	1.6	3960.6	−22	107.1	1.4
$\nu_{OH(H_2O)}$	3869	−15	14.3	1.1	3841.8	−18	15.4	1.4
ν_{OH}	3750	−122	498.0	12.0	3701.3	−151	547.4	11.1
$\nu_{CH(CH_3)}$	3186	−3	10.5	1.4	3194.9	−4	7.6	1.4
$\nu_{CH(CH_3)}$	3174	5	15.2	1.1	3183.6	3	10.9	1.0
$\nu_{CH(CH_3)}$	3079	1	9.4	1.0	3088.9	0	7.4	1.0
ν_{CH}	3058	−8	21.7	1.1	3057.5	−12	18.7	1.2
ν_{CN}	2193	−4	5.6	0.7	2205.9	−4	4.0	0.7
δ_{HOH}	1647	18	65.9	1.2	1652.4	3	73.5	1.1
$\delta_{CH(CH_3)}$	1516	3	5.0	1.5	1519.8	4	6.3	1.9
$\delta_{CH(CH_3)}$	1511	3	4.1	0.7	1510.1	3	4.1	0.7
$\delta_{CH/OH}$	1460	29	16.1	0.8	1460.1	31	21.0	1.0
$\delta_{CH(CH_3)}$	1419	−6	11.4	1.6	1413.6	−6	10.5	1.2
δ_{CH}	1368	−3	15.1	1.4	1359.9	−1	6.0	1.0
$\delta_{CH/OH}$	1318	49	58.8	1.3	1312.5	49	52.2	1.2
ν_{CO}	1166	14	80.2	0.7	1161.8	16	93.9	0.8
$\delta_{CH/OH}$	1135	4	27.9	3.3	1128.0	1	17.2	2.0
$\delta_{CH/CH}$	1074	6	6.1	1.1	1076.4	10	6.7	1.4
δ_{CCH}	954	3	21.2	0.8	952.0	4	19.1	0.7
δ_{CCH}	816	0	2.5	0.7	819.6	2	1.5	0.7
OH tors	693		157.2		711.2		122.0	
δ_{CCN}	586	2	3.8	0.8	591.0	5	3.8	0.7
δ_{CCN}	555	4	0.8	0.2	562.0	4	0.8	0.5
δ_{OCC}	406	6	6.6	0.8	404.1	6	5.6	0.6
OH tors	310	18	126.3	75.7	304.0	14	23.2	9.4
intermol	288		107.2		265.3		160.2	
CH3 tors	236	6	12.8	1.1	239.7	0	42.0	1.4
CH3 tors	208	17	13.6	0.2	206.7	−9	9.8	0.1
skeleton	200	18	2.9	0.1	200.8	10	5.5	2.7
intermol	149		1.8		150.4		1.3	
intermol	108		31.9		99.7		42.2	
intermol	47		4.7		50.6		6.0	
intermol	14		0.4		24.5		0.3	

the OH torsional mode in these systems. For the isolated lactonitrile molecule, the calculated frequencies corresponding to this stretching mode are 338 cm^{-1} (323 cm^{-1}), 331 cm^{-1} (316 cm^{-1}), and 292 cm^{-1} (290 cm^{-1}), for rotamers **A**, **B**, and **C**, with MP2/6-311++G(d,p) [MP2/6-311++G(2df,2p)], respectively. After hydrogen bond formation these frequencies are blue shifted by 14 cm^{-1} (63 cm^{-1}), 48 cm^{-1} (74 cm^{-1}), and 18 cm^{-1} (14 cm^{-1}), respectively. However, the presence of the bonded water makes a resonant OH torsional mode appearing in the lactonitrile molecule lying at 684 cm^{-1} (669 cm^{-1}) for **A**−OH···OH$_2$, 688 cm^{-1} (657 cm^{-1}) for **B**−OH···OH$_2$, and 693 cm^{-1} (711 cm^{-1}) for **C**−OH···OH$_2$, with MP2/6-311++G(d,p) [MP2/6-311++G(2df,2p)], respectively.

The calculated infrared spectrum of **A**−OH···OH$_2$ is given in Table 5. We additionally present the ratios between the infrared intensities for the intramolecular vibrational modes. As expected, the largest shift is found for the OH stretching mode (ν_{OH}) of the hydrogen bond donor. This is red shifted by 141 and 166 cm^{-1}, calculated at the MP2/6-311++G(d,p) and MP2/6-311++G(2df,2p) levels, respectively. The ratio of the intensities of this mode increases correspondingly by a large factor of 7.5 or 6.8. The other modes of the complex that suffer red shifts are the stretching in water, varying between 28 and 35 cm^{-1} at the MP2/6-311++G(d,p) level and 39−52 cm^{-1} at the MP2/6-311++G(2df,2p) level. The OH stretching frequencies of water are red shifted. We cannot discard that this shift has a contribution from the N···H hydrogen bond. A curious aspect is observed with the HOH bending mode (δ_{HOH}) of the bonded water: using the MP2/6-311++G(d,p) method this mode is found to be blue shifted by 10 cm^{-1}, whereas using the MP2/6-311++G(2df,2p) method the δ_{HOH} mode is estimated to be red shifted by 3 cm^{-1}. This is also observed in a lesser degree for the calculated CH wagging mode (δ_{CH}) of **A**−OH···OH$_2$, which is blue shifted by 2 cm^{-1} at the MP2/6-311++G(d,p) and is red shifted by 3 cm^{-1} at the MP2/6-311++G(2df,2p) levels. Unfortunately, no experimental result seems to be available for this complex to evaluate the accuracy of the theoretical methods.

The vibrational changes in the complex **B**−OH···OH$_2$ are similar to those in complex **A**−OH···OH$_2$. As can be seen in Table 6, the ν_{OH} mode of the hydrogen bond donor is red shifted by 137 and 154 cm^{-1} (with ratio of intensities of 7.2 and 6.5), calculated at the MP2/6-311++G(d,p) and MP2/6-311++G(2df,2p) levels, respectively. In general, as can be seen in Tables 5 and 6, the vibrational modes and infrared intensities of the complex **B**−OH···OH$_2$ are perturbed similarly to those for the complex **A**−OH···OH$_2$. The vibrational spectrum of **C**−OH···OH$_2$ is reported in Table 7. This is the less strongly bonded complex in the rotamer series of lactonitrile. As can be seen, the stretching modes of the H$_2$O subunit, acting as a proton acceptor, are less red shifted than in the complexes **B**−OH···OH$_2$ and **A**−OH···OH$_2$. In the **C**−OH···OH$_2$ case the red shifts of these modes are estimated in the 15−20 cm^{-1} range at MP2/6-311++G(d,p) and in the 18−22 cm^{-1} range at MP2/6-311++G(2df,2p). The OH stretching of the hydrogen bond donor is found to be red shifted by 122 and 151 cm^{-1} (with ratio of intensities of 12 and 11, respectively), considering the two levels of calculations reported in this study. Indeed, this shift indicates yet that **C**−OH···OH$_2$ is a moderately strongly bound complex. In general, the changes in the vibrational spectrum of **C**−OH···OH$_2$ are very similar to that observed for the other two complexes.

Conclusions

The conformational stability of the hydrogen bonded complexes of lactonitrile rotamers and water has been investigated by ab initio calculations at the MP2 level of theory. Our results show that the relative stability between rotamers **A** and **B** is significantly reduced from 0.36 to 0.1 kcal mol^{-1} upon complexation. Conformers **A** and **B** have the same binding to water, within 0.1 kcal mol^{-1}, and both are more strongly bonded to water than **C**, by ~2 kcal mol^{-1}. However, the calculated binding energies at the MP2 level indicate that the three rotamers are strong hydrogen bond donor systems. This information is of importance in connection with the dissociation of lactonitrile forming HCN and CH_3CHO. It is also interesting to note that the aqueous environment can alter the conformational stability of lactonitrile, so that we might expect to identify preferentially the structures **A**−OH···OH_2 and **B**−OH···OH_2. This is opposite to a recent study[20] in the conformational equilibrium of furfural in water. We have noted that hydrogen bond, although important, has the same strength for every rotamer in furfural and therefore does not play an important role is ascribing a preferential conformation.

In supplement, analyzing the calculated infrared spectra of these complexes, we have estimated frequency shifts and intensity ratios for the OH stretching mode of the hydrogen bond donor. These vibrational changes are typical for strongly bonded complexes, showing a correlation with the binding energies.[21] In general, comparing the results obtained at MP2 level using the 6-311++G(d,p) and 6-311++G(2df,2p) basis sets, the predicted changes in the spectra of these complexes give a similar description. This theoretical work is an attempt to provide important predictions and to aid in the future experimental and theoretical studies toward the understanding of lactonitrile−water complexes and the role of hydrogen bond in conformational equilibrium of molecular aggregates.

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