Polish J. Chem., **77**, 1587–1598 (2003)

Infrared Matrix Isolation Studies and *Ab Initio* Calculations of Acetohydroxamic Acid*

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(Received April 30th, 2003; revised manuscript June 26th, 2003)

The infrared absorption spectra of acetohydroxamic acid ($CH_3CONHOH$) and its deuterated analogue ($CH_3CONDOD$) 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 intramolecular hydrogen bond in solid argon and nitrogen. Theoretical studies of the structure and spectral characteristics of the acetohydroxamic acid molecule, carried out on both MP2 and B3LYP levels with the 6-311++G(2d,2p) basis set, are in accordance with the experimental data.

Key words: acetohydroxamic acid, matrix isolation, infrared spectra, *ab initi*o calculations

Hydroxamic acids have been recently the subject of growing interest, which is mainly stimulated by their biological activities [1–4]. 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 theoretical and experimental work performed so far leads to the conclusion that the stabilities of different isomers of hydroxamic acids are strongly dependent on the environment [5–7]. For example, the NMR studies of monoalkylhydroxamic acids and their O- and N-substituted derivatives showed that the acids in different solvents exist in both keto and iminal forms [5,6]. The equilibrium between the tautomers depends on the type of the acid and on the nature of the solvent. The infrared spectra of various hydroxamic acids in solid state and in various solvents suggest that the acids in the solid state and in polar solvents exist in the keto form, but in non polar solvents the iminal form is also present [6–9].

Recently, many reliable *ab initio* calculations, concerning the structural properties of the formohydroxamic acid and its derivatives, have been reported [10–15]. The results of the calculations refer to the system in the gas phase. The comparison of the calculated properties with the experimental gas phase data is particularly important in the case of hydroxamic acids due to strong sensitivity of their structural properties on the environment. Unfortunately, no experimental gas phase data have been reported for formohydroxamic acid (FHA) and its simple derivative, acetohydroxamic acid

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* Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

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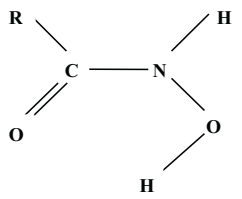
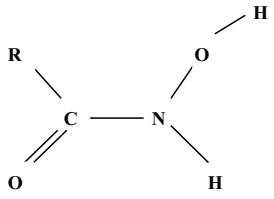
(AHA). This is due to instability of both acids at room temperature, which decompose violently above their melting points and are not soluble in nonpolar solvents.

Recently, we applied a matrix isolation technique combined with FT-IR spectroscopy to study the spectral characteristics and structural properties of formohydroxamic acid [16,17]. We proved that the *cis* keto conformer with an intramolecular hydrogen bond (1Z) and the *trans* keto conformer (1E) of formohydroxamic acid exist in equilibrium in the gas phase at room temperature with the population ratio equal to (1E)/(1Z) = 0.035 ± 0.009. The *trans* keto (1E) isomer was identified for the first time and spectral characteristics of both 1Z and 1E isomers was presented. Scheme 1 presents the *cis* keto (1Z) and *trans* keto (1E) conformers of formohydroxamic acid.



1Z



1E

In the work presented in this paper we applied matrix isolation technique combined with FT-IR spectroscopy to the study of acetohydroxamic acid. The spectral characteristics and the structural properties of the acid are presented. The experimental data are supported by *ab initio* calculations of the structure and the vibrational characteristics of the AHA molecule at the MP2/6-311++G(2d,2p) and B3LYP/6-311++G(2d,2p) levels.

EXPERIMENTAL

Infrared matrix isolation studies. Acetohydroxamic acid was commercially available (99% Fluka). Deuterated acetohydroxamic acid was prepared by multiple dissolving of AHA in D_2O (99%).

The $CH_3CONHOH/Ar$ (N_2) and $CH_3CONDOD/Ar$ (N_2) matrices were obtained by simultaneous deposition of acetohydroxamic acid vapour and argon (or nitrogen). Two methods were applied to introduce the vapour of the acid into vacuum chamber of the cryostat. In the first method, the solid sample of the acid was placed in the small bulb that was connected to the cryostat *via* tube, both bulb and tube were made of stainless steel. The temperature of the bulb and the tube were kept at 70°C during matrix deposition. In the second method, the solid sample was placed in the microprobe inside the cryostat, the microprobe was kept at 28°C by the adapted heater during matrix deposition. 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 0.5 cm^{-1} by means of a Bruker 113v FTIR spectrometer using liquid N_2 cooled MCT detector (4000–600 cm^{-1}).

Computational details. *Ab initio* calculations were carried out using the GAUSSIAN 98 [18] package of computer codes. Electron correlation was considered *via* the Mőller-Plesset perturbation theory [19,20] to the second order (MP2(FC)) and *via* the DFT method. The DFT exchange functional used to

study the acetohydroxamic acid molecular properties was the Becke hybrid method [21,22] based on the standard Becke exchange functional [23]. The correlation functional was the gradient-corrected functional by Lee, Yang, and Parr (LYP) [24]. The notation used to write the whole DFT functional was B3LYP [25].

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 [26,27] augmented with diffuse [28] and polarization [29] functions on all atoms to give the 6-311++G(2d,2p) basis set.

RESULTS AND DISCUSSION

Infrared matrix isolation studies: The spectra of matrices, obtained by deposition of the vapour above solid acetohydroxamic acid ($CH_3CONHOH$) or its deuterated analogue ($CH_3CONDOD$) diluted with argon, are shown in Figures 1 and 2. The frequencies of the bands present in the spectra are collected in Table 1.

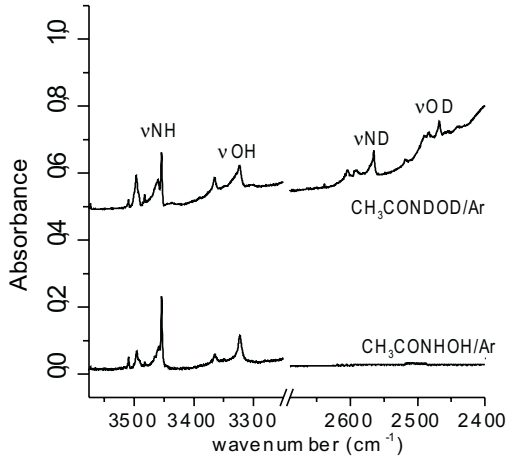


Figure 1. The 3600–2400 cm^{-1} region in the infrared spectra of acetohydroxamic acid and its deuterated analogue ($CH_3CONHOH$ and $CH_3CONDOD$) isolated in solid argon.

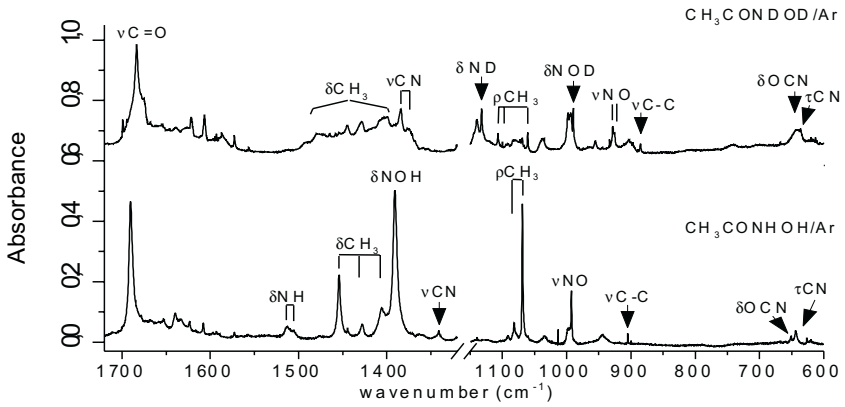


Figure 2. The 1720–600 cm^{-1} region in the spectra of the same matrices as presented in Figure 1.

Table 1. Observed frequencies (cm^{-1}) of acetohydroxamic acid and its deuterated analogue in argon matrices and frequencies calculated for these molecules at the B3LYP/6-311++G(2d,2p) level.

Assignment[a]	$CH_3CONHOH$		$CH_3CONDOD$	
	Exp.	Calc.	Exp.	Calc.
νNH, νND	3454.0	3623	2566.0	2658
νOH, νOD	3323.0	3565	2468.5	2594
$\nu_{as}CH_3$	3009.0	3126	3009.0	3126
$\nu_{as}CH_3$	3002.0	3124	3002.0	3124
$\nu_{s}CH_3$	2948.0	3054	2948.0	3054
Amide I (νCO)	1690.5	1718	1682.5	1709
Amide II (δNH/ND)	1513.5 1505.5	1553	1132.0	1161
$\delta_{as}CH_3$	1454.0	1494	1479.5 1465.0 1458.0	1498
$\delta_{as}CH_3$	1428.5	1474	1445.0	1474
$\delta_{s}CH_3$	1406.0	1403	1408.0 1402.5 1399.0	1408
δNOH, δNOD	1391.0	1414	989.5	945
Amide III (νCN)	1341.5	1277	1384.0 1375.5	1391
ρCH_3	1081.5	1055	1107.5 1100.0	1058
ρCH_3	1069.0	1091	1060.5	1113
νNO	992.5	1006	928.5 925.5	1006
νC–C	904.5	953	885.5	897
Amide IV (δOCN)	651.5	650	639.0	636
τCN	643.5	632	636.5	622

[a]Abbreviations: ν – stretching, δ – in plane bending, ρ – rocking, τ – torsion.

The molecule of acetohydroxamic acid is characterized by 24 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 18 vibrations of AHA; the other are assumed to occur below 600 cm^{-1}. They represent the OH, NH and CO out of plane deformation modes, CCN and CNO bending modes and CH_3 twisting mode.

The spectral region 4000–2900 cm^{-1} shows five fundamentals of AHA. The bands observed at 3454.0 and 3323.0 cm^{-1} (Figure 1) correspond to the NH and OH stretching modes. These modes are characterized by similar frequencies as the corresponding modes in the formohydroxamic acid molecule isolated in solid argon matrices (3482.5 and 3380.0 cm^{-1}, respectively) [16]. Deuteration of the N–H and O–H groups of acetohydroxamic acid shifted down the stretching vibrations to 2566.0 cm^{-1} for the ND group, and to 2468.5 cm^{-1} for the OD group. The isotopic shift ratios

for the ν(ND) and ν(OD) modes are equal to 1.35. The same value was observed in the case of formohydroxamic acid.

The relatively low frequency of the OH stretching mode (3323.0 cm^{-1}) suggests that the OH group in AHA acts as a proton donor in intramolecular hydrogen bond. In similar compounds which contain nonbonded NOH group, like hydroxylamine [30,31] or formaldoxime [32], the ν(OH) vibration is observed at 3634.7 and at 3620 cm^{-1}, respectively. The analogy with the formohydroxamic acid molecule allows us to claim the existence of the intramolecular C=O · · ·H–O hydrogen bond in the acetohydroxamic acid molecule.

The stretching vibrations of the CH_3 group of AHA were observed as very weak absorptions at 3009.0 and 3002.0 cm^{-1}, $\nu_{as}(CH_3)$, and at 2948.0 cm^{-1}, $\nu_s(CH_3)$. The bands were not sensitive to N- and O-deuteration of the $CH_3CONHOH$ molecule. Similar behaviour exhibited the $\nu_{as}(CH_3)$ modes of acetamide [33], which were observed at 2989 and 2943 cm^{-1}.

Several fundamentals of the AHA molecule appear in the 1800–1100 cm^{-1} spectral region (Figure 2). The most intense band at 1690.5 cm^{-1} originates from the Amide I mode, to which the main contribution gives the OCN antisymmetric stretching coordinate (marked for simplicity as ν(CO)). The deuteration of AHA shifts this absorption to 1682.5 cm^{-1}. The isotopic shift value (–8 cm^{-1}) for this fundamental is similar to that observed by Knudsen *et al*. for the Amide I mode of acetamide (–10 cm^{-1}) [33]. The position of the 1690.5 cm^{-1} band and its high intensity are very characteristic for carbonyl compounds, so there is no doubt that the acetohydroxamic acid molecule exists in the keto form in solid argon.

The weak bands at 1513.5 cm^{-1} (with the site band at 1505.5 cm^{-1}) and at 1341.5 cm^{-1} arise from the Amide II and Amide III modes, respectively. The Amide II and Amide III modes correspond to the coupled NH in plane bending and OCN symmetric stretching vibrations and are marked, for simplicity, as δ(NH) and ν(CN). The frequencies of the Amide II, Amide III modes of AHA have similar values to the frequencies of the corresponding modes in the formohydroxamic acid molecule (1505.0 and 1292.5 cm^{-1}, respectively). The counterparts of the 1513.5, 1341.5 cm^{-1} bands appear in the spectra of deuterated acid at 1384.0 cm^{-1} (with the satellite at 1375.5 cm^{-1}) and at 1132.0 cm^{-1} and are assigned to the CN stretching and ND bending modes, respectively. In $CH_3CONDOD$, the coupling between ND bending and OCN stretching coordinates is less pronounced than between the corresponding coordinates in nondeuterated acid molecule, similar situation was observed in the case of formohydroxamic acid. The Amide II and Amide III modes of acetamide isolated in solid argon [33] show similar behaviour. In the spectrum of CH_3COND_2 the 1148 cm^{-1} band (corresponding to the mode with large ND_2 bend contribution) is 437 cm^{-1} red shifted with respect to the Amide II band and the band at *ca*. 1339 cm^{-1} (corresponding mainly to CN stretch) is 25 cm^{-1} blue shifted with respect to Amide III band in CH_3CONH_2 spectrum.

The strong band at 1391.0 cm^{-1} originates from the NOH in plane deformation mode of AHA. The band appears at similar frequency as the corresponding band in the spectra of formohydroxamic acid (1372.0 cm^{-1}) and is slightly blue shifted with respect to the corresponding vibrations in hydroxylamine (1350.7 cm^{-1}) [30,31] or formaldoxime (1313 cm^{-1}) [32]. The blue shift of this band with respect to the δ(NOH) absorptions in hydroxylamine and formaldoxime confirms the existence of intramolecular hydrogen bond in the acetohydroxamic acid molecule. In the spectra of $CH_3CONDOD$/Ar matrices a band corresponding to the δ(NOD) mode appears at 989.5 cm^{-1} with the isotopic shift ratio 1391.0/989.5 = 1.41.

The bending modes of the CH_3 group of AHA appear in the 1500–1400 cm^{-1} spectral range. Two well defined bands observed at 1454.0, 1428.5 cm^{-1} are assigned to the $\delta_{as}(CH_3)$ modes and the band at 1406.0 cm^{-1} is attributed to $\delta_s(CH_3)$ mode. For acetamide isolated in solid argon [33] the $\delta_{as}(CH_3)$ modes were observed at 1433 cm^{-1} and the $\delta_s(CH_3)$ mode was detected at 1368 cm^{-1}. In the spectra of trans N-methylacetamide isolated in nitrogen matrices [34] the corresponding bands occurred at 1432 and 1370 cm^{-1}. In the case of N,N-dimethylacetamide [35] the $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$ modes were observed at 1440, 1428 and 1352 cm^{-1}. The N- and O-deuteration shifted the absorptions of the CH_3 group of AHA toward higher wavenumbers. The broad absorption at *ca*. 1465 cm^{-1} with subpeaks at 1479.5, 1465.0 and 1458.0 cm^{-1} is tentatively assigned to the $\delta_{as}(CH_3)$ mode, the band at 1445.0 cm^{-1} is attributed to the $\delta_{as}(CH_3)$ mode and the broad band at *ca*. 1405 cm^{-1} with subpeaks at 1408.0, 1402.5 and at 1399.0 cm^{-1} is assigned to the $\delta_s(CH_3)$ mode of the $CH_3CONDOD$ molecule.

The rocking modes of the CH_3 group of AHA were observed at 1081.5 and at 1069.0 cm^{-1}. Their counterparts in the spectra of deuterated acid occurred at 1107.5, 1100.0 cm^{-1} and at 1060.5 cm^{-1}. In the spectra of the CH_3CONH_2 molecule isolated in solid argon the $\rho(CH_3)$ bands appeared at 1035 and 968 cm^{-1} and were shifted to 1036 and 1026 cm^{-1}, respectively, in the spectra of the CH_3COND_2 molecule.

The other bands due to the AHA fundamentals were observed in the 1000–600 cm^{-1} region (Figure 2). The band at 992.5 cm^{-1} is assigned to the NO stretching mode and the absorption at 904.5 cm^{-1} is attributed to the C–C stretching vibration. The band at 651.5 cm^{-1} corresponds to the Amide IV mode (associated with the OCN deformation), and the 643.5 cm^{-1} band is assigned to the CN torsion. After deuteration the ν(NO) band is shifted to 928.5, 925.5 cm^{-1} and the ν(C–C) absorption to 885.5 cm^{-1}, the Amide IV and the τ(CN) bands occur at 639.0, 636.5 cm^{-1}, respectively.

The ν(NO) vibration of acetohydroxamic acid occurs at higher frequency (992.5 cm^{-1}) than the corresponding modes of formohydroxamic acid (841.0 cm^{-1}) or hydroxylamine (895.9 cm^{-1}). In all three molecules the frequency of the ν(N–O) mode is strongly affected by deuteration. In HCONDOD and ND_2OD molecules the ν(N–O) frequency was *ca*. 40 and 80 cm^{-1} red shifted with respect to the ν(N–O) frequency of nondeuterated molecule. In the case of acetohydroxamic acid molecule the ν(N–O) band shows *ca*. 65 cm^{-1} red shift after deuteration. Such a large shift indicates that deuterium motion also contributes to this mode. The δ(NOD) bending and the ν(N–O)

stretching vibrations are characterized by close frequency values (989.5, 928.5 cm^{-1}) which suggests that the NOD bending coordinate may contribute to the NO stretching mode in the $CH_3CONDOD$ molecule.

The Amide IV mode is observed at 651.5 cm^{-1} for AHA and was detected at 658 cm^{-1} in N-methylacetamide in solid nitrogen [34] and at 587 cm^{-1} in N,N-dimethylacetamide in solid argon [35]. The deuterium shift of δ(OCN) in $CH_3CONDOD$ (–12.5 cm^{-1}) may be due to small contribution of deuterium motion to this mode. For comparison, a 20 cm^{-1} deuterium red shift of δ(OCN) was observed in solid N-deuterated amides [36,37], and the corresponding mode exhibited quite significant 37 cm^{-1} red shift in the N-deuterated acetamide molecule isolated in solid argon [33,38].

The band at 643.5 cm^{-1} in the spectra of $CH_3CONHOH$ is assigned to the τ(CN) mode. The corresponding band was observed at 595.0 cm^{-1} for formohydroxamic acid and at 619 cm^{-1} for N-methylacetamide in solid argon. In the spectra of $CH_3CONDOD$ the τ(CN) mode is shifted to 636.5 cm^{-1} showing 7 cm^{-1} deuterium red shift. In the spectra of formohydroxamic acid [16] and in the spectra of solid amides [36,37] the CN torsion also shows small sensitivity to deuterium substitution.

Annealing of the AHA/Ar matrix to 33K resulted in a decrease of the intensities of the fundamental bands that were discussed above. However, there were some bands which grew after annealing; they were observed at 3365.0, 3244.0, 1678.0, 1670.0, 1658.0 and 995.5 cm^{-1}. These bands were assigned to the associates of acetohydroxamic acid. The method of preparing of $CH_3CONHOH$/Ar matrices by deposition of the vapour above heated solid acetohydroxamic acid diluted with argon explains the formation of the AHA associates.

The spectrum of acetohydroxamic acid in nitrogen matrices is shown in Figure 3 and the frequencies are collected in Table 3. The bands of AHA monomer in nitrogen are broader and slightly shifted with respect to the corresponding bands in solid argon.

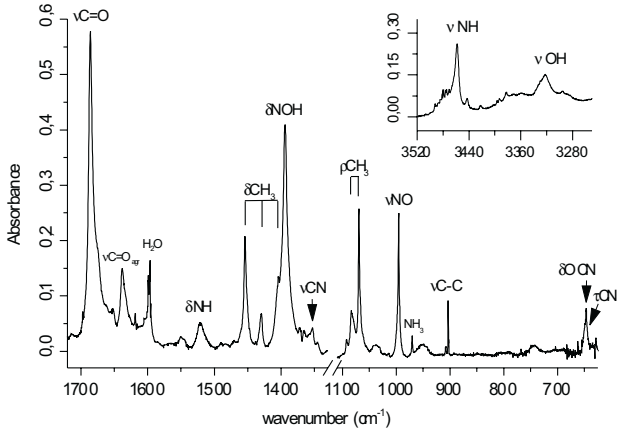


Figure 3. The 3520–3250 cm^{-1} and 1720–620 cm^{-1} spectral regions of acetohydroxamic acid isolated in solid nitrogen.

Table 2. Equilibrium structures[a] of acetohydroxamic acid at the MP2 and B3LYP levels of theory employing the 6-311++G(2d,2p) basis set.

property	MP2	B3LYP
r(C=O)	1.2293	1.2247
r(CN)	1.3671	1.3636
r(NO)	1.4040	1.4001
r(C–H_3)	1.0860	1.0890
r(C–C)	1.5030	1.5062
r(N–H_1)	1.0067	1.0076
r(O–H_2)	0.9769	0.9787
r(O···H_2)	1.9590	1.9800
θ(O=C–N)	119.98	119.72
θ(C–N–O)	115.00	115.85
θ(O=C–C)	124.41	124.19
θ(C–C–N)	115.52	116.03
θ(C–N–H_1)	119.18	121.02
θ(H_1–N–O)	110.67	110.96
θ(N–O–H_2)	100.68	101.37
θ(O···H_2–O)	120.37	118.85
θ(C=O···H_2)	81.47	81.95
ϕ(OCNH_1)	146.49	149.58
ϕ(OCNO)	11.54	10.53
ϕ(CCNO)	–171.60	–172.00
ϕ(CCNH_1)	–36.65	–32.95
ϕ(CNOH_2)	–4.58	–4.54
ϕ(H_1NOH_2)	–143.25	–147.57
μ	3.76	3.35

[a]The bond distances are given in Å, the angles in degrees, dipole moments in Debyes.

Table 3. Calculated and observed vibrational spectra (in cm^{-1}) of acetohydroxamic acid[a].

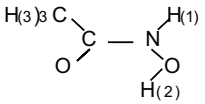
Assignment[b]	MP2	B3LYP	Argon[c]	Nitrogen
νNH	3654 (79)	3623 (64)	3454.0 (0.32)	3458.5 (0.47)
νOH	3595 (57)	3565 (64)	3323.0 (0.28)	3322.5 (0.26)
$\nu_{as}CH_3$	3193 (2)	3126 (12)	3009.0 (0.01)	3008.5 (0.02)
$\nu_{as}CH_3$	3192 (6)	3124 (2)	3002.0 (0.02)	2996.5 (0.01)
$\nu_{s}CH_3$	3098 (4)	3054 (5)	2948.0 (0.02)	2943.0 (0.01)
Amide I (νCO)	1725 (199)	1718 (226)	1690.5 (1.0)	1685.5 (1.0)
Amide II (δNH)	1557 (42)	1553 (46)	1513.5 (0.16)	1521.0 (0.12)
$\delta_{as}CH_3$	1515 (29)	1494 (25)	1454.0 (0.32)	1454.5 (0.24)
$\delta_{as}CH_3$	1495 (7)	1474 (7)	1428.5 (0.07)	1430.0 (0.06)
$\delta_{s}CH_3$	1412 (46)	1403 (19)	1406.0 (0.11)	1404.5 sh

Table 3 (continuation)

δNOH	1434 (160)	1414 (181)	1391.0 (0.96)	1394.0 (0.85)
Amide III (νCN)	1293 (9)	1277 (8)	1341.5 (0.05)	1353.0 (0.03)
ρCH_3	1068 (8)	1055 (9)	1081.5 (0.08)	1083.0 (0.06)
ρCH_3	1095 (50)	1091 (63)	1069.0 (0.33)	1069.0 (0.18)
νNO	1014 (14)	1006 (16)	992.5 (0.13)	995.5 (0.23)
νC–C	957 (15)	953 (15)	904.5 (0.01)	903.0 (0.02)
Amide IV (δOCN)	656 (21)	650 (15)	651.5 (0.02)	647.0 (0.02)
τCN	635 (17)	632 (15)	643.5 (0.05)	643.0 (0.03)
Amide V (γNH)	485 (114)	432 (156)		
γOH	430 (153)	479 (51)		
δCCN	418 (42)	413 (65)		
δCNO	293 (26)	286 (28)		
γC=O	248 (1)	241 (2)		
$\tau C–CH_3$	95 (0)	100 (0)		

[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 integral intensities for experimental spectra.
[b] Only the internal coordinate giving the main contribution to P.E.D. is given, abbreviations: ν – stretching, δ – in plane bending, ρ – rocking, τ – torsion, γ – out of plane bending.
[c] Only the frequencies of the most intense bands are given; the component bands corresponding to different sites were included in the intensity measurement.

Theoretical studies: The equilibrium geometry of the 1Z keto conformer of the acetohydroxamic acid molecule calculated at the MP2(FC) and B3LYP levels using 6-311++G(2d,2p) basis set is reported in Table 2. It was revealed in earlier studies [15] that the 6-311++G(2d,2p) basis set well reproduces the experimental gas phase proton dissociation energy value of acetohydroxamic acid. The scheme presented below shows the numbering of hydrogen atoms employed in the AHA molecule.



Comparison of the DFT and MP2 results shows that bond distances between hydrogen atoms and heavy atoms are slightly longer and those between heavy atoms (C=O, C–N, C–C and N–O bonds) are shorter at the DFT level than at the MP2 level of theory.

The harmonic vibrational frequencies computed for the AHA molecule at the MP2 and B3LYP levels of theory are presented in Table 3 and compared with experimental data. The calculated frequencies reproduce well the observed acetohydroxamic acid frequencies with the exception of the frequencies of the OH, NH and CH_3 stretching vibrations, 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 to be the least intense one in agreement with experimental data. In Table 3 only the internal coordinate giving the main contribution to the normal mode is presented (except amide I, II, III and IV vibrations). However, the theoretical calculations demonstrate that strong coupling between internal coordinates in the molecule of the acid occurs similar to that observed for formohydroxamic acid [16].

Data presented in Table 3 clearly indicate that the level of *ab initio* calculations used in this paper well reproduces the experimental spectra, which we find important due to the lack of the structural data for acetohydroxamic acid molecule derived from microwave measurements.

Bonding and structure: The spectra of acetohydroxamic acid in solid argon and nitrogen provide strong evidence for the 1Z keto tautomeric structure with intramolecular hydrogen bond. The presence of the bands characteristic for the C=O and NH group vibrations and a lack of the band due to the C=N stretch prove that the acid exists in the matrix as a keto tautomer. The low value of the OH stretching frequency provides strong evidence for an intramolecular hydrogen bond between OH group and an oxygen atom of a carbonyl group. The OH stretching vibration appears in the region above 3450 cm^{-1} if the OH group is not involved in the hydrogen bond. The decrease of the OH stretching frequency in the acetohydroxamic acid (3323.0 cm^{-1}) is accompanied by an increase of the NOH in plane bending frequency (1391.0 cm^{-1}) that is expected for a hydrogen bond. The intramolecular hydrogen bond is probably also responsible for the relatively low frequency of the C=O stretching vibration in acetohydroxamic acid (1691.0 cm^{-1} for AHA in solid argon). The C=O stretch was identified at 1777.9 cm^{-1} in the spectra of formamide [39] in solid argon and at 1726 cm^{-1}, 1721 cm^{-1} in the spectra of acetamide [33,38] and N-methylformamide [34] in solid argon, respectively. All other AHA vibrations (except γ(OH) that was not identified) are less sensitive to formation of intramolecular hydrogen bond.

It should be noted that the X-ray diffraction of crystals of acetohydroxamic acid hemihydrate also supported the 1-Z keto tautomer with the OH bond in the *syn* conformation [40].

CONCLUSIONS

In this work we applied matrix isolation technique combined with FT-IR spectroscopy to study the spectral characteristics of $CH_3CONHOH$ and its deuterium analogue $CH_3CONDOD$. The experimental results show that acetohydroxamic acid exists as the keto tautomer with 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 intramolecular CO$\cdots$HON hydrogen bond.

Theoretical studies of the 1-Z keto structure of the acetohydroxamic acid molecule carried out on 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.

Acknowledgment

We gratefully acknowledge financial support from the Polish State Committee for Scientific Research (Grant KBN No. 3T09 A 062 18).

REFERENCES

1. Miller M.J., *Chem. Rev*., **89**, 1563 (1989).
2. Steward A.O. and Martin J.G., *J. Org. Chem*., **54**, 1221 (1989).
3. Bauer L. and Exner O., *Angew. Chem., Int. Ed. Engl*., **13**, 376 (1974) and references therein.
4. Kaczka E.A., Gitterman C.O., Dulaney E.L. and Falkers K., *Biochemistry*, **1** , 340 (1962).
5. (a) Brown D.A., Glass W.K., Mageswaran R. and Girmay B., *Magn. Reson. Chem*., **26**, 970 (1988); (b) Brown D.A., Glass W.K., Mageswaran R. and Mohammed S.A., *Magn. Reson. Chem*., **29**, 40 (1991).
6. Brown D.A., Coogan R.A., Fitzpatrick N.J., Glass W.K., Abukshima D.E., Ahlgrén M., Smolander K., Pakkanen T.T., Pakkanen T.A. and Peräkylä M., *J. Chem. Soc., Perkin Trans. 2*, 2673 (1996).
7. Artemenko A.I., Anufriev E.K., Tikunova L. and Exner O., *Zh. Prikl. Spektr*., **33**, 131 (1980).
8. Exner O. and Horak M., *Coll. Czech. Chem. Commun*., **24**, 968 (1959).
9. HadŽi D. and Prevoršek D., *Spectrochim. Acta*, **10**, 38 (1957).
10. Fitzpatrick N.J. and Mageswaran R., *Polyhedron*, **8**, 2255 (1989).
11. Turi L., Dannenberg J.J., Rama J.B. and Ventura O.N., *J. Phys. Chem*., **96**, 3709 (1992).
12. Ventura O.N., Rama J.B., Turi L. and Dannenberg J.J., *J. Am. Chem. Soc*., **115**, 5754 (1993).
13. Remko M., Mach P., Schleyer P.v.R. and Exner O., *J. Mol. Struct. (THEOCHEM)*, **279**, 139 (1993).
14. Ventura O.N., Rama J.B., Turi L. and Dannenberg J.J., *J. Phys. Chem*., **99**, 131 (1995).
15. (a) Wu D.-H. and Ho J.-J., *J. Phys. Chem. A* , **102**, 3582 (1998); (b) Guo J.X. and Ho J.-J., *J. Phys. Chem. A*, **103**, 6433 (1999); (c) Yen S.-J., Lin C.-Y. and Ho J.-J., *J. Phys. Chem. A*, **104**, 11771 (2000).
16. Sałdyka M. and Mielke Z., *J. Phys. Chem. A*, **106**, 3714 (2002).
17. Sałdyka M. and Mielke Z., *Chem. Phys. Lett*., **371**, 713 (2003).
18. Frish M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheesman J.R., Zakrzewski V.G., Montgomery Jr., J.A., Stratmann R.E., Burant J.C., Dapprich S., Millam J.M., Daniels A.D., Kudin K.N., Strain M.C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford S., Ochterski J., Petersson G.A., Ayala P.Y., Cui Q., Morokuma K., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Cioslowski J., Otriz J.V., Baboul A.G., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts M., Martin R.L., Fox D.J., Keith T., Al.-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.M., Andres J.L., Gonzales C., Head-Gordon M., Replogle E.S. and Pople J.A., GAUSSIAN 98, REVISION A.9, Gaussian Inc., Pittsburgh PA, 1998.
19. Mőller C. and Plesset M.S., *Phys. Rev*., **46**, 618 (1934).
20. Binkley J.S. and Pople J.A., *Int. J. Quantum Chem*., **9**, 229 (1975).
21. Becke A.D., *J. Chem. Phys*., **98**, 1372 (1993).
22. Becke A.D., *J. Chem. Phys*., **98**, 5648 (1993).
23. Becke A.D., *Phys. Rev. A*, **38**, 3098 (1988).
24. Lee C., Yang W. and Parr R.G., *Phys. Rev. B*, **37**, 785 (1988).
25. Johnson B.G., Gill P.M.W. and Pople J.A., *J. Chem. Phys*., **98**, 5612 (1993).
26. McLean A.D. and Chandler G.S., *J. Chem. Phys*., **72**, 5639 (1980).
27. Krishnan R., Binkley J.S., Seeger R.S. and Pople J.A., *J. Chem. Phys*., **72**, 650 (1980).
28. Clark T., Chandrasekhar J., Spitznagel G.W. and Schleyer P.v.R., *J. Comput. Chem*., **4**, 294 (1983).
29. Frish M. and Pople J.A. and Binkley J.S., *J. Chem. Phys*., **80**, 3265 (1984).

30. Withnall R. and Andrews L., *J. Phys. Chem*., **92**, 2155 (1988).
31. (a) Yeo G.A. and Ford T.A., *J. Mol. Struct*., **217**, 307 (1990); (b) Yeo G.A. and Ford T.A., *Spectrochim. Acta*, **47A**, 919 (1991); (c) Yeo G.A. and Ford T.A., *Vibrational Spectrosc*., **2**, 173 (1991).
32. Heikkilä A., Pettersson M., Lundell J., Khriachtchev L. and Räsänen M., *J. Phys. Chem. A*, **103**, 2945 (1999).
33. Knudsen R., Sala O. and Hase Y., *J. Mol. Struct*., **321**, 187 (1994).
34. Ataka S., Takeuchi H. and Tasumi M., *J. Mol. Struct*., **113**, 147 (1984).
35. Mielke Z., Ratajczak H., Wiewiórowski M., Barnes A.J. and Mitson S.J., *Spectrochim. Acta*, **42A**, 63 (1986).
36. Miyazawa T., Shimanouchi T. and Mizushima S.-I ., *J. Chem. Phys*., **29**, 611 (1958).
37. Miyazawa T., Shimanouchi T. and Mizushima S.-I, *J. Chem. Phys*., **24**, 408 (1956).
38. Bohn R.B. and Andrews L., *J. Phys. Chem*., **93**, 5684 (1989).
39. (a) Räsänen M., *J. Mol. Struct*., **101**, 275 (1983); (b) Lundell J., Krajewska M. and Räsänen M., *J. Phys. Chem*., **102**, 6643 (1998).
40. Brecker B.H. and Small R.W.H., *Acta Cryst. B*, **26**, 1705 (1970).