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Matrix Infrared Spectra and ab Initio Calculations of the Formohydroxamic Acid Complexes with HF and HCl

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Argon matrix infrared spectra of the complexes formed between formohydroxamic acid (HCONHOH) or its isotopic analogues (HCONDOD, HCO^{15}NHOH) and hydrogen halides (HF, HCl) have been recorded. The experimental results indicate formation of a very strong binary complex in which the hydrogen halide molecule acts as a proton donor toward the carbonyl group of formohydroxamic acid. The H−X stretches and several perturbed HCONHOH, HCONDOD, and HCO^{15}NHOH vibrations were identified for the two HX complexes; for the HF complex two librational HF modes were also observed. Theoretical studies of the structure and spectral characteristics of the HCONHOH···HF and HCONHOH···HCl complexes were carried out on the electron correlation level with the 6-311++G(2d,2p) basis set. The calculated vibrational frequencies for the complexes present in matrixes are in good agreement with the experimental data. The calculations demonstrate also the stability of the other three binary complexes. In the cyclic structure the HX molecule acts as a proton donor for the C═O group and a proton acceptor for the NOH group, and in the two less stable structures the HX is attached to the oxygen or nitrogen atom of the NOH group.

Introduction

Hydroxamic acids have been recently the subject of growing interest which is stimulated by their properties as iron chelators with therapeutic potential,[1] their photochemical properties,[2] and their characteristics as specific enzyme inhibitors.[3] Among the problems that attracted the most attention of the researchers is the identity of the preferred structure of the hydroxamic acid and its acidity. The amount of theoretical and experimental work performed so far leads to the conclusion that both the stability of different isomers of hydroxamic acids[4−6] and their behavior as N- or O-acids[7−10] are strongly dependent on the environment. The recent theoretical calculations showed that formo- and acetohydroxamic acids should behave as N-acids in the gas phase,[11−13] but as O-acids in aqueous solutions.[11] Ventura et al.[14] performed a comparative ab initio study of gas-phase structure and acidity of formohydroxamic acid and formamide and concluded that the OH group in formohydroxamic acid stabilizes the enol form with respect to the keto one, in comparison with the analogous situation in formamide.

Hydroxamic acids are *N*-hydroxy substituted derivatives of amides and involve, like amides, the fragment of the simplest protein structure HNC═O. The hydrogen bonding abilities and, in particular, the site of protonation for amides[15] have been examined extensively in the literature due to the biological importance of amides. It is now a well-recognized fact that the carbonyl oxygen is the predominant basic center in amides[15,16] but the nitrogen atom may also act as a proton acceptor in complexes with strong proton donors.[15,17] In addition to the two basic centers characteristic for the HNC═O group, hydroxamic acids have a third basic center, which is the oxygen atom of the hydroxyl group. Despite extensive studies of the basicity of amides, the basicity of hydroxamic acids and, in particular, the influence of *N*-hydroxy substituent on the two basic centers of the HNC═O group have not been studied so far.

In our recent paper[18] we showed that formohydroxamic acid (FHA) trapped from the gas phase into solid argon or nitrogen exists in matrixes preferentially in the keto form with an intramolecular hydrogen bond. To evaluate the proton acceptor abilities of the three basic centers of the formohydroxamic acid molecule, we have performed infrared and ab initio studies of the formohydroxamic acid complexes with strong proton donors: hydrogen fluoride and hydrogen chloride. The experiments were carried out also for the complexes of isotopically substituted formohydroxamic acid: HCONDOD···HX and HCO^{15}NHOH···HX. The matrix infrared spectra provide information about the geometry of the energetically favored complexes trapped in the matrix. The results of ab initio calculations indicate all probable structures of the HCONHOH···HX binary complexes and their interaction energies providing information on the relative basicity of the three basic sites in the formohydroxamic acid molecule. The results of our study are presented in this paper.

Experimental Section

Infrared Matrix Isolation Studies. Formohydroxamic acid was prepared and purified by the method previously described.[19] Deuterated formohydroxamic acid was prepared by multiply dissolving FHA in D_2O (99%). The 50% enriched ^{15}N-substituted formohydroxamic acid was synthesized from $H_2NOH{\cdot}HCl$ (50%) + $H_2{}^{15}NOH{\cdot}HCl$ (50%) (Cambridge Isotope Laboratories, Inc.).

The HF/Ar or HCl/Ar and HCONHOH/Ar (HCONDOD/Ar or HCO^{15}NHOH/Ar) gas mixtures were co-deposited simultaneously through two separate spray-on lines. Formohydroxamic acid was evaporated from the glass bulb kept at room temperature, which was connected to the cryostat via a glass tube. The HF/Ar and HCl/Ar mixtures were prepared by standard manometric technique; the concentration of HF/Ar and HCl/Ar varied in the range 1/100−1/2000.

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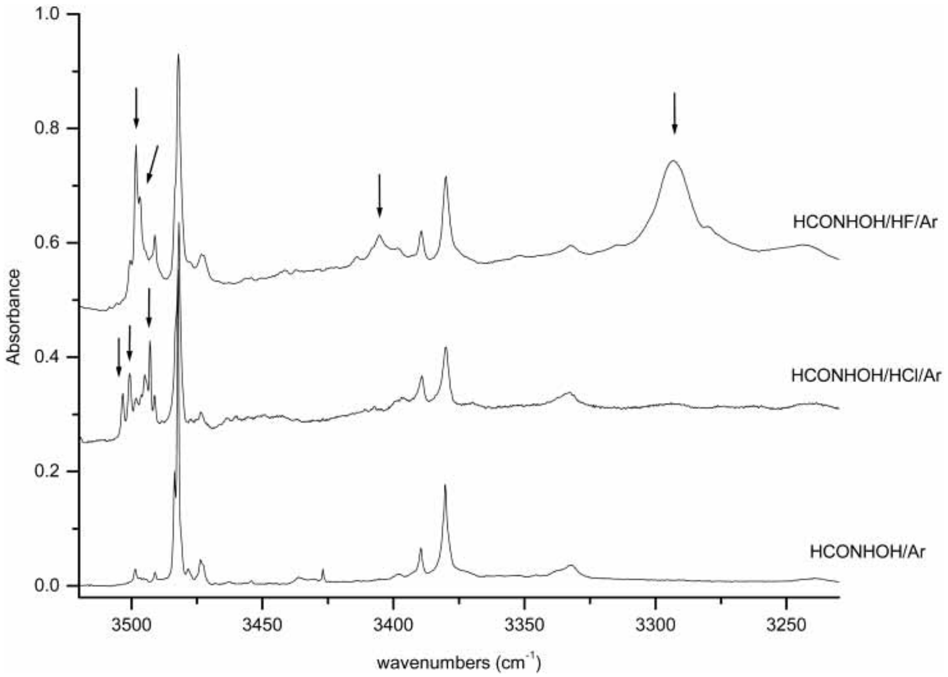

Figure 1. The 3520−3230 cm^{-1} region in the infrared spectra of matrixes obtained by co-deposition of vapor pressure above solid formohydroxamic acid (T = 300 K) with Ar and with HF/Ar = 1/200, HCl/Ar = 1/300 gas mixtures.

Gold-plated copper mirror was used as a sample holder and was maintained at 20 K (12 K for IR measurements) by means of a closed-cycle helium refrigerator (Air Products, Displex 202A). Infrared spectra were recorded in a reflection mode with a resolution of 0.5 cm^{-1} by means of a Bruker 113v FTIR spectrometer using a liquid N_2 cooled MCT detector (4000−600 cm^{-1}).

Computational Details. Ab initio calculations were carried out using the GAUSSIAN 98 package of computer codes.[20] Electron correlation was considered via the Möller−Plesset perturbation theory[21,22] to the second order (MP2(FC)). The structures of the isolated monomers, HCONHOH and HX (X = F, Cl), and the structures of formohydroxamic acid complexes with HX were fully optimized by using the 6-311++G(2d,2p) basis set.[23,24] Vibrational frequencies and intensities were computed both for the monomers and for the complexes. Interaction energies were corrected by the Boys−Bernardi full counterpoise correction.[25]

Results

Experimental Spectra. The spectra of FHA/Ar and HX/Ar (X = F, Cl) matrixes were recorded before the study of complexes was undertaken. In the spectra of FHA/Ar matrixes weak bands due to formohydroxamic acid decomposition products (NH_2OH, NH_3, $HCONH_2$, HCOOH, CO_2) were also present,[18] but the concentration of contaminants was low and thus permitted the study of the formohydroxamic acid complexes.

The spectra of FHA/HX/Ar (X = F, Cl) matrixes showed a number of prominent new absorptions as compared to the spectra of HX/Ar and FHA/Ar matrixes. Most of the product absorptions appeared in the vicinity of the FHA monomer bands and were assigned to the perturbed vibrations of FHA in the complex. Additional product bands were also observed for the ν_s(HF), ν_{libr}(HF), and ν_s(HCl) vibrations as discussed below. The representative regions of the HCONHOH/HX/Ar spectra are shown in Figures 1−3.

Formohydroxamic Acid···HF Complexes. In the spectra of HCONHOH/HF/Ar matrixes the new absorptions appeared at 3498.5, 3497.0, 3405.5, 2948.5, 1662.5, 1390.0 1352.5, 860.0, 775.0, and 599.0 cm^{-1} in the vicinity of the HCONHOH vibrations. On the broad 1390.0 cm^{-1} band a subpeak occurred at 1393.5 cm^{-1}, and the very weak 775 cm^{-1} band showed a shoulder at 774 cm^{-1}. In addition, a strong, broad band appeared at 3293.0 cm^{-1} and two strong, characteristic bands were observed at 796.0 and 742.5 cm^{-1} (see Figures 1−3). The relative intensities of the new product bands were not sensitive to matrix annealing and were independent of matrix concentration.

Several experiments were performed with HCONDOD. When HF/Ar mixture was co-deposited with HCONDOD, the new absorptions appeared at 2601.5, 2599.5, 2521.0, 1658.5, 1656.0, 1354.5, 1344.0, 1121.5, 969.5, and 597.5 cm^{-1} in the vicinity of the HCONDOD molecule vibrations. Additional bands that occurred at 3290.5, 792.5, and 743.0 cm^{-1} corresponded to 3293.0, 796.0, and 742.5 cm^{-1} absorptions in experiments with nondeuterated HCONHOH sample.

In addition, a number of experiments were performed with ^{15}N-substituted formohydroxamic acid. In the spectra of HCO-^{15}NHOH/HF/Ar matrixes new product bands were observed at 3491.5, 3490.0, 3405.5, 1660.0, 1380.5, 1351.5, 855.0, 770.0, 769.0, and 596.0 cm^{-1} in the vicinity of the HCO^{15}NHOH vibrations. The 3293.5, 796.0, and 742.0 cm^{-1} absorptions appeared at frequencies very close to the corresponding absorptions in the HCONHOH experiments.

Formohydroxamic Acid···HCl Complexes. In the spectra of HCONHOH/HCl/Ar matrixes the product absorptions were observed at 3503.5, 3500.5, 3493.0, 1654.5, 1647.5, 1391.0, 1388.0, 1349.0, 855.0, 853.5, and 771.5 cm^{-1} in the vicinity of the HCONHOH molecule vibrations (see Figures 1−3). An additional broad and diffuse band was detected at ca. 2380 cm^{-1}. The above absorptions were observed for all concentrations studied. With an increase of HCl concentration in the matrix, all product bands grew at the same rate.

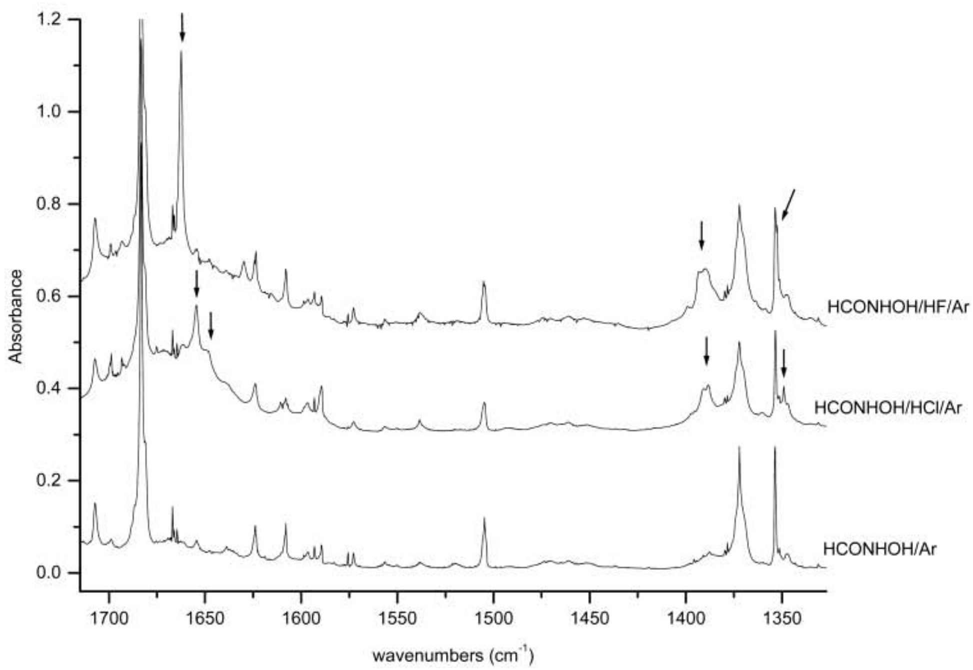

Figure 2. The 1720−1320 cm^{-1} region in the spectra of the same matrixes as presented in Figure 1.

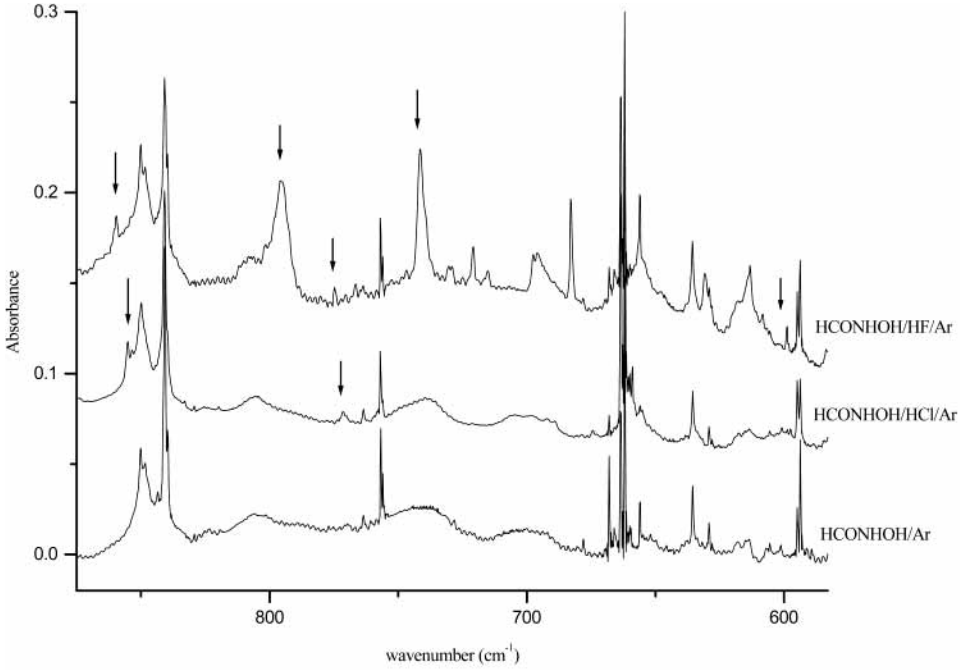

Figure 3. The 900−550 cm^{-1} region in the spectra of the same matrixes as presented in Figure 1.

The spectra of HCONDOD/HCl/Ar matrixes also showed new absorptions in the vicinity of the HCONDOD vibrations at 2598.0, 2596.0, 2518.0, 1651.0, 1644.5, 1351.5, 1340.0, and 1122.0 cm^{-1}.

The spectra of HCO^{15}NHOH/HCl/Ar matrixes showed the product bands at 3486.0, 3484.0, 1650.5, 1380.0, 1377.0, and 1348.0 cm^{-1}.

The frequencies of all product absorptions observed in the spectra of HCONHOH (HCONDOD, HCO^{15}NHOH)/HF/Ar and HCONHOH(HCONDOD, HCO^{15}NHOH)/HCl/Ar matrixes are collected in Tables 1 and 2, respectively.

Ab Initio Calculations. *Monomers.* The calculated data for HCONHOH, HF, and HCl are reported in Table 3 together with the available experimental data for HF and HCl. Comparison of the calculated and experimental values of geometrical parameters for HF and HCl shows that the theoretical approach used in this study well reproduces the experimental data. As is evident in Table 3, also the calculated MP2 dipole moments of the HF and HCl molecules are in reasonable agreement with the experimental values. The structure of formohydroxamic acid in the gas phase has not yet been determined; however, it was revealed in earlier studies[12] that the basis set used in this study well reproduces the experimental gas-phase proton dissociation energy of acetohydroxamic acid.[10]

The harmonic vibrational frequencies computed for the isolated molecules are presented in Tables 5 and 6.

Complexes. The results of geometry optimizations of formohydroxamic acid complexes with the HF and HCl subunits are collected in Table 4. Four stationary points for the HCONHOH···HX complexes calculated at the MP2 level with the

TABLE 1: Observed Frequencies and Frequency Shifts, $\Delta\nu^{a} = \nu_{\mathrm{complex}} - \nu_{\mathrm{monomer}}$, for Formohydroxamic Acid−Hydrogen Fluoride Complex in Solid Argon (cm^{-1})^{b}

HCONHOH/HF	HCONHOH···HF		HCONDOD	HCONDOD···HF		HCO^{15}NHOH	HCO^{15}NHOH· ·HF		
monomers	ν	$\Delta\nu$	monomer	ν	$\Delta\nu$	monomer	ν	$\Delta\nu$	assignment^{c}
3919.5	3293.0	−626.5		3290.5	−629.0		3293.5	−626.0	HF stretch
3483.5 s	3498.5	+15.0	2575.5	2601.5	+25.0	3474.0	3491.5	+17.0	NH stretch
3482.0	3497.0		2572.0 s	2599.5			3490.0		
3389.0 s	3405.5	+21.0	2507.5	2521.0	+16.0	3389.0 s	3405.5	+21.0	OH stretch
3380.0			2503.5 s			3380.0			
2912.0	2948.5	+36.5	2909.0			2912.0			CH stretch
1683.0	1662.5	−20.5	1682.0	1658.5	−24.0	1681.0	1660.0	−21.0	amide I (C═O stretch)
1681.5 sh				1656.0					
1505.0			1117.0	1121.5	+4.5	1494.5			amide II (NH bend)
1374.0 sh	1393.5	+19.0	944.0	969.5	+26.5	1360.5 sh	1380.5	+21.5	NOH bend
1372.0	1390.0		942.0 s			1359.0			
1369.5 sh									
1354.0	1352.5	−1.5	1356.0	1354.5	−1.5	1353.0	1351.5	−1.5	CH i.p. bend
1292.5			1325.5 s	1344.0	+20.0	1288.6			amide III (CN stretch)
1291.0 s			1324.0			1287.0 s			
1186.0			1181.5			1183.0			CH o.p. bend
841.0	860.0	+20.0	802.0			834.5	855.0	+20.5	NO stretch
839.5 s									
	796.0			792.5			796.0		HF libr sym
756.5	775.0	+18.0	690.5			752.0	770.0	+18.0	amide IV (OCN bend)
756.0 s	774.0						769.0		
	742.5			743.0			742.0		HF libr asym
595.0	599.0	+4.0	593.0	597.5	+5.0	591.5	596.0	+6.0	CN torsion
594.0 s			592.0 s			589.0 s			

[a] In the case of doublets or triplets observed for one fundamental, the average of the frequencies is taken into account. [b] s: the less intense of the two component bands corresponding to each fundamental. [c] Only the internal coordinate giving the main contribution to the normal mode is given.

TABLE 2: Observed Frequencies and Frequency Shifts, $\Delta\nu^{a} = \nu_{\mathrm{complex}} - \nu_{\mathrm{monomer}}$, for Formohydroxamic Acid−Hydrogen Chloride Complex in Solid Argon (cm^{-1})^{b}

HCONHOH/HCl	HCONHOH···HCl		HCONDOD	HCONDOD···HCl		HCO^{15}NHOH	HCO^{15}NHOH···HCl		
monomer	ν	$\Delta\nu$	monomer	ν	$\Delta\nu$	monomer	ν	$\Delta\nu$	assignment^{c}
2887.0	∼2380	−507							HCl stretch
3483.5 s	3503.5	+16.0	2575.5	2598.0	+22.0	3474.0	3486.0	+11.0	NH stretch
3482.0	3500.5		2572.0 s	2596.0			3484.0		
	3493.0								
3389.0 s			2507.5	2518.0 sh	+13.0	3389.0 s			OH stretch
3380.0			2503.5 s			3380.0			
2912.0			2909.0			2912.0			CH stretch
1683.0	1654.5	−31.0	1682.0	1651.0	−31.0	1681.0	1650.5	−31.0	amide I (C═O stretch)
1681.5 sh	1647.5			1644.5 sh					
1505.0			1117.0	1122.0	+5.0	1494.5			amide II (NH bend)
1374.0 sh	1391.0	+18.0	944.0			1360.5 sh	1380.0	+18.5	NOH bend
1372.0	1388.0		942.0 s			1359.0	1377.0		
1369.5 sh									
1354.0	1349.0	−5.0	1356.0	1351.5	−4.5	1353.0	1348.0	−5.0	CH i.p. bend
1292.5			1325.5 s	1340.0	+15.0	1288.6			amide III (CN stretch)
1291.0 s			1324.0			1287.0 s			
1186.0			1181.5			1183.0			CH o.p. bend
841.0	855.0	+14.0	802.0			834.5			NO stretch
839.5 s	853.5								
756.5	771.5	+15.0	690.5			752.0			amide IV (OCN bend)
756.0 s									
595.0			593.0			591.5			CN torsion
594.0 s			592.0 s			589.0 s			

[a] In the case of doublets or triplets observed for one fundamental, the average of the frequencies is taken into account. [b] s: the less intense of the two component bands corresponding to each fundamental. [c] Only the internal coordinate giving the main contribution to the normal mode is given.

6-311++G(2d,2p) basis set are presented in Figure 4. Structures I and III describe the hydrogen bonded complexes with the HX molecule playing the role of proton donor and directed along one of the two electron pairs of the oxygen atom of the C═O or OH groups, respectively. Structure II describes the cyclic complex with seven-membered ring in which HX acts as a proton donor for the oxygen atom of the C═O group and as a proton acceptor for the OH group. The three complexes are nonplanar. In structure IV the HX molecule is hydrogen bonded to the nitrogen atom and is located perpendicularly to the FHA plane.

The MP2 optimized intermolecular distances, *R*, between two heavy atoms involved in the hydrogen bridge are in the range 2.55−2.81 Å for the HF complexes and 3.04−3.35 Å for the HCl ones. There are no available experimental structures for these systems. The calculated intermolecular distances for the

TABLE 3: Calculated Properties of Isolated Molecules[a]

HCONHOH

property	calcd	property	calcd
r(C=O)	1.2252	$\theta(H_1{-}C{-}N)$	113.02
r(CN)	1.3574	$\theta(C{-}N{-}H_2)$	120.15
r(NO)	1.4011	$\theta(H_2{-}N{-}O)$	111.48
$r(C{-}H_1)$	1.0939	$\theta(N{-}O{-}H_3)$	101.25
$r(N{-}H_2)$	1.0062	$\theta(O\cdots H_3{-}O)$	118.78
$r(O{-}H_3)$	0.9750	ϕ(OCNO)	−11.20
$r(O\cdots H_3)$	2.0260	$\phi(H_1CNO)$	171.73
θ(O=C−N)	122.10	$\phi(H_1CNH_2)$	32.97
θ(C−N−O)	115.84	$\phi(CNOH_3)$	3.79
$\theta(O{=}C{-}H_1)$	124.82	$\phi(H_2NOH_3)$	146.01
		μ	3.283

property	calcd	exptl
	HF	
R	0.918	0.917[b]
μ	1.873	1.83[b]
	HCl	
R	1.270	1.275[b]
μ	1.183	1.09[b]

[a] Bond lengths are in angstroms, angles in degrees, dipole moments in debyes, and frequencies in cm^{-1}. [b] From ref 26.

HCONHOH···HX complexes are close to the experimental values for strongly hydrogen bonded complexes between oxygen bases and hydrogen halides.[27−31] The experimentally determined distances between two heavy atoms involved in the hydrogen bridge are equal to 2.662 and 3.215 Å for the $H_2O\cdots HX$ complexes[27,28] where HX = HF and HCl, respectively.

The largest elongation of the H−X bond, Δr(HX), upon complex formation occurs for the cyclic structures and is equal to 0.038 Å for HF and 0.039 Å for HCl complexes. In the complexes with HX bonded to carbonyl group this perturbation is also significant: 0.022 Å for HF and 0.029 Å for HCl system. The least Δr(HX) elongation is calculated for the structures in which the oxygen or nitrogen atoms of the NOH group play the role of proton acceptor: 0.015 or 0.013 Å for HF and 0.017 or 0.012 Å for HCl complexes, respectively.

Counterpoise-corrected MP2 interaction energies, ΔE^{CP}, are also presented in Table 4. The comparison of the interaction energy values shows that HF complexes are much more stable than HCl ones. Among the four stable HF complexes the cyclic complex II is characterized by the lowest value of the interaction energy, $\Delta E^{CP} = -8.40$ kcal mol^{-1}. The next one with respect to the value of interaction energy is complex I for which $\Delta E^{CP} = -7.72$ kcal mol^{-1}. Thus, the energy difference between complex I and complex II is equal to 0.68 kcal mol^{-1}. The zero-point vibrational energy corrections reduced the energy difference between structures I and II to 0.03 kcal mol^{-1}. We performed for these two structures single point calculations at the MP2 level with the more extended basis set 6-311++G-(3df,3pd). The obtained interaction energy values, ΔE^{CP}, were equal to −8.78 and −7.93 kcal mol^{-1} for structures II and I, respectively. In the case of HCl complexes the lowest value of the interaction energy corresponds to structure I in which the HX subunit is hydrogen bonded to the oxygen atom of the carbonyl group of HCONHOH. Complex I ($\Delta E^{CP} = -3.23$ kcal mol^{-1}) is calculated to be 0.6 kcal mol^{-1} more stable than the

TABLE 4: Calculated Properties of HCONHOH···HX (X = F, Cl) Complexes[a]

	HCONHOH···HF				HCONHOH···HCl			
property	structure I	structure II	structure III	structure IV	structure I	structure II	structure III	structure IV
$R((C)O\cdots X)$	2.622	2.551			3.087	3.042		
$R(N\cdots X)$				2.815				3.355
$R((N)O\cdots X)$		2.776	2.707			3.280	3.215	
r(HX)	0.939	0.956	0.933	0.931	1.299	1.309	1.287	1.282
Δr(HX)	0.022	0.038	0.015	0.013	0.029	0.039	0.017	0.012
r(C=O)	1.239	1.235	1.223	1.215	1.237	1.228	1.223	1.219
Δr(C=O)	0.014	0.010	−0.002	−0.010	0.012	0.005	−0.002	−0.006
r(CN)	1.333	1.338	1.365	1.388	1.336	1.348	1.364	1.376
r(NO)	1.389	1.384	1.413	1.412	1.391	1.388	1.410	1.408
$r(CH_1)$	1.091	1.094	1.093	1.094	1.092	1.096	1.093	1.094
$r(NH_2)$	1.003	1.004	1.011	1.012	1.004	1.005	1.010	1.010
$r(OH_3)$	0.974	0.975	0.979	0.975	0.974	0.970	0.979	0.975
$\Delta r(OH_3)$	0.001	0.0	0.004	0.0	0.001	0.005	0.004	0.0
θ(OCN)	121.2	125.9	121.7	121.9	121.4	125.8	121.7	121.9
θ(CNO)	118.7	123.6	113.4	113.8	118.3	121.5	113.9	114.6
$\theta(OCH_1)$	124.4	122.5	125.0	125.1	124.3	123.0	125.0	125.0
$\theta(H_1CN)$	114.3	111.5	113.2	112.9	114.2	111.1	113.2	113.0
$\theta(CNH_2)$	124.7	121.9	118.9	114.9	124.1	120.9	119.1	117.0
$\theta(H_2NO)$	113.5	113.3	110.2	109.1	113.2	113.1	110.5	110.0
$\theta(NOH_3)$	101.6	105.5	101.2	102.1	101.5	105.1	101.0	101.8
$\Theta(C{=}O\cdots H)$	108.8	114.6			106.1	115.1		
$\Theta(O{-}N\cdots H)$				106.2				97.3
$\Theta(H\cdots OH_3)$			121.3				117.5	
$\Theta(H\cdots CN)$				107.9				108.8
$\Theta(O\cdots HX)$	168.5	162.3	151.7		167.1	164.5	153.9	
$\Theta(N\cdots HX)$				172.6				174.1
$\Phi(CO\cdots HX)$	2.1	3.7			1.63	15.3		
$\Phi(CN\cdots HX)$				−67.5				−88.9
$\Phi(ON\cdots HX)$				170.0				152.0
$\Phi(H\cdots OCN)$	178.0	28.1			177.9	33.8		
$\Phi(CNO\cdots H)$			119.8				114.1	
$\Phi(HF\cdots OH_3)$		−18.0	119.0			−17.9	119.2	
μ	4.866	4.394	1.744	3.679	4.241	4.132	1.801	3.3728
ΔE^{CP}	−7.72	−8.40	−4.39	−2.59	−3.23	−2.62	−0.93	−0.22
ΔE^{CP}(ZPVE)	−5.73	−5.76	−2.22	−0.68	−1.78	−0.93	0.60	0.99

[a] Bond lengths are in angstroms, angles in degrees, dipole moments in debyes, and energies in kcal mol^{-1}.

TABLE 5: Calculated Frequencies and Frequency Shifts of HCONHOH···HF Complexes (cm^{-1})

HCONHOH/HF monomer	complex structure I		complex structure II		complex structure III		complex structure IV		assignment
	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	
Intramolecular									
4165.3	3674.7	−490.6	3346.0	−819.3	3824.0	−341.3	3843.2	−322.1	HF stretch
3663.1	3707.3	+44.2	3689.3	+26.2	3608.8	−54.3	3577.7	−85.4	NH stretch
3629.9	3655.0	+25.1	3632.2	+2.3	3557.7	−72.2	3639.2	+9.3	OH stretch
3081.2	3123.4	+42.2	3087.8	+6.6	3098.8	+17.6	3091.1	+9.9	CH stretch
1726.3	1707.8	−18.5	1727.5	+1.2	1728.4	+2.1	1745.3	+19.0	amide I (C═O stretch)
1558.7	1588.8	+30.1	1579.6	+20.9	1405.0	−153.7	1532.6	−26.1	amide II (NH bend)
1415.2	1439.0	+23.8	1503.4	+88.2	1548.5	+133.3	1380.6	−34.6	NOH bend
1393.3	1391.4	−1.9	1419.0	+25.7	1388.9	−4.4	1405.3	+12.0	CH i.p. bend
1221.6	1242.1	+20.5	1270.1	+48.5	1213.9	−7.7	1184.4	−37.2	amide III (CN stretch)
1016.1	1011.7	−4.4	1019.3	+3.2	1026.4	+10.3	1037.4	+21.3	CH o.p. bend
969.3	995.6	+26.3	985.1	+15.8	964.8	−4.5	948.3	−21.0	NO stretch
858.1	878.2	+20.1	833.1	−25.0	860.8	+2.7	854.6	−3.5	amide IV (OCN bend)
510.3	531.4	+21.1	531.0	+20.7	552.7	+42.4	351.4	−158.9	CN torsion
411.0	214.2	−196.8	284.3	−126.7	420.2	+9.2	565.0	+154.0	amide V (NH o.p. bend)
376.9	330.5	−46.4	491.4	+114.5	481.9	+105.0	456.6	+79.7	OH o.p. bend
294.4	340.8	+46.4	338.3	+43.9	332.9	+38.5	307.1	+12.7	CNO bend
Intermolecular									
	814.6		1015.7		780.0		774.6		HF in plane
	757.5		880.8		680.5		652.5		HF o.o. plane
	184.4		178.1		204.7		163.7		stretch
	51.0		94.3		89.3		63.7		HCONHOH in plane
	44.4		229.8		43.7		51.0		HCONHOH o.o. plane

TABLE 6: Calculated Frequencies and Frequency Shifts of HCONHOH···HCl Complexes (cm^{-1})

HCONHOH/HCl monomer	complex structure I		complex structure II		complex structure III		complex structure IV		assignment
	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	
Intramolecular									
3002.2	2603.3	−398.9	2481.8	−520.4	2774.1	−228.1	2826.4	−175.8	HCl stretch
3663.1	3699.9	+36.8	3672.2	+9.1	3613.8	−44.3	3606.7	−56.4	NH stretch
3629.9	3650.7	+20.8	3690.8	+60.9	3567.3	−62.6	3634.4	+4.5	OH stretch
3081.2	3108.8	+27.6	3062.4	−18.8	3095.4	+14.2	3087.5	+6.3	CH stretch
1726.3	1703.0	−23.3	1728.8	+2.5	1727.0	+0.7	1735.4	+9.1	amide I (C═O stretch)
1558.7	1583.9	+25.2	1534.6	−24.1	1405.5	−153.2	1538.8	−19.9	amide II (NH bend)
1415.2	1435.2	+10.0	1475.3	+60.1	1551.9	+136.7	1386.5	−28.7	NOH bend
1393.3	1393.5	+0.2	1419.4	+26.1	1389.7	−3.6	1405.0	+11.7	CH i.p. bend
1221.6	1239.5	+17.9	1251.3	+29.7	1212.7	−8.9	1198.3	−23.3	amide III (CN stretch)
1016.1	1011.8	−4.3	1022.5	+6.4	1021.7	+5.6	1026.6	+10.5	CH o.p. bend
969.3	991.1	+21.8	986.1	+16.8	964.6	−4.7	954.9	−14.4	NO stretch
858.1	863.7	+5.6	848.9	−9.2	859.1	+1.0	852.5	−5.6	amide IV (OCN bend)
510.3	528.6	+18.3	514.1	+3.8	517.8	+7.5	353.6	−156.7	CN torsion
411.0	238.4	−172.6	261.0	−150.0	447.3	+36.3	626.0	+215.0	amide V (NH o.p. bend)
376.9	348.0	−28.9	389.8	+12.9	371.4	−5.5	478.9	+102.0	OH o.p. bend
294.4	323.0	+28.6	312.9	+18.5	317.4	+23.0	301.3	+6.9	CNO bend
Intermolecular									
	625.3		695.0		604.9		410.2		HCl in plane
	566.7		600.2		502.8		373.3		HCl o.o. plane
	133.6		161.8		149.5		107.6		stretch
	52.8		128.2		76.3		42.5		HCONHOH in plane
	42.7		74.4		28.5		33.5		HCONHOH o.o. plane

Figure 4. Optimized structures of formohydroxamic acid complexes with hydrogen halides.

cyclic complex II ($\Delta E^{CP} = -2.62$ kcal mol^{-1}). The zero-point vibrational energy corrections increased the energy difference between these two structures to 0.81 kcal mol^{-1}.

The HF complexes described by structures III and IV are 4.0 and 5.8 kcal mol^{-1} less stable, respectively, than the most stable HF complex described by structure II. In turn, the HCl complexes III and IV are 2.3 and 3.0 kcal mol^{-1} less stable, respectively, than complex I corresponding to the global minimum on the potential energy surface. The obtained results indicate that carbonyl oxygen in formohydroxamic acid as in formamide is the strongest basic center and the oxygen atom of the NOH group exhibits stronger basic properties than the nitrogen atom.

The calculated vibrational frequencies of formohydroxamic acid complexes with the HF and HCl subunits are collected in Tables 5 and 6, respectively.

Discussion

Formohydroxamic Acid−Hydrogen Fluoride. The set of bands observed in the spectra of HCONHOH/HF/Ar matrixes at 3498.5, 3497.0, 3405.5, 2948.5, 1662.5, 1393.5, 1390.0, 1352.5, 860.0, 775.0 (with a shoulder at 774 cm^{-1}), and 599.0 cm^{-1} close to the HCONHOH absorptions and the characteristic

TABLE 7: Frequencies (cm^{-1}) of ν_s(HX) and ν_{libr}(HX) Vibrations in a Series of Complexes between Carbonyl Compounds and Hydrogen Halides in Solid Argon

		HF complexes			HCl complexes	
base	PA[a] (kJ/mol)	ν_s	ν_{libr}	ref	ν_s	ref
H_2CO	713	3750	612; 602	32		
$CH_3(H)CO$	769	3416	722; 693	32		
CH_3COOH	784	3406	736; 699	33		
CH_3COOCH_3	822	3351	756; 728	33	2450	36
$(CH_3)_2CO$	812	3302	778; 756	32	2392	35
HCONHOH	834	3293.0	796.0; 742.5	this work	~2380	this work
$HCONH_2$	822	3242	864; 772	16		
CH_3CONH_2	864	3160	848; 805	16		
$CH_3CON(CH_3)_2$	908	3072	877; 826	16	740	15
$HCON(CH_3)_2$	888				~1600−700	34

[a] From ref 39.

product bands observed at 3293.0, 796.0, and 742.5 cm^{-1} can be assigned with confidence to the 1:1 HCONHOH···HF complex. The relative intensities of the bands do not depend on matrix concentration and remain constant after matrix annealing. The appearance of the 3498.5, 3497.0, 1393.5, 1390.0, and 775.0, 774.0 cm^{-1} doublets is most probably due to the site splitting.

The 3498.5 and 3497.0 cm^{-1} doublet in the spectra of HCONHOH/HF/Ar matrixes is due to the perturbed NH stretching vibration in the HCONHOH···HF complex as confirmed by the observed isotopic shifts. The doublet is 7 cm^{-1} red shifted to 3491.5 and 3490.0 cm^{-1}, respectively, after ^{15}N substitution. It appears at 2601.5, 2599.5 cm^{-1} in the spectra of deuterated formohydroxamic acid with the isotopic shift ratio ν(NH)/ν(ND) = 1.34. The 3498.5, 3497.0 cm^{-1} pair shows ca. 15 cm^{-1} blue shift with respect to the corresponding band of the HCONHOH monomer. The band appearing at 3405.5 cm^{-1} in a vicinity of the ν(OH) band of HCONHOH is assigned to the perturbed OH stretching vibration in the complex. The band is not sensitive to ^{15}N substitution but is shifted to 2521 cm^{-1} after deuteration with the isotopic shift ratio ν(OH)/ν(OD) = 1.34. The 3405.5 cm^{-1} mode is ca. 21 cm^{-1} blue shifted as compared to the monomer absorption. The band observed at 2948.5 cm^{-1} corresponds to the perturbed ν(CH) mode in the complex. This feature is 36.5 cm^{-1} blue shifted with respect to the free FHA molecule. The corresponding band was not observed either in ^{15}N experiment or in ^{2}H experiments.

Significant perturbation was observed for the HCONHOH vibrations occurring in the 1800−1300 cm^{-1} region in the HCONHOH···HF complex. The sharp product band at 1662.5 cm^{-1} is assigned to the amide I mode of the formohydroxamic acid molecule in the complex. The band is 20.5 cm^{-1} shifted toward lower frequencies with respect to the amide I mode of FHA. In the HCONDOD experiments the amide I mode of the complex appears as a doublet at 1658.5, 1656 cm^{-1} that is ca. 23.5 cm^{-1} red shifted with respect to the amide I band of HCONDOD. In ^{15}N experiments the corresponding band appeared at 1660.0 cm^{-1} showing a 21 cm^{-1} red shift with respect to the nonperturbed vibration of a free molecule. The broad absorption at 1390.0 cm^{-1} with a 1393.5 cm^{-1} subpeak is attributed to the perturbed NOH in plane bending vibration. The absorption shows ca. 19 cm^{-1} blue shift with respect to the corresponding band of FHA. In ^{15}N experiments the corresponding band is identified at 1380.5 cm^{-1} and in ^{2}H experiments at 969.5 cm^{-1}. The observed isotopic shifts confirm the proposed assignment of the broad band. The CH in plane bending mode of the complex occurs at 1352.5 cm^{-1} in HCONHOH experiments and is 1.5 cm^{-1} shifted toward lower frequencies from the corresponding monomer absorption. The corresponding band appears at 1351.5 cm^{-1} in ^{15}N experiments and at 1354 cm^{-1} in ^{2}H experiments, showing the same 1.5 cm^{-1} shift with respect to the nonperturbed vibration in all three isotopically substituted complexes.

In the spectral region below 900 cm^{-1} the bands due to the perturbed HCONHOH vibrations in the HCONHOH···HF complex were identified at 860.0, 775.0, and 599.0 cm^{-1}. These absorptions are assigned to the NO stretching, amide IV, and CN torsion vibrations and are ca. 19, 18, and 4 cm^{-1} blue shifted with respect to the corresponding absorptions of the FHA monomer, respectively. The corresponding bands appear at 855.0, 770.0 (with satellite at 769.0), and 596 cm^{-1} in ^{15}N experiments showing ca. 5.0, 5.0, and 3.0 cm^{-1} ^{15}N red shifts, respectively. In ^{2}H experiments only the band corresponding to the CN torsion mode was identified at 597.5 cm^{-1}.

In the spectra of the HCONDOD···HF complexes two additional product bands due to the perturbed FHA vibrations were observed that were not identified in the spectra of the HCONHOH and HCO^{15}NHOH complexes. The bands appearing in the spectra of deuterated sample at 1121.5 and 1344.0 cm^{-1} are attributed to the amide II (NH bend) and amide III (CN stretch) vibrations. The 1121.5 and 1344.0 cm^{-1} bands are 4.5 and 20 cm^{-1} blue shifted with respect to the corresponding absorptions of HCONDOD.

The strong, broad band observed in the spectra of the HCONHOH···HF complexes at 3293.0 cm^{-1} is assigned with confidence to the HF stretching vibration. The strong bands appearing at 796.0 and 742.5 cm^{-1} are due to the HF librational modes. The frequencies of the perturbed HF modes in the studied complex have values close to the frequencies of the corresponding modes in HF complexes with other carbonyl compounds[16,32,33] (see Table 7) and especially with amides. For the formamide−HF complex[16] ν_s(HF), $\nu_{libr\,sym}$(HF), and $\nu_{libr\,asym}$(HF) were identified at 3242, 864, and 772 cm^{-1}, and for the acetamide−HF complex[16] these modes were identified at 3160, 848, and 805 cm^{-1}, respectively.

In the spectra of the HCO^{15}NHOH−HF complexes the perturbed HF stretch and two HF librational modes appear at 3293.5, 796.0, and 742.5 cm^{-1}, and in the spectra of the HCONDOD−HF complexes they appear at 3290.5, 792.5, and 743.0 cm^{-1}, respectively.

Formohydroxamic Acid−Hydrogen Chloride. The set of bands observed at 3503.5, 3500.5, 3493.0, 1654.5, 1647.5, 1391.0, 1388.0, 1349.0, 855.0, 853.5, and 771.5 cm^{-1} in the vicinity of the HCONHOH bands and the broad, diffuse band at 2380 cm^{-1} are assigned to the 1:1 HCONHOH···HCl complex. The appearance of triplets and doublets is attributed to multiple trapping sites in an argon matrix.

The absorption due to the perturbed NH stretch vibration occurs in the spectrum of the HCONHOH···HCl complex as a triplet at 3503.5, 3500.5, and 3493.0 cm^{-1}, showing ca. 16 cm^{-1}

blue shift with respect to the monomer band. The corresponding bands in ^{15}N and ^{2}H experiments appear as doublets at 3486.0, 3484.0 cm^{-1} and at 2598.0, 2596.0 cm^{-1}, respectively. The 1654.5, 1647.5 cm^{-1} pair is assigned to the perturbed amide I vibration; the corresponding band is identified at 1650.5 cm^{-1} in ^{15}N experiment and at 1651.0 cm^{-1} (with a shoulder at 1644.5 cm^{-1}) in ^{2}H experiment. In all three isotopically substituted complexes (H, ^{15}N, ^{2}H) the perturbed amide I vibration is ca. 31 cm^{-1} red shifted with respect to the corresponding monomer mode. The NOH in plane bending vibration of the complex is identified at 1391.0 cm^{-1} with its lower frequency component at 1388.0 cm^{-1}. These bands are ca. 18 cm^{-1} blue shifted from the absorption due to the δ(NOH) vibration in HCONHOH. The counterparts of these bands appear at 1380.0, 1377.0 cm^{-1} in ^{15}N experiments; they were not identified in ^{2}H spectra. The perturbed CH in plane bending mode is observed at 1349.0 cm^{-1}, which gives a 5 cm^{-1} red shift with respect to the monomer absorption. The corresponding mode appeared at 1348.0 cm^{-1} in ^{15}N spectra and at 1351.5 cm^{-1} in ^{2}H spectra, with similar red shifts (5.0, 4.5 cm^{-1}) from the corresponding FHA absorptions. The 855.0 (with its satellite at 853.5 cm^{-1}) and 771.5 cm^{-1} bands are assigned to the NO stretching and amide IV modes of the HCONHOH···HCl complex. These bands are ca. 14 and 15 cm^{-1} blue shifted as compared to the corresponding absorptions of formohydroxamic acid. The corresponding absorptions were not identified either in ^{15}N or in ^{2}H experiments.

In the spectra of the HCONDOD···HCl complexes two additional product bands appeared at 1122.0 and 1340.0 cm^{-1} in the vicinity of the amide II (1117 cm^{-1}) and amide III (1324 cm^{-1}) bands of ^{2}H-substituted FHA monomer. The bands are assigned to the corresponding, perturbed vibrations in the complex.

The weak, diffuse, and broad band observed in the high-frequency region at ca. 2380 cm^{-1} is assigned to the perturbed HCl stretch in the complex with formohydroxamic acid.

Bonding and Structure. The infrared spectra of the formohydroxamic acid···HF and HCl complexes share common features. In both HF and HCl complexes the perturbed NH and OH stretching, NOH in plane bending, NO stretching, and amide IV modes of formohydroxamic acid exhibit blue shifts whereas the amide I vibrations show significant red shifts. The ν_s(HX) vibration is strongly red shifted in both complexes (−626.5, −507 cm^{-1} in HF, HCl complexes, respectively). The observed perturbations of both submolecules after complex formation point to the structure in which HX acts as a strong proton donor and HCONHOH acts as a proton acceptor.

The HCONHOH molecule has three basic centers: the oxygen atom of the C═O group and the oxygen and nitrogen atoms of the NOH group. Since HCONHOH is a simple derivative of formamide, the oxygen atom of the carbonyl group of formohydroxamic acid is the most probable site of attachment of hydrogen fluoride or hydrogen chloride. The red frequency shifts of the perturbed amide I mode in the formohydroxamic acid···HF complexes (−20.5, −24, and −21 cm^{-1} in ^{1}H, ^{2}H, and ^{15}N complexes, respectively; see Table 1) and in the formohydroxamic acid···HCl complexes (−31 cm^{-1} in all three isotopically substituted complexes; see Table 2) as well as the blue shifts of the identified amide III vibrations in the HCONDOD···HF and HCONDOD···HCl complexes (+20, +15 cm^{-1}, respectively) are characteristic for attachment of the HX subunit to the oxygen atom of carbonyl group in the amide···HX complexes. In the formamide···HF complex isolated in solid argon the amide I mode is shifted 18 cm^{-1} toward lower frequencies and the amide III mode is shifted 38 cm^{-1} toward higher frequencies after complex formation.[16] For acetamide···HF and *N*,*N*-dimethylacetamide···HF complexes, the 47 and 32 cm^{-1} red shifts of the amide I modes were observed, respectively, and the perturbed amide III mode in acetamide···HF complex was 34 cm^{-1} blue shifted from the monomer acetamide absorption.[16] In *N*,*N*-dimethylacetamide···HCl and *N*,*N*-dimethylformamide···HCl complexes isolated in solid argon, the perturbed amide I mode was found to be ca. 70 and 40 cm^{-1} red shifted with respect to the corresponding monomer vibration.[15,34] The perturbed amide III modes were not identified for these complexes.

The perturbation of the amide IV mode is also characteristic for the site of HX attachment in amides. In amide···HF,[16] *N*,*N*-dimethylacetamide···HCl,[15] and *N*,*N*-dimethylformamide···HCl[34] complexes this vibration was found to be 25−40, 15, and 6 cm^{-1} blue shifted, respectively, from the corresponding monomer vibrations. In the HCONHOH···HF and HCONHOH···HCl complexes the corresponding modes exhibit 18 and 15 cm^{-1} blue shifts, respectively.

The 3293.0, 796.0, and 742.5 cm^{-1} bands assigned to the ν_s(HF), $\nu_{\text{libr sym}}$(HF), and $\nu_{\text{libr asym}}$(HF) modes in the formohydroxamic acid···HF complex are in typical frequency ranges for the HF vibrations in the complexes of carbonyl compounds with HF (see Table 7). The 626.5 cm^{-1} red shift observed for the HF stretch in the HCONHOH···HF complex indicates that this complex has strength comparable to that of the hydrogen bond to the HF complexes with acetone and formamide. In the latter two complexes the HF stretch was 617 and 677 cm^{-1} shifted toward lower frequencies from its monomer value.[16,32] The values of the ν_{libr} frequencies identified for formohydroxamic acid complexes are in accord with this conclusion. The deuterium substitution of formohydroxamic acid has a small effect on the frequencies of the HF submolecule in the complex. The 2.5 and 3.5 cm^{-1} red shifts of the ν_s(HF) and $\nu_{\text{libr sym}}$(HF) frequencies in the HCONDOD···HF complex as compared to the HCONHOH···HF one are similar to those observed for deuterated amides···HF complexes and suggest slightly stronger HF interaction with HCONDOD than with HCONHOH.

The weak and broad band at 2380 cm^{-1} that is assigned to the HCl stretch in the HCONHOH···HCl complex appears at a frequency similar to that of the ν_s(HCl) absorption in the spectra of the acetone···HCl system in solid argon (2393 cm^{-1}).[35] In *N*,*N*-dimethylacetamide···HCl[15] and *N*,*N*-dimethylformamide···HCl[34] a very strong hydrogen bond is formed with the proton shared between the oxygen and chlorine atoms (see Table 7).

Ab initio calculations predict two stable structures (I, II) in which the HX subunit interacts with the oxygen atom of the carbonyl group of HCONHOH. In structure I hydrogen halide interacts with the oxygen atom of the carbonyl group only, and in structure II a seven-membered ring is formed in which HX interacts both with the oxygen atom of the C═O group and with the hydrogen atom of the OH group. Comparison of the calculated frequency shifts for structures I and II (see Tables 5 and 6) with the observed frequency shifts for the complexes isolated in solid argon (see Tables 1 and 2) indicates that the HF and HCl complexes trapped in the matrix have structure I. Red shifts of the amide I and CH in plane bending vibrations and blue shifts of the amide IV mode are observed for the HF and HCl complexes in solid argon. The observed shifts are in accord with the calculated frequency shifts for these modes in the complex with structure I whereas the blue shifts of the amide I and CH in plane bending vibrations and red shift of the amide

IV mode are predicted for structure II. The other perturbed modes are calculated to be shifted in the same direction in both complexes; structure II is characterized by much larger frequency shifts of the HX stretching and NOH bending modes than structure I.

Ab initio calculations predict structure I of the HCONHOH···HCl complex to be the most stable one among the four stable structures. The counterpoise-corrected interaction energies (ΔE^{CP}) are equal to −3.23, −2.62, −0.93, and −0.22 kcal/mol and the zero-point vibrational energies calculated from the harmonic frequencies are equal to −1.78, −0.93, 0.60, and 0.99 kcal/mol for structures I, II, III, and IV, respectively. Inclusion of the ZPVE correction did not affect significantly the differences in the interaction energies between the four complexes. In the case of the HCONHOH···HF system the values of the interaction energies (ΔE^{CP}) point to the cyclic structure II as the most stable one; the ΔE^{CP} values are equal to −7.72, −8.40, −4.39, and −2.59 kcal/mol for structures I, II, III, and IV, respectively. The differences in the proton affinity values of the F^- and Cl^- anions (1554 and 1395 kJ/mol)[37] and in the magnitudes of the fluorine and chlorine atomic radiuses might explain the lower interaction energy for the cyclic HCONHOH···HF complex II as compared to complex I. However, the calculations show that the ZPVE correction reduces significantly the energy difference between structures I and II. The zero-point energies calculated from the harmonic frequencies are equal to −5.73, −5.76, −2.22, and −0.68 kcal/mol for structures I, II, III, and IV, respectively. Therefore, complexes I and II have comparable zero-point energies, which justifies the presence of the HCONHOH···HF complexes with structure I in the studied matrixes; the matrix environment may favor structure I. It is also interesting to note that in the case of the HF complexes the calculated dipole moment for structure I is larger than that for structure II (see Table 4). It has been found that the complexes with larger dipole moments are more effectively stabilized by matrix environment.[38] The difference between the calculated dipole moments for structures I and II of the HF complexes is rather small (0.472 D), but a larger dipole moment of structure I may favor the stabilization of this complex in the matrix as compared to structure II when the interaction energy of the two complexes is comparable.

Conclusions

FTIR studies have shown that formohydroxamic acid and hydrogen fluoride or hydrogen chloride form hydrogen bonded complexes in argon matrixes in which the hydrogen halide molecule acts as a proton donor toward the carbonyl group of HCONHOH. Several perturbed HCONHOH vibrations, one HCl (ν_s) and three HF vibrations (ν_s, $\nu_{\text{libr sym}}$, $\nu_{\text{libr asym}}$), were identified for the hydrogen chloride and hydrogen fluoride complexes. The studies of the complexes with isotopically substituted formohydroxamic acid (HCONDOD and $HCO^{15}NHOH$) helped us to assign the perturbed vibrations of the HCONHOH molecule. The stronger perturbation of the formohydroxamic acid vibrations in the hydrogen fluoride complexes indicates higher interaction energy for the hydrogen fluoride complexes than for the hydrogen chloride ones.

Ab initio calculations performed for the formohydroxamic acid···hydrogen fluoride/hydrogen chloride systems demonstrate the stability of the four HCONHOH···HX complexes (structures I, II, III, and IV). In the complex with structure I the HX submolecule is attached to the oxygen atom of the carbonyl group along one of its electron pairs. In complex II the seven-membered cyclic ring is formed with HX interacting with both the C═O and NOH groups of formohydroxamic acid. In complexes III and IV hydrogen halide is bonded either to an oxygen or to a nitrogen atom of the NOH group. All four structures are nonplanar: in structure IV the HX molecule is located perpendicularly toward the plane of formohydroxamic acid. Structure I is calculated to have the lowest interaction and zero-point vibrational energies among the four stable HCl structures, and structures I and II are found to have comparable zero-point energies in the case of HF complexes with structure II characterized by the lower interaction energy. Structures III and IV correspond to much more weakly bound HX complexes than structures I and II; structure IV is the least stable one among the four structures. The calculations indicate that carbonyl oxygen in formohydroxamic acid as in formamide is the strongest basic site and the oxygen atom of the NOH group exhibits stronger basic properties than the nitrogen atom.

Comparison of the calculated frequency shifts for the three structures with the observed frequency shifts of the complexes trapped in the matrixes clearly indicates that both HF and HCl complexes have structure I with the HX molecule attached to the oxygen atom of the C═O group of formohydroxamic acid. Matrix environment favors structure I, which is characterized by a slightly larger dipole moment than structure II.

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