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Infrared Matrix Isolation Studies and Ab Initio Calculations of Formhydroxamic Acid

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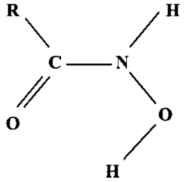
The infrared absorption spectra of formhydroxamic acid (HCONHOH) and its isotopic analogues (HCONDOD, $HCO^{15}NHOH$) isolated in argon and nitrogen matrices have been recorded for the first time. The infrared spectra prove that this molecule exists as the keto tautomer with an intramolecular hydrogen bond in solid argon and nitrogen. The normal coordinate analysis indicated strong coupling between amide grouping vibrations. Theoretical studies of the structure and spectral characteristic of the formhydroxamic acid molecule, carried out on both MP2 and B3LYP levels with the 6-311++G(2d,2p) basis set, were in accordance with the experimental data.

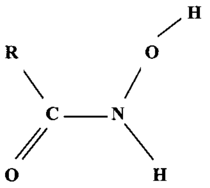
Introduction

Hydroxamic acids (RCONHOH) are chemical compounds first reported by Lossen in 1869.[1] Extensive work has been carried out on their formations, reactions, and structure in the ground state.[2,3] The main reason for this interest is that this type of molecule contains the fragment of the simplest protein structure: $HNC{=}O$. The progress in hydroxamic acids chemistry has been stimulated by the isolation of naturally occurring acids, which are active as antibiotics, antitumor and antifungal agents, and specific enzyme inhibitors.[4] They also play an important role in iron uptake and metabolism.[5] Hydroxamic acids serve as bidentate ligands toward many metal ions and therefore are useful in colorimetric analyses.[3]

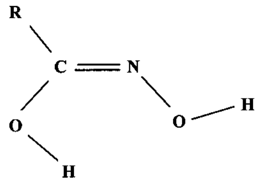
Formhydroxamic acid (HCONHOH) is the simplest hydroxamic acid, which can exist in two keto tautomeric forms, 1-*Z* and 1-*E*, and two iminol forms, 2-*Z* and 2-*E*.



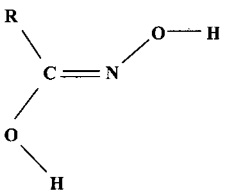
1-Z



1-E



2-Z



2-E

The X-ray diffraction of crystals of formhydroxamic acid[6] shows that 1-*Z* is the stable tautomer in the crystalline phase. The structure is almost planar with the OH bond in the anti orientation. The X-ray diffraction of acetohydroxamic acid hemihydrate[7] also supported the tautomer 1-*Z*, but with the OH bond in the syn conformation. An ^{17}O NMR study of benzohydroxamic acids[8] led to a similar conclusion that the keto form 1 is predominant in various solvents. More recent NMR studies[9,10] showed that monoalkylhydroxamic acids and their O- and N-substituted derivatives in different solvents exist in both keto and iminol forms. The equilibrium between the tautomers depends on the type of acid and on the nature of the solvent. The infrared spectra of various hydroxamic acids in solid state and in CCl_4, $CHCl_3$, dioxane, CH_3CN solutions were also studied.[10−12] The spectra suggest that acids in the solid state and in polar solvents exist in the keto form, but in nonpolar solvents the iminol form is also present. The infrared absorption spectrum of a solid film of formhydroxamic acid was recorded by Orville-Thomas et al.[13] for the first time. The spectrum showed that the molecule has a keto transplanar structure. Later, Fritz et al.[14] reported the IR spectra of HCONHOH in KBr plate and in a Nujol mull, which confirmed the existence of this molecule in the keto form in the solid state.

Recently, many reliable ab initio studies of hydroxamic acids have been reported.[15−20] Low-quality calculations suggest that hydroxamic acids exist mainly as the 1-*E* tautomers in the gas phase;[15,16] however, the highest quality calculations performed so far, MP2/6-311++G(2d,2p) and SCF/6-311++G(2d,2p),[19] predict the following order of stability of the structures: 1-*Z* > 1-*E* > 2-*Z* > 2-*E*. The planar hydrogen-bonded structure of formhydroxamic acid is predicted to be the most stable one in the gas phase.

The structure of anions has also been a subject of discussion. Some authors indicate hydroxamic acids to be O-acids,[21−24] but several authors suggested that hydroxamic acids are N-acids.[25−27] This phenomena is strongly dependent on the environment used in the experiments. Recently, Decouson et al.[27] measured gas-phase acidities of acetohydroxamic acid and its *O*-methyl and *N*-methyl derivatives and concluded that $CH_3CONHOH$ essentially behaves as an N-acid in the gas phase. Theoretical calculations at both MP2/6-311++G(2d,2p) and CBS-Q levels[17,20,28] showed that both formo- and acetohydroxamic acids should behave as NH acids in the gas phase.

Formhydroxamic acid (FHA) molecule was extensively studied by theoretical methods, as discussed above, but no experimental data have been reported for the molecule in the gas phase and the data reported for other phases are scarce.

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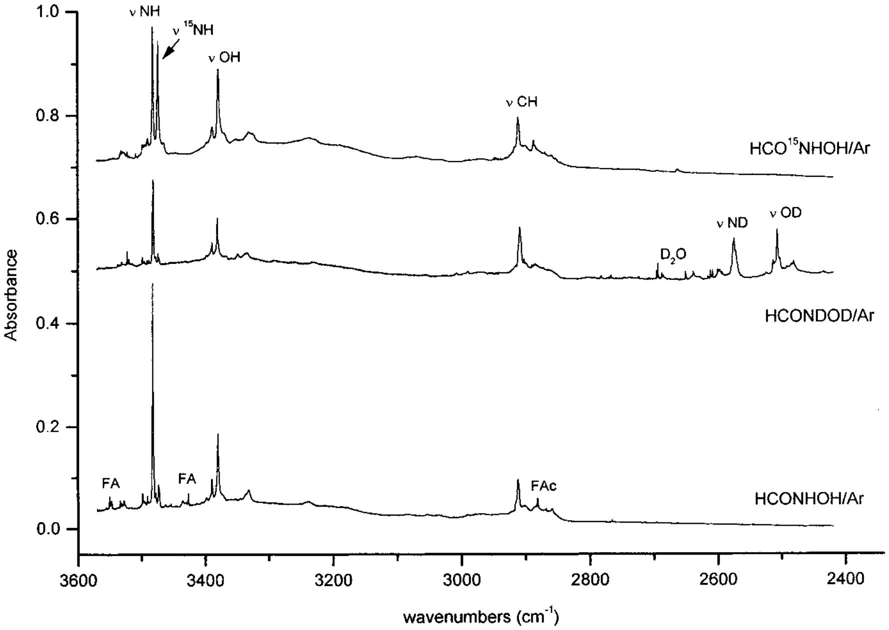


Figure 1. The 3600−2400 cm^{-1} region in the infrared spectra of formhydroxamic acid and its deuterated and 50% N-15-enriched analogues (HCONHOH, HCONDOD, and HCO^{15}NHOH) isolated in solid argon. FA, FAc indicate bands due to formamide and formic acid contaminants (see text).

This is because formhydroxamic acid is not stable at room temperature, decomposes violently above its melting point, and is not soluble in nonpolar solvents. We applied a matrix isolation technique combined with FT-IR spectroscopy to study the spectral characteristic of this molecule. In this paper we present and discuss the infrared spectra of formhydroxamic acid and its isotopic analogues in solid argon and nitrogen. The results of normal coordinate analysis and theoretical studies of possible structures and the vibrational assignment at the MP2/6-311++G(2d,2p) and B3LYP/6-311++G(2d,2p) levels are also included.

Experimental Section

Infrared Matrix Isolation Studies. Formhydroxamic acid was prepared and purified by the method previously described.[29] Elemental analysis (C, H, N) and melting point were used as criteria of purity and were as follows (theoretical values are in parentheses): mp 78−80 °C (76−79 °C); C, 19.75 (19.68); H, 4.79 (4.95); N, 22.85 (22.95). Deuterated formhydroxamic acid was prepared by multiple dissolving of FHA in D_2O (99%). Enriched (50% N-15) formhydroxamic acid was synthesized from $H_2{}^{15}NOH{\cdot}HCl$ (50%) + $H_2NOH{\cdot}HCl$ (50%) (Cambridge Isotope Laboratories, Inc.).

The HCONHOH/Ar (N_2), HCONDOD/Ar (N_2), and HCO^{15}NHOH/Ar (N_2) matrices were obtained by simultaneous deposition of formhydroxamic acid vapor and argon (nitrogen). The acid was evaporated from a glass bulb kept at room temperature, which was connected to a cryostat via a glass tube. The monomer concentration was controlled by comparing the spectra obtained at different deposition conditions.

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[30] package of computer codes. Electron correlation was considered via the Möller−Plesset perturbation theory[31,32] to the second order (MP2(FC)) and via the DFT method. The DFT exchange functional used to study the formhydroxamic acid molecular properties was the Becke hybrid method[33,34] based on the standard Becke exchange functional.[35] The correlation functional was the gradient-corrected functional by Lee, Yang, and Parr (LYP).[36] The notation used to write the whole DFT functional was B3LYP.[37]

The harmonic wavenumbers were calculated analytically both at the MP2 and B3LYP levels. The applied basis sets were the standard split-valence, 6-311-type Gaussian functions[38,39] augmented with diffuse[40] and polarization[41] functions on all atoms to give the 6-311++G(2d,2p) basis set.

Results and Discussion

Infrared Matrix Isolation Studies. All bands observed in the spectra of matrices obtained by deposition of the vapor above solid formhydroxamic acid (FHA) diluted with argon are shown in Figures 1 and 2 and are listed in Table 1. The observed bands reveal several species; in addition to FHA, also products of FHA decomposition were identified. Matrix isolated carbon dioxide (CO_2), ammonia (NH_3), hydroxylamine (Hy), formamide (FA), and formic acid (FAc) were detected together with formhydroxamic acid. The conditions of deposition (temperature of the solid FHA sample and the rate of Ar (N_2) deposition) have been varied in order to reduce the process of decomposition of FHA and to obtain matrices with minimum impurities. We were able to identify the bands of FHA in solid argon because the matrix spectra of FHA decomposition products are well-known from previous studies (CO_2,[42,43] NH_3,[44] $HCONH_2$,[45,46] HCOOH,[47] NH_2OH[48,49]). The relative intensities of FHA bands with respect to the impurities' absorptions have been varying from one experiment to another and were larger in experiments in which the FHA decomposition process was strongly reduced.

Figures 1 and 2 present the spectra of FHA monomer in solid argon in the whole spectral range. In Figure 1 the NH stretching bands of FHA and formamide contaminant are presented, and in Figure 2 the ν(C=O) bands of FHA, formamide, and formic acid can be compared. As can be seen (see also Table 1) the

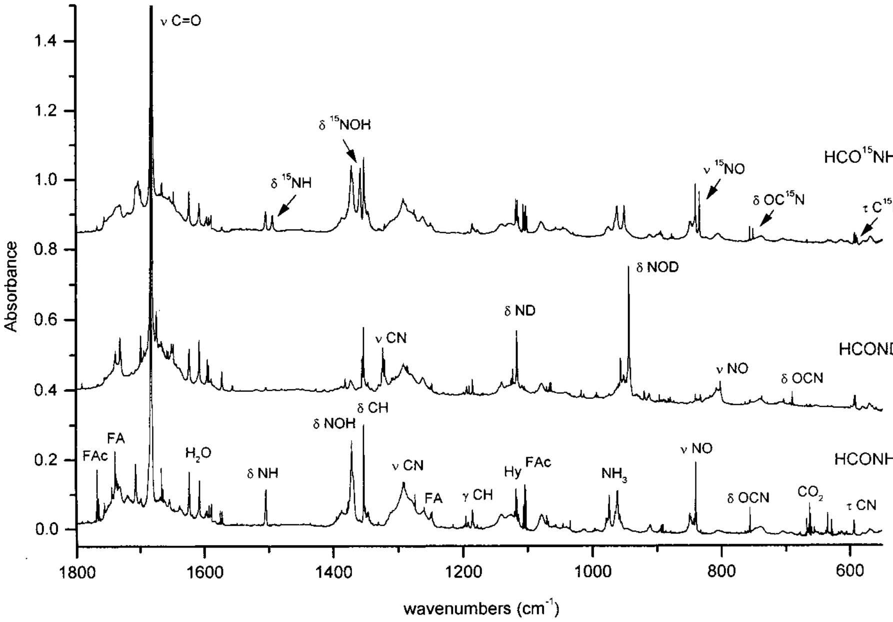


Figure 2. The 1800−550 cm^{-1} region in the spectra of the same matrices as presented in Figure 1. FA, FAc, Hy indicate bands due to formamide, formic acid and hydroxylamine contaminants (see text).

TABLE 1: Frequencies (cm^{-1}) and Absorbances of the Absorptions Appearing after Deposition of HCONHOH Equilibrium Vapor Pressure Diluted with Argon

freq	A	assignment	freq	A	assignment	freq	A	assignment	freq	A	assignment
3776.5	0.07	H_2O	2882.0	0.03	$HCONH_2$	1575.5	0.04	$HCONH_2$	1035.0	0.03	$NH_3{\cdot}H_2O$
3756.5	0.16	H_2O	2868.5	0.01	$HCONH_2$	1505.0	0.11	HCONHOH	974.5	0.15	NH_3
3711.0	0.09	H_2O	2345.5	0.94	CO_2	1387.5	0.02	$HCONH_2$	961.5	0.10	NH_3 + ?
3702.5	0.01	$NH_3{\cdot}H_2O$	2339.0	0.50	CO_2	1380.0	0.01	HCOOH	894.5	0.02	NH_2OH
3635.0	0.01	NH_2OH	1768.0	0.06	HCOOH	1378.5	0.03	$HCONH_2$	887.3	0.01	$HCONH_2$
3573.5	0.02	NH_3	1767.0	0.25	HCOOH	1372.0	0.41	HCONHOH	841.0	0.15	HCONHOH
3550.5	0.03	$HCONH_2$	1765.0	0.06	HCOOH	1354.0	0.28	HCONHOH	839.5	0.02	HCONHOH
3547.0	0.01	HCOOH	1744.5	0.09	$HCONH_2$	1292.5		HCONHOH	756.5	0.07	HCONHOH
3483.5	0.06	HCONHOH	1739.5	0.19	$HCONH_2$	1291.0		HCONHOH	756.0	0.01	HCONHOH
3482.5	0.57	HCONHOH	1738.0	0.09	$HCONH_2$	1196.5	0.04	$HCONH_2$	668.0	0.05	$CO_2{\cdot}H_2O$
3435.5	0.01	$NH_3{\cdot}H_2O$	1707.0	0.11	?	1192.5	0.01	$HCONH_2$	663.5	0.13	CO_2
3427.0	0.03	$HCONH_2$	1683.0	1.13	HCONHOH	1186.0	0.05	HCONHOH	662.0	0.24	CO_2
3398.0	0.01	NH_3	1654.5	0.02	NH_3	1118.5	0.16	NH_2OH	635.5	0.11	HCOOH
3389.0	0.05	HCONHOH	1624.0	0.16	H_2O	1117.0	0.06	NH_2OH	628.0	0.06	HCOOH
3380.0	0.19	HCONHOH	1608.0	0.17	H_2O	1105.0	0.16	HCOOH	595.0	0.04	HCONHOH
2953.0	0.01	HCOOH	1593.0	0.04	H_2O	1103.5	0.20	HCOOH	594.0	0.02	HCONHOH
2912.0	0.10	HCONHOH	1589.5	0.05	H_2O						

concentration of FHA decomposition products is relatively low, which makes possible the studies of formhydroxamic acid monomer.

Formhydroxamic acid, a seven-atom molecule, is characterized by 15 vibrations, all of them active in the IR spectrum. The spectral region 4000−600 cm^{-1} in our studies was determined by using the MCT detector working in this range. We were able to recognize 12 vibrations of FHA; the other three are assumed to occur below 500 cm^{-1} and represent the OH and NH out-of-plane deformation modes and CNO bending mode. The frequencies of the observed absorption bands of isotopic analogues of FHA in argon matrices are collected in Table 2, and the frequencies of the bands observed for FHA in nitrogen matrices are presented in Table 4.

The spectral region 4000−2900 cm^{-1} shows three fundamentals of FHA isolated in solid argon (Figure 1). The first one is observed at 3482.5 cm^{-1} with a satellite band at 3483.5 cm^{-1}, the second fundamental appears at 3380.0 cm^{-1} with a higher frequency component at 3389.0 cm^{-1}, and the third one is detected at 2912.0 cm^{-1}. These bands correspond to the NH, OH, and CH stretching modes, respectively. The small magnitude of the band splitting indicates that the origin of the splitting lies possibly in different trapping sites for the FHA molecule in solid argon. The NH and CH stretching modes appear at frequencies observed for amides monomers.[45,46] Deuteration of the N−H and O−H groups of formhydroxamic acid shifted down the stretching vibrations to 2575.5 and 2572.0 cm^{-1} for the ND group and to 2507.5 and 2503.5 cm^{-1} for the OD group. The isotopic shift ratios for the ν(ND) and ν(OD) modes are equal to 1.35 (3482.5/2575.5 = 1.35, 3380.0/2507.5 = 1.348). For comparison, the $\nu_s(NH_2)$ band of formamide was shifted after N-deuteration[45] from 3427 to 2498 cm^{-1}, which gives a very similar isotopic shift as found for the NH stretching vibration in the HCONDOD molecule. A small shift of the ν(CH) stretching absorption from 2912.0 to 2909.0 cm^{-1} and the lack of the ν(CD) band indicate that only N- and O-deuteration takes place. The spectra of N-15 substituted formhydroxamic acid in solid argon show one new band at 3474.0 cm^{-1} in this area that can be assigned to the ^{15}NH stretching mode in the HCO^{15}NHOH molecule. The position of this band clearly confirms the assignment of the NH stretch at 3482.5 cm^{-1}. The value of the isotopic shift (−8.5 cm^{-1}) of this mode is the same as observed for the ν(NH) mode of ^{15}*N*-methyl-

TABLE 2: Comparison between Observed[a] and Calculated[b] Isotopic Frequencies (cm^{-1}) of Formhydroxamic Acid[c]

HCONHOH		HCO^{15}NHOH		HCONDOD		
obsd	calcd	obsd	calcd	obsd	calcd	assignment [PED][d,e]
3483.5 s	3489.4	3474.0	3480.8	2575.5	2574.8	ν(NH) [98]
3482.5				2572.0 s		
3389.0 s	3424.9	3389.0 s	3424.9	2507.5	2506.6	ν(OH) [97]
3380.0		3380.0		2503.5 s		
2912.0	2913.3	2912.0	2912.8	2909.0	2913.5	ν(CH) [99]
1683.0	1685.9	1681.0	1685.3	1682.0	1680.7	ν(C=O) [77], δ(CH) [12]
1681.5 sh						
1505.0	1518.6	1494.5	1506.3	1117.0	1120.0	δ(NH) [50], ν(CN) [26], δ(NOH) [15]
						{δ(ND) [60], ν(CN) [18], ν(NO) [10]}
1374.0 sh	1379.5	1359.0	1363.8	944.0	970.5	δ(NOH) [59], ν(CN) [18], δ(NH) [10]
1372.0				942.0 s		{δ(NOD) [70], δ(ND) [25]}
1369.5 sh						
1354.0	1345.9	1353.0	1340.2	1356.0	1343.3	δ(CH) [53], ν(C=O) [19], δ(NOH) [19]
						{δ(CH) [61], ν(C=O) [16], ν(CN) [11]}
1292.5	1286.2	1288.5	1282.4	1325.5 s	1379.3	ν(CN) [53], δ(NH) [24]
1291.0 s		1287.0 s		1324.0		{ν(CN) [66], δ(ND) [12], ν(NO) [11]}
1186.0	1192.2	1183.0	1190.7	1181.5	1180.4	γ(CH) [77]
841.0	849.7	834.5	830.1	802.0	795.3	ν(NO) [60], δ(O=CN) [26]
839.5 s						{ν(NO) [67], δ(NOD) [15], δ(O=CN) [11]}
756.5	763.1	752.0	759.2	690.5	675.2	δ(O=CN) [50], ν(NO) [23], δ(CH) [10]
756.0 s						{δ(O=CN) [59], ν(NO) [10], γ(CH) [14]}
595.0	611.7	591.5	609.5	593.0	593.7	τ(CN) [37], γ(CH) [20], δ(O=CN) [16]
594.0 s		589.0 s		592.0 s		{τ(CN) [39], γ(CH) [11], δ(O=CN) [20]}

[a] Measurements were performed in solid argon; s = less intense of the two-component bands corresponding to each fundamental [b] Calculations were made using the Schachtschneider Force Constant Adjustment Program, ref 58. [c] The following are the best fit force constants (units: N m^{-1} × 10^{-2} for stretch−stretch, N rad^{-1} ×•10^{8} for stretch−bend, and N m rad^{-2} × 10^{18} for bend−bend). Diagonal: F(C=O) = 11.10, F(CN) = 8.72, F(NO) = 3.70, F(CH) = 4.59, F(NH) = 6.72, F(OH) = 6.55, F(OCN) = 1.40, F(OCH) = 0.99, F(CNH) = 1.00, F(NOH) = 0.88, F(γCH) = 0.78, F(τCN) = 0.18. Off-diagonal: F(CO/CN) = −0.65, F(CO/NO) = 0.35, F(CO/OCN) = −0.15, F(CO/CNH) = 0.25, F(CN/OCN) = 1.40, F(CN/OCH) = 0.70, F(CN/CNH) = 0.30, F(CN/NOH) = −0.25, F(OCN/CNH) = −0.20, F(OCN/CNO) = −0.25, F(OCN/NOH) = −0.20, F(OCN/γCH) = 0.48, F(OCN/γNH) = 0.3, F(OCN/γOH) = −0.23, F(OCH/CNO) = −0.45, F(OCH/NOH) = −0.07, F(CNH/NOH) = −0.08, F(γNH/τCN) = 0.17, F(τCN/γOH) = 0.19. [d] All values less than 10% have been omitted. [e] The assignment obtained for the HCONDOD molecule is given in braces.

TABLE 3: Equilibirum Structures[a] of Formhydroxamic Acid at the MP2 and B3LYP Levels of Theory Employing the 6-311++G(2d,2p) Basis Set

	MP2		B3LYP	
property	planar	nonplanar	planar	nonplanar
r(C=O)	1.2302	1.2252	1.2229	1.2190
r(CN)	1.3412	1.3574	1.3408	1.3533
r(NO)	1.3917	1.4011	1.3913	1.3979
r(CH$_1$)	1.0935	1.0939	1.0979	1.0980
r(NH$_2$)	1.0015	1.0062	1.0034	1.0076
r(OH$_3$)	0.9758	0.9750	0.9766	0.9765
r(O•••H$_3$)	2.0484	2.0260	2.0827	2.0582
θ(O=CN)	121.73	122.10	121.98	122.21
θ(CNO)	118.36	115.84	118.91	116.81
θ(O=CH$_1$)	125.05	124.82	124.85	124.71
θ(H$_1$CN)	113.22	113.02	113.16	113.04
θ(CNH$_2$)	127.25	120.15	127.29	121.76
θ(H$_2$NO)	114.38	111.48	113.80	111.73
θ(NOH$_3$)	100.50	101.25	101.47	101.96
θ(O•••H$_3$O)	118.43	118.78	116.63	117.11
θ(C=O•••H$_3$)	80.97	81.12	81.01	81.23
ϕ(OCNH$_2$)	180.0	−149.96	180.0	−153.23
ϕ(OCNO)	0.0	−11.20	0.0	−10.02
ϕ(H$_1$CNO)	180.0	171.73	0.0	172.40
ϕ(H$_1$CNH$_2$)	0.0	32.97	0.0	29.19
ϕ(CNOH$_3$)	0.0	3.79	0.0	3.80
ϕ(H$_2$NOH$_3$)	180.0	146.01	180.0	150.56
μ	3.503	3.283	3.130	2.943
E	−243.804720	−243.805897	−245.144257	−245.144795
ΔE^b	0.74		0.34	
ΔE^c(ZPVE)	0.28		−0.09	

[a] The bond distances are given in angstroms, the angles in degrees, dipole moments in Debyes, total energies in hartrees, and relative energies in kcal/mol. [b] ΔE is the energy difference between planar and nonplanar structures at the given level of theory. [c] ΔE(ZPVE) is the energy difference between planar and nonplanar structures at the given level of theory including ZPVE correction.

acetamide isolated in argon matrixes.[50] No other changes were recognized in this spectral region after N-15 isotopic substitution in FHA.

The position of the OH stretching mode at 3380.0 cm^{-1} suggests that the OH group in FHA acts as proton donor in an intramolecular hydrogen bond. In similar compounds that

TABLE 4: Calculated and Observed Vibrational Spectra (in cm^{-1}) of Formhydroxamic Acid[a]

	MP2		B3LYP			
assignment[b]	planar	nonplanar	planar	nonplanar	argon[c]	nitrogen
ν(NH)	3728.2 (135)	3633.1 (103)	3686.5 (100)	3628.2 (91)	3482.5 (0.57)	3469.5 (0.06)
ν(OH)	3626.8 (54)	3629.9 (36)	3608.1 (57)	3603.9 (35)	3380.0 (0.20)	3376.0 (0.10)
ν(CH)	3089.9 (42)	3081.2 (39)	3013.8 (50)	3015.7 (47)	2912.0 (0.10)	2915.5 (0.03)
amide I [ν(CO)]	1714.4 (328)	1726.3 (268)	1715.7 (332)	1731.3 (294)	1683.0 (1.13)	1684.5 (0.23)
amide II [δ(NH)]	1585.8 (30)	1558.7 (36)	1576.5 (34)	1556.5 (37)	1505.0 (0.11)	1525.0 (0.01)
δ(NOH)	1433.2 (87)	1415.2 (81)	1416.1 (93)	1404.5 (93)	1372.0 (0.41)	1372.5 (0.06)
δ(CH)	1390.4 (25)	1393.3 (34)	1379.3 (23)	1381.6 (25)	1354.0 (0.28)	1352.0 (0.10)
amide III [ν(CN)]	1217.3 (13)	1221.6 (10)	1208.1 (12)	1208.1 (9)	1292.5	1294.0 (0.04)
γ(CH)	993.8 (2)	1016.1 (17)	981.7 (1)	1000.9 (28)	1186.0 (0.05)	1188.0 (0.01)
ν(NO)	988.8 (86)	969.3 (40)	983.8 (86)	965.5 (37)	841.0 (0.17)	847.5 (0.07)
amide IV [δ(OCN)]	856.4 (16)	858.1 (40)	852.4 (18)	855.3 (35)	756.5 (0.08)	766.5 (0.01)
τ(CN)	523.4 (4)	510.3 (50)	514.2 (6)	504.4 (31)	595.0 (0.06)	611.0 (0.01)
amide V [γ(NH)]	−323.3 (140)	411.0 (83)	−285.9 (134)	376.8 (89)		
γ(OH)	377.4 (92)	376.9 (206)	376.9 (91)	395.5 (71)		
δ(CNO)	286.3 (27)	294.4 (36)	278.5 (27)	282.4 (43)		

[a] In all calculations the 6-311++G(2d,2p) basis set was used; the numbers in parentheses are the IR intensities expressed in km·mol^{-1} for calculated spectra and the relative intensities for experimental spectra [b] Only the internal coordinate giving the main contribution to PED is given. [c] Only the frequencies of the most intense bands are given; the component bands corresponding to different sites were included in the intensity measurement.

contain a nonbonded NOH group like hydroxylamine[48,49] or formaldoxime,[51] ν(OH) is observed at 3634.7 or 3620 cm^{-1} in the argon matrix spectra, respectively. Our result allows us to claim the existence of an intramolecular $C{=}O\cdots H{-}O$ hydrogen bond in the formhydroxamic acid molecule.

There are several fundamentals of the FHA molecule in the 1800−1100 cm^{-1} spectral region (Figure 2). The most intense band at 1683.0 cm^{-1} with the shoulder at 1681.5 cm^{-1} originates from the amide I mode. The absorptions arising from vibrations of the amide grouping $O{=}C{-}N{-}H$ are qualitatively described as the amide bands. The amide I band is associated principally with the OCN antisymmetric stretching vibration [named as ν(CO) for simplicity]. In agreement with its assignment, the 1683.0 cm^{-1} band shows small 1 and 2 cm^{-1} red shifts after deuterium and N-15 substitution, respectively. The position of this band and its high intensity are very characteristic for carbonyl compounds, so there is no doubt that the formhydroxamic acid molecule exists in the keto form in solid argon.

The weak bands at 1505.0 and 1292.5 cm^{-1} with the site band at 1291.0 cm^{-1} arise from the amide II and III modes and are related to the interaction of the NH in-plane bending and OCN symmetric stretching vibrations [determined as δ(NH) and ν(CN) for simplicity]. In amides,[52,53] the δ(NH) and ν(CN) modes are strongly coupled, since their unperturbed frequencies lie close to one another. The normal coordinate analysis that we have performed for FHA shows the contributions of the NH bending and CN stretching coordinates to the 1505.0 and 1292.5 cm^{-1} normal modes (see Table 2). In deuterated molecule the coupling between ND bending and CN stretching coordinates is less pronounced than between their nondeuterated analogues, and the bands appearing at 1325.5 and 1117.0 cm^{-1} can be assigned to the CN stretching and ND bending modes, respectively. Similar behavior is exhibited by the amide II and III bands in the spectra of formamide[45] isolated in solid argon. In the spectrum of $HCOND_2$, the 1086 cm^{-1} band corresponding to the mode with large ND_2 bend contribution is 491 cm^{-1} red-shifted, and the other one at 1297 cm^{-1} corresponding mainly to CN stretch is 45 cm^{-1} blue-shifted as compared to the $HCONH_2$ spectrum. In the spectra of N-15-substituted formhydroxamic acid, the amide II band appears at 1494.5 cm^{-1}. The observation of the weak amide III band at 1288.5 cm^{-1} was difficult because of the broad absorption at ca. 1280 cm^{-1} arising from the amide III band of formamide. The N-15 isotopic shift values for these two fundamentals are similar to those observed by Shimanouchi et al. for solid N-15-substituted polyglycines $(NHCH_2CO)_n$,[54] where the isotopic shifts were −13 and −4 cm^{-1} for the amide II and III modes, respectively.

The relatively broad band at 1372.0 cm^{-1}, with shoulders at 1374.0 and 1369.5 cm^{-1}, originates from the NOH in-plane deformation mode of FHA. This frequency is slightly blue-shifted with respect to the frequency of the corresponding vibration in hydroxylamine (1350.7 cm^{-1})[48,49] or formaldoxime (1313 cm^{-1})[51] in argon matrices. The position and the shape of this band confirm the existence of an intramolecular hydrogen bond in the formhydroxamic acid molecule. In the spectra of HCONDOD/Ar matrices, a band corresponding to the δ(NOD) mode appears at 944.0 cm^{-1} with isotopic shift ratio 1372.0/944.0 = 1.45. After N-15 substitution, the frequency of the NOH in-plane bending mode is shifted to 1359 cm^{-1}.

Two bending modes of the CH group of FHA appear in the 1500−1100 cm^{-1} spectral range. The CH in-plane bending vibration in amides[45,55,56] typically appears around 1400 cm^{-1} in solid argon. A medium strong band at 1354.0 cm^{-1} is assigned to the δ(CH) mode in our spectra and the out-of-plane motion of the CH bond is identified as a very weak absorption at 1186.0 cm^{-1}. The frequency of the latter mode seems to be dependent on the type of substituent at the nitrogen atom of amides. For formamide isolated in solid argon,[45] the γ(CH) mode was observed at 1047 cm^{-1}; for trans *N*-methylformamide isolated in nitrogen matrices,[55] the corresponding band was detected at 880 cm^{-1}; and for *N*,*N*-dimethylformamide, γ(CH) was recorded at 835 cm^{-1} in argon and nitrogen matrices.[56] The δ(CH) and γ(CH) modes identified for FHA show small sensitivity to deuteration (2 and −4.5 cm^{-1} shift, respectively) and to N-15 substitution (−1 and −3 cm^{-1} shifts, respectively).

The other three weak bands due to FHA fundamentals are observed in the region 900−600 cm^{-1} (Figure 2). The bands are split, possibly due to trapping site effects in solid argon. The band at 841.0 with an accompanying one at 839.5 cm^{-1} is assigned to the NO stretching mode, the absorption at 756.5

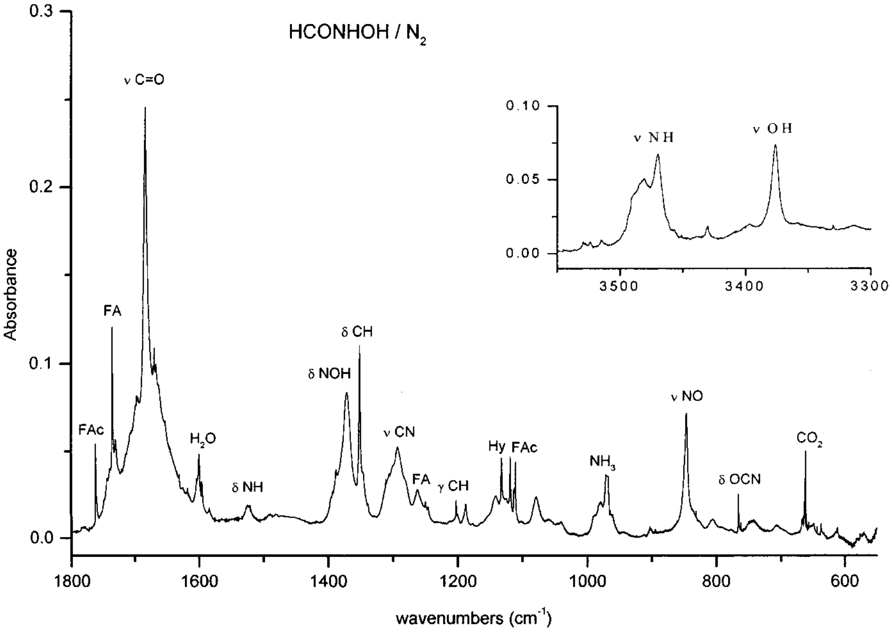


Figure 3. The 3550−3300 and 1800−550 cm^{-1} spectral regions of formhydroxamic acid isolated in solid nitrogen.

with a weaker one at 756.0 cm^{-1} is attributed to the amide IV mode (associated with the OCN deformation vibration), and the bands at 595.0 and 594.0 cm^{-1} are assigned to the CN torsional mode of FHA. All above absorptions are sensitive to the N-15 substitution: the 841.0 cm^{-1} NO stretch is shifted to 834.5 cm^{-1}, the 756.5 cm^{-1} amide IV band is shifted to 752.0 cm^{-1}, and the 595.0 and 594.0 cm^{-1} bands assigned to CN torsion are shifted to 591.5 and 589.0 cm^{-1}, respectively. Deuteration also affects the spectra of the FHA molecule in this region; the NO stretching and amide IV absorptions are shifted to 802.0 and 690.5 cm^{-1}, respectively; the CN torsion is only slightly affected by deuteration and appears at 593.0 and 592.0 cm^{-1}.

The ν(NO) vibration occurs in the region characteristic for this mode. It was identified at 886 cm^{-1} for formaldoxime[51] in argon and at 895.9 cm^{-1} for hydroxylamine[48] in argon. In deuterated hydroxylamine molecule (ND_2OD), the corresponding vibration was found to be shifted to 818.2 cm^{-1} and in N-15-substituted molecule to 880.5 cm^{-1}. The normal coordinate analysis performed for FHA shows that in deuterated HCONDOD molecule the NOD bending coordinate contributes to the 802.0 cm^{-1} mode. This fact might explain the almost 40 cm^{-1} shift of the ν(NO) vibration in deuterated formhydroxamic acid (see Table 2).

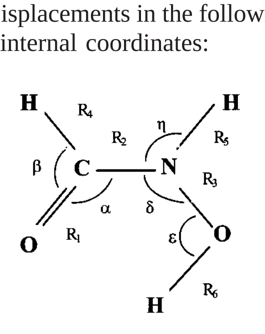
The amide IV mode appears around 550 cm^{-1} in simple amides isolated in solid argon,[45,46] at 761 cm^{-1} in *N*-methylformamide in solid nitrogen,[55] at 654 cm^{-1} in *N*,*N*-dimethylformamide in argon and nitrogen matrices,[56] and at 587 cm^{-1} in *N*,*N*-dimethylacetamide in solid argon.[57] A 20 cm^{-1} deuterium red shift of δ(OCN) was observed in solid N-deuterated amides,[52,53] and the corresponding mode exhibited a quite significant 37 cm^{-1} red shift in the N-deuterated acetamide molecule isolated in solid argon.[46] The large deuterium shift (−66 cm^{-1}) of δ(OCN) in HCONDOD cannot be explained straightforward by the contribution of deuterium motion to this mode, since the normal coordinate analysis shows that only the OCN bending, NO stretching, and CH out-of-plane deformation coordinates contribute to the 690.5 cm^{-1} mode of deuterated FHA. However, we cannot exclude the contributions of the OD or ND out-of-plane deformation coordinates to the 690.5 cm^{-1} mode of HCONDOD. This issue requires further studies. An observed N-15 isotopic shift (−4.5 cm^{-1}) of δ(OCN) in HCO^{15}NHOH is slightly larger than the N-15 shift of the corresponding mode (−3 cm^{-1}) in solid N-15-substituted polyglycines.[54]

As can be seen from the normal coordinate analysis, the 595.0 cm^{-1} mode of FHA corresponds to strongly coupled CN torsional, OCN bending, and CH out-of-plane deformation vibrations. The small deuterium and N-15 red shifts (2 and 3.5 cm^{-1}, respectively) of the CN torsional mode observed for isotopically substituted FHA are similar to those exhibited in the spectra of solid amides or polyglycines.[52−54]

The spectrum of formhydroxamic acid in nitrogen matrices is shown in Figure 3, and the frequencies are collected in Table 4. As can be seen, the bands of FHA monomer in nitrogen are broader and slightly shifted with respect to the corresponding bands in solid argon. In contrast with the argon spectra, the bands are not split in the FHA/N_2 matrices spectra.

Annealing of the FHA/Ar matrix to 33 K resulted only in a slight growth of the satellite bands and decrease of the intensities of the corresponding main bands, respectively. The annealing experiments and the presence of single bands in the spectra of FHA/N_2 matrices confirm our assumptions about the existence of multiple trapping sites for the FHA molecule in solid argon.

Normal Coordinate Analysis. The geometry of the nonplanar HCONHOH molecule determined from the theoretical studies at the MP2/6-311++G(2d,2p) level was used in the normal coordinate analysis (see Table 3). The calculations were performed using the Schachtschneider Force Constant Adjustment Program.[58] Displacements in the following 11 coordinates were taken as the internal coordinates:



The other four out of plane coordinates were γ(CH), γ(NH), γ(OH), and τ(CN). The initial force constants were transferred from *N*-methylformamide,[55] *N*-methylacetamide,[52] formamide,[53] and hydroxylamine.[48]

Table 2 compares measured and calculated frequencies for HCONHOH and its isotopes HCONDOD and $HCO^{15}NHOH$. There is a good agreement between these sets of values considering that the frequencies were assumed to be harmonic. The fit force constants are also presented in Table 2.

The diagonal force constants for the FHA molecule have similar values to the corresponding force constants of *N*-methylformamide.[55] The force constants calculated for the NOH group can be compared to those calculated for hydroxylamine;[48] the small differences between the values of the corresponding constants may be due to the presence of an intramolecular hydrogen bond and to the contribution of the NOH group vibrations to the amide modes of the formhydroxamic acid molecule. The off-diagonal force constants appeared to be important to reproduce the deuterium and N-15 isotopic shifts of the NOH, NH, and OCN bending and NO stretching frequencies of HCONDOD and $HCO^{15}NHOH$.

The normal coordinate analysis allowed us to propose the reliable assignment for all observed bands of formhydroxamic acid in argon matrix. The calculations confirm the strong coupling between the NH bending and CN stretching coordinates in the amide II and III modes of FHA (their contributions are 50% and 26% for the amide II mode and 24% and 53% for the amide III mode, respectively). As can be seen in Table 2, deuteration affects the potential energy distribution and changes the observed coupling in such a way that the contribution of one internal coordinate to the particular mode increases significantly. This phenomena is clearly exhibited in the spectra of HCONDOD, where the new sharp bands of ν(CN) and δ(ND) appear. Similar results were obtained by Schimanouchi et al.[52] for liquid *N*-methylacetamide; the NH bending and CN stretching coordinates gave contributions of 60% and 40% to the amide II mode and 29% and 35% to the amide III vibration, respectively. The amide IV mode in *N*-methylacetamide corresponded to coupled OCN bending (42%) and CH_3–C stretching (28%) modes. In formhydroxamic acid molecule, the OCN bending, NO stretching, and CH out-of-plane deformation coordinates give contributions of 50%, 23%, and 10% to the amide IV mode at 756.5 cm^{-1}, respectively. However the amide I mode at 1683.0 cm^{-1} remains mostly the C=O stretching vibration with the small 12% addition of the CH bending coordinate, and this result is very characteristic for amide compounds.[52,53,55]

Theoretical Studies. The equilibrium geometry of the 1-*Z* keto tautomer of the formhydroxamic acid molecule calculated at the MP2(FC) and B3LYP levels using the 6-311++G(2d,2p) basis set is reported in Table 3. For both levels, the planar and nonplanar symmetry results are included. It was revealed in earlier studies[20] that the 6-311++G(2d,2p) basis set well-reproduces the experimental gas-phase proton dissociation energy value for acetohydroxamic acid. Another ab initio study at the SCF and MP2(Full) levels using the 6-311++G(2d,2p) basis set[19] predicted the global minimum on the potential energy surface of FHA as a nonplanar conformation around the nitrogen atom and a quasilinear hydrogen bond between both oxygen atoms. The fully planar hydrogen-bonded structure was found as a transition state with the 0.41 kcal/mol height of this state over the symmetrically located minima.

The performed MP2 and B3LYP calculations indicated the energy difference between the planar and nonplanar conformers as 0.74 kcal/mol at the MP2 level and 0.34 kcal/mol at the B3LYP level; the zero point vibrational energy correction (ZPVE) changes this energy difference to 0.28 and −0.09 kcal/mol at the MP2 and B3LYP levels, respectively. The predicted nonplanar FHA molecule has a pyramidal nitrogen atom. The torsional angle [φ(CNOH)] is about 4° and is low enough to make possible the formation of the O···H−O hydrogen bond in this conformer. Comparison of the DFT and MP2 results shows that bond distances for all hydrogen atoms are slightly longer at the DFT level. Simultaneously, the C=O, C−N, and N−O bonds are shorter at the B3LYP level than at the MP2 level. The bond angles are predicted to be almost equal at the MP2 and B3LYP levels.

The harmonic vibrational frequencies computed for the FHA molecule at the MP2 and B3LYP levels of theory are presented in Table 4 and compared with experimental data. As a transition state on a shallow potential energy surface, the planar structure shows one negative eigenvalue corresponding to the γ(NH) mode. All other vibrational frequencies of the nonplanar and planar structures have similar values. The B3LYP-calculated spectrum is qualitatively similar to the MP2 one. The calculated frequencies reproduce well the observed formhydroxamic acid frequencies with the exception of the observed OH and NH stretching frequencies, which are lower than the predicted ones, owing to their strong anharmonicity. Both MP2 and B3LYP predict the C=O stretch to be the most intense absorption and the CN stretching and the CH out-of-plane bending to be the least intense ones in the calculated spectrum, which is in agreement with experimental data. Data presented in Table 4 clearly indicate that the level of ab initio calculations used in this paper is able to reproduce the experimental results, which we find very important when lacking the data derived from microwave measurements concerning the formhydroxamic acid molecular properties.

Bonding and Structure. The spectra of the formhydroxamic acid in solid argon and nitrogen provide strong evidence for the 1-*Z* keto tautomeric structure with an intramolecular hydrogen bond. The presence of the bands characteristic for the C=O and NH group vibrations and lack of the band due to C=N stretch prove that the acid exists in the matrix as the keto tautomer. The reduction observed in the OH stretching fundamental provides strong evidence for an intramolecular hydrogen bond between the OH group and the oxygen atom of the carbonyl group. The OH stretch vibrations are found in the region above 3450 cm^{-1} if the OH group is not involved in the hydrogen bond. The small value of the OH stretching frequency in the formhydroxamic acid is accompanied by the enlarged value of the NOH in-plane bending frequency that is expected for an intramolecular hydrogen bond. As mentioned earlier, both in hydroxylamine[48,49] and formaldoxime[51] molecules isolated in argon the corresponding modes have lower frequencies than in formhydroxamic acid. The intramolecular hydrogen bond is probably also responsible for the relatively low frequency of the C=O stretching vibration in the formhydroxamic acid (1683.0 cm^{-1} for FHA in solid argon). The C=O stretch was identified at 1777.9 cm^{-1} in the spectra of formamide[45] in solid argon and at 1726 and 1721 cm^{-1} in the spectra of acetamide[46,59] and *N*-methylformamide[55] in solid argon, respectively. All other FHA vibrations [except γ(OH), which was not identified] are less sensitive to formation of an intramolecular hydrogen bond.

Conclusions

In this work we applied a matrix isolation technique combined with FT-IR spectroscopy to study the spectral characteristic of HCONHOH and its isotopic analogues HCONDOD and $HCO^{15}NHOH$. The experimental results show that formhydroxamic acid exists as the keto tautomer with an intramolecular hydrogen bond in solid argon and nitrogen. The existence of the keto form is confirmed by the presence of the bands due to NH and C═O groups and lack of the bands characteristic of the C═N vibrations. The bands characteristic of free NH and associated OH groups prove the existence of an intramolecular CO···HON hydrogen bond. The normal coordinate analysis allowed us to obtain a reliable assignment of the observed bands of fromhydroxamic acid and showed strong coupling between amide grouping vibrations.

Theoretical studies of the 1-*Z* keto structure of the formhydroxamic acid molecule carried out at both MP2 and B3LYP levels with the 6-311++G(2d,2p) basis set were in accordance with experimental data. The calculated spectra reproduce well the frequencies and the intensities of the measured spectra.

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