# Photochemistry of Acetohydroxamic Acid in Solid Argon. FTIR and Theoretical Studies

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**Supporting Information** 

**ABSTRACT:** The products formed during exposure of the CH<sub>3</sub>CONHOH/Ar (AHA/Ar) matrices to the full output of the Xe lamp and to 225 nm OPO radiation are studied. The irradiation promotes the isomerization,  $1Z \rightarrow 1E$ , and AHA photodissociation reactions. Four pairs of coproducts are experimentally found to appear in the photolysis, they form the complexes: CH<sub>3</sub>OH… HNCO (1), H<sub>2</sub>O…CH<sub>3</sub>NCO (2), H<sub>2</sub>O…CH<sub>3</sub>CNO (3) and CO… CH<sub>3</sub>NHOH (4). The structures of the complexes were optimized at the MP2 computational level with the 6-311++G(2d,2p) and augcc-pVTZ basis sets. Three local minima were predicted for the complex (1), two for the complexes (2) and (3) and four local minima were found for the complex (4). The comparison of the



theoretical spectra with the experimental ones allowed us to determine the structures of the complexes formed in the matrix. The mechanisms of the reaction channels leading to formation of the four coproducts are proposed. It is concluded that the first step in formation of the (1), (2) and (3) complexes is the scission of the N–O bond whereas the creation of the complex (4) is due to the cleavage of the C–N bond.

## 1. INTRODUCTION

Hydroxamic acids (HA, RCONR'OH; R, R' = H, aryl, or alkyl) constitute the major class of structures with a wide spectrum of biological activities.<sup>1,2</sup> One of the first substantial applications of hydroxamic acids was associated with their use as siderophores, low molecular weight iron binding agents.<sup>3,4</sup> However, the biomedical applications of HA are no longer exclusively related to the uptake or removal of iron from the organism. There has been increasing interest in their roles as specific enzymes inhibitors, because HA possesses a moiety that has been demonstrated as a key structural element in many highly potent and selective inhibitors against a variety of biocatalysts such as matrix metalloproteases, peroxidases, hydrolases, ureases, and lipoxygenases.<sup>5,6</sup> A number of hydroxamic acids also have hypotensive, anticancer, antimalarial, antituberculosis, and antifungal properties and have been identified as compounds of potential chemotherapeutics aiming at cardiovascular diseases, Alzheimer's disease, and HIV.<sup>7</sup> Acetohydroxamic acid (AHA), known as Lithostat, is the only one among many compounds that has been clinically used for the treatment of urinary tract infections by urease inhibition.<sup>9</sup> AHA also shows many applications as a chelating agent in coordination chemistry and is often used as a small structural analogue of desferrioxamine B in biomedical investigations.<sup>10,11</sup> Recently, we reported the structural and tautomerical properties of AHA in the ground electronic state showing that acetohydroxamic acid trapped from the gas phase into solid argon or nitrogen exists mainly in the *Z-keto* form with an intramolecular hydrogen bond.<sup>12,13</sup> The broad spectrum of biomedical applications of AHA raises questions about the influence of UV–vis irradiation on the structure, isomeric equilibrium, and photochemical properties of acetohydroxamic acid.

Literature reports indicate that a photolytic scission of the N-O bond is the main photodissociation channel of hydroxamic acids. This reaction was already observed in the sixties by Walling and Naglieri<sup>14</sup> for N,O-diacylbenzoylhydroxylamine. The formation of anilides and amides after photoirradiation of N-substituted naphthalene-hydroxamic acids<sup>15</sup> and *N*-phenylbenzenehydroxamic  $\operatorname{acids}^{16,17}$  as well as 2-(arylthio)benzenehydroxamic  $\operatorname{acids}^{18,19}$  and 2-(aryloxy)benzenehydroxamic acids<sup>20</sup> is also consistent with the initial homolysis of the N-O bond. For benzyl N-methylbenzohydroxamate<sup>21</sup> or benzyl benzohydroxamate<sup>22</sup> a photoelimination in the singlet state through a mechanism involving the N-O bond cleavage was also proposed. Besides this reaction pathway, other mechanisms of the photolysis of hydroxamic acids have also been reported. It was suggested that the photoirradiation of selected naphthalenehydroxamic acids<sup>23</sup> leads to acylaminoxyl radical generation and not to the scission

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of the N–O bond. It has been implied that acylaminoxyl radicals are primary intermediates in the photochemical reaction of N-substituted hydroxamic acids containing the hydroxyl groups.<sup>15,17</sup>

Our recent studies showed that the UV–vis photode composition of the simplest representative of hydroxamic acids, namely, formohydroxamic acid<sup>24</sup> as well as its aminosubstituted derivative, namely, *N*-hydroxyurea<sup>25</sup> in low-temperature matrices leads to the products whose observation suggests two photodissociation channels proceeding through the scission of the N–O or C–N bonds in these molecules. If the acetohydroxamic acid molecule exhibits similar mechanisms of photodissociation, then the photodissociation of AHA should produce the HNCO–CH<sub>3</sub>OH and CH<sub>3</sub>NHOH–CO complexes as photoproducts. In this paper, the full spectroscopic characteristics of the 1*Z* and 1*E* isomers of AHA is given and, for the first time, the photochemical behavior of acetohydroxamic acid in an argon matrix is presented.

#### 2. EXPERIMENTAL SECTION

**Infrared Matrix Isolation Study.** The studies were performed for CH<sub>3</sub>CONHOH/Ar and CH<sub>3</sub>CONDOD/Ar samples. The solid sample of AHA was placed in a small electric oven assembled inside the cryostat. The temperature of the oven was controlled by the dc regulated power supply (NDN instruments). Matrices were prepared by codeposition of AHA vapor coming out of the oven with a large excess of argon onto the cold CsI window. The low temperature was maintained by means of a closed cycle helium refrigerator (ARS-2HW). FTIR spectra were recorded between 4000 and 500 cm<sup>-1</sup> in a transmission mode by means of a Bruker 66 FTIR spectrometer with a resolution of 0.5 cm<sup>-1</sup> and using a liquid N<sub>2</sub> cooled MCT detector.

After the infrared spectra of the initially deposited matrices were recorded, the samples were exposed to the full output radiation of a Xe arc lamp (Osram, XBO 450 W) for up to 120 min. A 5 cm water filter served to reduce the amount of infrared radiation reaching the matrix. Photochemical reactions in AHA/Ar and ADA/Ar matrices were also induced by UV radiation of a pulsed optical parametric oscillator Vibrant (Opotek, Inc.) (repetition rate 10 Hz, pulse duration 7 ns) pumped with a Nd:YAG laser (Quantel). The matrices were irradiated with the 225 and 243 nm UV lines for up to 125 min.

**Computational Details.** All calculations were performed using the Gaussian09 code.<sup>26</sup> Because most of the considered complexes are weakly bonded, the structures were optimized in two steps at the MP2 computational level with the 6-311+ +G(2d,2p) and aug-cc-pVTZ basis sets. First, standard geometry optimization of each complex was carried out. Afterward, all the structures found were reoptimized with the counterpoise correction (CP).<sup>27</sup> Both normal and CP-corrected harmonic wavenumbers and intensities were obtained for the optimized complexes. The anharmonic wavenumbers for the species identified in the performed experiments were also calculated on the MP2/aug-cc-pVTZ level. Energies of the lowenergy excited states were calculated using the time dependent density functional theory (TD-DFT).<sup>28,29</sup>

## 3. RESULTS AND DISCUSSION

Two photoprocesses occur simultaneously in matrices even during early stages of their irradiation:  $1Z \rightarrow 1E$  isomerization and photodissociation. We reported the study on AHA isomerization in our earlier paper.<sup>13</sup> However, the exposure of the AHA/Ar matrix to the 225 nm radiation emitted by the OPO gave much higher yield of 1*E* than irradiation with Xe lamp and allowed us to identify a number of weaker 1*E* bands that were not reported in our earlier paper. In addition to 1*Z* and 1*E* isomers, in matrices is also present a small amount of 2*Z* isomer of AHA but it is not affected, within experimental error, by the applied radiation (the band intensities of 2*Z* do not change during irradiation). In Figure 1 the decay of the 1*Z* 



**Figure 1.** Kinetic profiles showing changes of populations of 1*Z* (1690 cm<sup>-1</sup>) and 1*E* (1727 cm<sup>-1</sup>) AHA isomers and photoproducts CH<sub>3</sub>OH···HNCO (1025, 1052 cm<sup>-1</sup>), CO···CH<sub>3</sub>NHOH (2132, 2140, 2142, 2143 cm<sup>-1</sup>), H<sub>2</sub>O···CH<sub>3</sub>NCO (2284, 2290 cm<sup>-1</sup>), and H<sub>2</sub>O···CH<sub>3</sub>CNO (2305, 2311 cm<sup>-1</sup>) in the process of irradiation ( $\lambda = 225$  nm). The "amount of photoproducts" is proportional to the experimental integrated band intensities (divided by the calculated infrared intensity, *I*<sub>theor</sub> of the corresponding vibration).

isomer and the growth of the 1E one are presented. The bands due to the 1E isomer could be easily distinguished from those belonging to the dissociation products as they grew, in early stages of photolysis, with a much higher rate than those corresponding to photolysis products.

1Z–1E Isomerization of the Keto Tautomer of AHA. Among four minima located on the potential energy surface of acetohydroxamic acid (1Z, 1E, 2Z, 2E, Figure S1) the 1Z keto tautomer with intramolecular hydrogen bond is the most stable one (cf. our previous paper for details<sup>13</sup>). According to our previously reported computations, MP2/6-311++G(2d,2p), and those conducted here, MP2/aug-cc-pVTZ, the ZPEcorrected energy difference between the two keto isomers 1Z and 1E is equal to 5.6 and 8.8 kJ mol<sup>-1</sup> and the 1Z–1E conversion requires an activation energy of 70.3 and 67.4 kJ mol<sup>-1</sup>, respectively.

On the basis of the calculated relative Gibbs free energies at both levels of theory, it is estimated that the equilibrium gaseous mixture at evaporation temperature 301 K contains 92-91% 1*Z*, 4-2% 1*E*, and 4-6% 2*Z*, respectively.

The spectral regions in which the most characteristic and intense bands of the 1Z and 1E isomers occur are shown in



Figure 2. Positions of the bands observed for 1Z and 1E in solid argon together with the calculated wavenumbers are given in Table 1. The experimental populations, based on the integrated absorbance of the 1Z and 1E bands (divided by the absolute intensities calculated for the corresponding vibrations), are estimated to be ca. 92.5% and 2.3%, respectively. The relative abundance of the 2Z tautomer also present in the matrix (not affected by the radiation) is assessed to be equal to 5.1%. These values are in a very good agreement with the theoretically predicted abundances.

Exposing the AHA/Ar matrix to the OPO radiation at 225 nm promotes the  $1Z \rightarrow 1E$  transformation. According to the kinetic profiles presented in Figure 1, the 1Z isomer is efficiently converted into 1E form. Simultaneously, in addition to the isomeric interconversion, other AHA photoreactions leading to the sample decomposition take place in the studied matrices.

**Photodecomposition.** *Identification of Photoproducts.* Figure 3 shows the 2320–2120 cm<sup>-1</sup> region of the spectra of the CH<sub>3</sub>CONHOH/Ar matrix recorded directly after matrix deposition and after matrix exposure to  $\lambda = 225$  nm or to  $\lambda = 243$  nm radiation. In Figure S2, Supporting Information, the spectra of CH<sub>3</sub>CONDOD/Ar after deposition and after irradiation are presented. This is the key region as far as the identification of the products of photolysis is concerned. We can distinguish four groups of bands that grow in this region after the AHA/Ar matrix is exposed to the full output of the Xe lamp or to  $\lambda = 225$  nm radiation emitted by the OPO. One group of bands occurs on the high- and low-frequency sides of the 2138.7 cm<sup>-1</sup> absorption due to the CO monomer. The bands are observed at 2143.7, 2142.4, 2140.3 and 2134.3, 2132.3 cm<sup>-1</sup>. Another group involves broad absorption extending in the 2270–2230  $\rm cm^{-1}$  region with subpeaks at 2264.5, 2261.0, 2258.0, 2252.0, and 2251.0  $\rm cm^{-1}.$  The other two groups involve doublets at 2284.0, 2290.0  $\rm cm^{-1}$  and at 2311.5, 2305.0  $\rm cm^{-1}.$ 

The four groups of bands correspond to four pairs of photoproducts as will be discussed below.

The appearance of the bands due to the perturbed vibration of the carbon monoxide molecule suggests that in AHA a similar mechanism of photodissociation occurs, i.e., scission of the N–O bond, as in the case of formohydroxamic acid. The coproduct of CO in the case of formohydroxamic acid was hydroxylamine, NH<sub>2</sub>OH, and in the case of acetohydroxamic acid it is presumably N-methylhydroxylamine, CH<sub>3</sub>NHOH. The infrared spectrum of CH<sub>3</sub>NHOH has not been reported so far. As the two coproducts of photodissociation channel of AHA molecule are trapped in one cage, they may form a complex. So, we assumed that the six bands in the vicinity of the CO monomer band are due to the complexes formed between the two coproducts.

The broad band appearing after irradiation in the 2270–2230 cm<sup>-1</sup> region indicates formation of isocyjanic acid during AHA photolysis. From the five clear subpeaks that appear on the broad absorption at 2264.5, 2261.0, 2258.0 and at 2252.0, 2251.0 cm<sup>-1</sup>, the wavenumber of the central peak, at 2258.0 cm<sup>-1</sup>, corresponds to the NCO asymmetric stretch of the HNCO monomer isolated in an argon matrix.<sup>30–32</sup> The other four subpeaks are assigned to HNCO complexed with CH<sub>3</sub>OH whose presence is manifested in the OH stretching and CO stretching regions of the spectra recorded after AHA irradiation (Figure 4).

On the high-wavenumber side of the broad HNCO band appear two relatively sharp strong bands at 2290.0 and 2284.0 cm<sup>-1</sup> and another two less intense ones at 2311.5 and 2305.3 cm<sup>-1</sup>. The first two absorptions are with confidence assigned to the NCO asymmetric stretching vibration of methyl isocyanate, CH<sub>3</sub>NCO. The corresponding band was observed at ca. 2288 cm<sup>-1</sup> in the spectra of CH<sub>3</sub>NCO in the gas phase<sup>33</sup> and as a quadruplet with very intense peak at 2289 cm<sup>-1</sup> (accompanied by three much weaker components) in the spectra of methyl isocyanate isolated in solid nitrogen.<sup>34</sup> The quadruplet was interpreted in terms of coupling of  $\nu_{as}$ NCO with the torsion of



**Figure 2.** Selected regions of the IR spectra obtained for the AHA/Ar matrix: after deposition (black traces) and after 60 min of the  $\lambda$  = 225 nm irradiation (green traces) during which the highest concentration of 1*E* in the matrix was obtained.

Table 1. Observed Vibrational Wavenumbers in the Spectra of the AHA/Argon Matrix  $(cm^{-1})$  Compared with the Calculated Wavenumbers of the 1Z and 1E Isomers of Acetohydroxamic Acid<sup>*a*</sup>

	1Z			1E				
exptl	harmonic calcns	anharmonic calcns	exptl	harmonic calens	anharmonic calcns	assign. <sup>c</sup>		
3454.0	3635 (77) <sup>b</sup>	3469	3389.5	3571 (37)	3403	$\nu \rm NH$		
			3391.3					
3323.0	3536 (68)	3322	3586.3	3803 (66)	3613	νOH		
			3583.2					
3009.0	3187 (6)	3048	2994.5	3215 (3)	3075	$ u_{\rm as} {\rm CH}_3 $		
3002.0	3185 (1)	3045	2960.0	3176 (3)	3035	$\nu_{\rm as} {\rm CH}_3$		
2948.0	3089 (3)	2987		3092 (1)	2981	$\nu_{\rm s} {\rm CH}_3$		
1690.5	1733 (203)	1702	1727.3	1766 (233)	1735	νсο		
1513.5	1551 (33)	1504	1368.0	1424 (63)	1375	$\delta \mathrm{NH}$		
1505.5								
1454.0	1509 (33)	1466	1435.0	1497 (10)	1446	$\delta_{ m as}  m CH_3$		
1428.0	1490 (8)	1436	1429.0	1485 (9)	1438	$\delta_{ m as} { m CH}_3$		
1406.0	1401 (24)	1365	1379.0	1425 (86)	1383	$\delta_{ m s} { m CH}_3$		
1391.0	1428 (184)	1387	1383.7	1401 (50)	1360	$\delta$ NOH		
1251.0	1299 (7)	1250	1303.0	1331 (46)	1301	$\nu CN$		
1081.0	1060 (7)	1070		1061 (4)	1036	$\rho CH_3$		
1069.0	1098 (56)	1031		1036 (0)	1010	$\rho CH_3$		
992.5	1017 (13)	995	1053.0	1091 (38)	1055	$\nu NO$		
944.5	959 (14)	948	827.0	853 (18)	837	$\nu CC$		
644.0	659 (19)	644	537.0	546 (59)	535	$\delta$ OCN		
			535.5					
	635 (10)	611		186 (6)	176	$\tau CN$		
	428 (151)	416	610.0	680 (204)	632	γNH		
	489 (51)	358		364 (56)	344	γОН		
	414 (84)	379		486 (9)	479	$\delta$ CCN		
	290 (28)	278		282 (6)	288	$\delta$ CNO		
	251 (2)	234		591 (2)	581	γC=Ο		
	107 (0)	96		145 (0)	126	$\tau C$ — $CH_3$		

<sup>*a*</sup>In all calculations the MP2/aug-cc-pVTZ method was used. <sup>*b*</sup>The numbers in parentheses are the IR intensities expressed in km mol<sup>-1</sup>. <sup>*c*</sup>Abbreviations:  $\nu$ , bond stretching;  $\delta$ , bending, deformation in plane;  $\rho$ , rocking;  $\gamma$ , out-of-plane bending, torsion;  $\tau$ , twisting.



**Figure 3.** 2325–2120 cm<sup>-1</sup> region of the spectra of CH<sub>3</sub>CONHOH/ Ar matrix after deposition (a), after irradiation of the deposited matrix for 20 min with full output of Xe lamp (b), and after irradiation of the deposited matrix with  $\lambda$  = 225 nm for 120 min. (c) or with  $\lambda$  = 243 nm for 125 min. (d) The bands due to the complexes are labeled by arrows; the labels "c" indicate the <sup>13</sup>C counterparts of the <sup>12</sup>C absorptions and the labels "\*" and "+" indicate bands due to HNCO and CO monomers, respectively.

the methyl group. In addition, the authors managed to identify the absorption due to the CH<sub>3</sub>N<sup>13</sup>CO species, which allowed them to determine the <sup>13</sup>C isotopic shift for the  $\nu_{as}NCO$ vibration, the shift amounted to ca. 63.5 cm<sup>-1</sup>. We also identified in the recorded spectra very weak bands, at 2224.0 and 2217.5 cm<sup>-1</sup>, that exhibit ca. 66 cm<sup>-1</sup> red shift from the 2290.0 and 2284.0 cm<sup>-1</sup> absorptions. The shift agrees very well with the value of the <sup>13</sup>C shift calculated and observed for  $\nu_{as}$ NCO of CH<sub>3</sub>NCO<sup>34</sup> and provides strong evidence for the correct assignment of the 2290 and 2284 cm<sup>-1</sup> bands. The three much weaker components of the  $\nu_{as}$ NCO absorption, observed in an earlier report, may coincide with the broad band of the HNCO complexes and/or with a doublet corresponding to the CH<sub>3</sub>CNO ones. However, the CH<sub>3</sub> torsion vibrations are expected to have different values in the 2a, 2b complexes than in the CH<sub>3</sub>NCO and methyl torsion.

The two weaker bands at 2311 and 2305 cm<sup>-1</sup> are attributed to acetonitrile *N*-oxide. The IR spectra of CH<sub>3</sub>CNO both in the gas phase<sup>35</sup> and in argon matrix<sup>36</sup> were reported. The 2311.5 and 2305.3 cm<sup>-1</sup> wavenumbers match well the wavenumber of the  $\nu_{\rm as}$ CNO band (2309 cm<sup>-1</sup>) observed in the spectra of CH<sub>3</sub>CNO in an argon matrix.<sup>36</sup>

It can be expected that the coproduct accompanying formation of methyl isocyanate and acetonitrile *N*-oxide during photodissociation of AHA is the water molecule. As illustrated in Figure 4, water is also formed during AHA photolysis.

The presence of HOCN, which could be formed in a rearrangement process of HNCO, can be safely excluded even though its strongest absorption,  $\nu$ CN, was reported to occur at 2286.3 cm<sup>-1</sup> for the molecule trapped in an argon matrix.<sup>30,31</sup>

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**Figure 4.**  $3800-3100 \text{ cm}^{-1}$  (A),  $1750-1225 \text{ cm}^{-1}$  (B), and  $1210-600 \text{ cm}^{-1}$  (C) regions of the spectra of the same matrices whose spectra are shown in Figure 3 (a, b). The labels "\*" indicate bands due to water contamination, and the label "+" indicates a band tentatively assigned to the  $\delta$ NOH of MeHy monomer.

The 2290 and 2284 cm<sup>-1</sup> bands (assigned to the CH<sub>3</sub>NCO complexes) and the broad band in the 2275–2230 cm<sup>-1</sup> region (due to the HNCO complexes) appear simultaneously after short irradiation time (1 min). With prolonged irradiation time the overall intensity of the 2290 and 2284 cm<sup>-1</sup> bands decreases with respect to an overall absorption attributed to the  $\nu_{as}$ NCO of the HNCO complexes (Figure S3, Supporting Information). Such behavior is an evidence against assignment of the 2290 and 2284 cm<sup>-1</sup> bands to the secondary product of the AHA photolysis reaction. The second, strong evidence against the presence of HOCN in the matrix is the lack of absorption in the 3000–2700 cm<sup>-1</sup> region, which could be assigned to  $\nu$ (OH) of strong HOCN…CH<sub>3</sub>OH complex

(Figure S3). We optimized the structures of the HOCN···  $CH_3OH$  complex and calculated the frequencies of the two optimized structures. The results are presented in Table S1, Supporting Information. For the more stable structure, in which OH of HOCN is bonded to an oxygen atom of  $CH_3OH$  the OH stretch of HOCN is expected to shift ca. 730 cm<sup>-1</sup> toward lower frequencies and its intensity should increase ca. 15 times. No such band was identified in the 3000–2700 cm<sup>-1</sup> region that could be assigned to the HOCN···CH<sub>3</sub>OH complex. It has to be noted that for all four complexes formed after photolysis (CH<sub>3</sub>OH···HNCO, H<sub>2</sub>O···CH<sub>3</sub>NCO, H<sub>2</sub>O··· CH<sub>3</sub>CNO, CO···CH<sub>3</sub>NHOH) their most stable structures were identified.

Below, the theoretical spectra of the optimized structures of the  $CH_3OH$ ···HNCO,  $H_2O$ ··· $CH_3NCO$ ,  $H_2O$ ··· $CH_3CNO$ , and CO··· $CH_3NHOH$  complexes are compared with the recorded spectra in the whole middle infrared region. The comparison provides strong evidence for the formation of the abovementioned complexes in the studied matrices.

 $CH_3OH$ ···HNCO. The calculations resulted in three local minima on the potential energy surface of the isocyanic acid-methanol system that correspond to the stable structures presented in Figure 5. In the most stable structure, 1a ( $\Delta E^{CP}$  =



Figure 5. MP2/aug-cc-pVTZ optimized structures of the CH<sub>3</sub>OH… HNCO complex. The selected bond distances (Å) and interaction energies  $\Delta E^{CP}$  (kJ mol<sup>-1</sup>) are given.

-30.22 kJ mol<sup>-1</sup>), the NH group of HNCO serves as a proton donor toward the oxygen atom of methanol. In turn, in the 1b configuration, ( $\Delta E^{CP} = -13.65$  kJ mol<sup>-1</sup>), the OH group of methanol acts as a proton donor toward the nitrogen atom of HNCO. The cyclic structure, 1c ( $\Delta E = -16.32$  kJ mol<sup>-1</sup>), is stabilized by two weak hydrogen bonds, one is formed between NH group of HNCO and the oxygen atom of methanol and another one between an OH group of CH<sub>3</sub>OH and an oxygen atom of HNCO.

The geometrical parameters of the optimized structures 1a, 1b, and 1c and the full sets of vibrational wavenumbers are presented in Tables S2 and S3. In Table 2 the theoretical wavenumber shifts,  $\Delta \nu_{\text{theor}} = (\nu_{\text{comp}} - \nu_{\text{mon}})_{\text{theor}}$  for the three structures are compared with the experimental ones,  $\Delta \nu_{\text{exp}} = (\nu_{\text{compl}} - \nu_{\text{mon}})_{\text{expl}}$ . The experimental wavenumbers for the HNCO and CH<sub>3</sub>OH were taken from refs 31 and 37.

As can be seen in Table 2, the formation of the structure 1a in the matrix is very well documented by the appearance of the bands due to the strongly perturbed  $\nu$ NH and  $\delta$ HNC isocyanic acid modes. The broad band at ca. 3189 cm<sup>-1</sup> attributed to the

## Table 2. Wavenumbers (cm<sup>-1</sup>) of the Bands Identified for the 1a and 1b Structures of the CH<sub>3</sub>OH···HNCO Complexes<sup>a</sup>

structure 1a					structure 1b						1c		
CH <sub>3</sub> OH		CH <sub>3</sub> OD		CH <sub>3</sub> OH		CH <sub>3</sub> OD		СН <sub>3</sub> ОН	Σ.				
$\nu_{\rm exp}$	$\Delta \nu_{exp}^{\ b}$	$\Delta  u_{ m theor}$	$\nu_{\mathrm{exp}}$	$\Delta  u_{ m exp}$	$\Delta  u_{ m theor}$	$\nu_{\rm exp}$	$\Delta \nu_{\mathrm{exp}}$	$\Delta  u_{ m theor}$	$\nu_{exp}$	$\Delta  u_{ m exp}$	$\Delta  u_{ m theor}$	$\Delta  u_{ m theor}$	assign.
3671.0						3590	-77	-83	2643.2	-63	-70	-24	$\nu \mathrm{OH}/\mathrm{OD}$
3662.5	-4.5	-7	2702	-4	-5								$\nu OH/OD$
3016.0	+11	+12	3018.5	+12	+12			-9.5			-10.5	+0.5	$\nu CH_3$
2984.0	+22	+29	2987.5	+26	+29			-14			-14	+8.5	$\nu CH_3$
2854.0	+6	+17	2860	+15	+19			-10.5			-10	+5	$\nu CH_3$
1074.5	-2.2	-4	1233.8	+6.5									$\rho CH_3$
1027.5													νCO
1025	-9	-7	1028.2	-14.6	-18	1052.7	+18.5	+15.5			+7	+5	νCO
structure 1a							structu	ure 1b			1c		
HNCO DNCO				HNCO			DNCO		HNCO				
$ u_{\rm exp} $	$\Delta \nu_{exp}^{\ b}$	$\Delta  u_{ m theor}$	$\nu_{\rm exp}$	$\Delta  u_{\mathrm{exp}}$	$\Delta  u_{ m theor}$	$\nu_{\rm exp}$	$\Delta  u_{ m exp}$	$\Delta  u_{ m theor}$	$ u_{\rm exp} $	$\Delta  u_{ m exp}$	$\Delta  u_{ m theor}$	$\Delta \nu_{ m theor}$	assign.
3199													$\nu \mathrm{NH}/\mathrm{ND}$
3189	~-330	-314	2400	-207	-200			-31	2587?	-20	-25	-28	$\nu \mathrm{NH}/\mathrm{ND}$
3167													$\nu \mathrm{NH}/\mathrm{ND}$
2261	+2	+4				2251	-7						$\nu_{\rm as} { m NCO}$
2264.5	+5.5	+4	2218	-13	-17	2252	-8	-1.5	2249.5	+18.5	+2	-6	$\nu_{\rm as} { m NCO}$
850.5	+80.5	+88			-13	825.2	+55	+60			+28	+28	$\delta$ HNC/DNC

<sup>a</sup>The experimental wavenumber shifts,  $\Delta \nu_{exp}$  for 1a, and 1b and the theoretical shifts,  $\Delta \nu_{theor}$ , for 1a, 1b, and 1c are also presented.  $^{b}\Delta \nu$  indicates the differences between the wavenumber of the complex and the corresponding wavenumber of the HNCO or CH<sub>3</sub>OH monomers. The experimental wavenumbers for the monomers in solid argon were taken from refs 31and 37.

perturbed NH stretching vibration is ca. 330 cm<sup>-1</sup> red-shifted and the absorption assigned to  $\delta$ HNC is 80 cm<sup>-1</sup> blue-shifted with respect to the corresponding modes of the HNCO monomer in agreement with the shifts predicted for this structure (-314 and +88 cm<sup>-1</sup>, respectively). In turn the absorption due to the NCO asymmetric stretch exhibits ca. 5 cm<sup>-1</sup> blue shift with regard to the corresponding band of HNCO, which also matches the calculated shift (+4 cm<sup>-1</sup>). The experimental wavenumber shifts of the identified  $\nu$ OH and  $\nu$ CO modes of CH<sub>3</sub>OH (-4.5, -9 cm<sup>-1</sup>) are also in accord with the calculated ones (-7 cm<sup>-1</sup> for both modes). And, similarly, the experimental and theoretical  $\Delta \nu$  values for the other bands assigned to the 1a structure exhibit a good agreement. The deuterium sensitive modes were identified in the spectra of matrices containing CH<sub>3</sub>CONDOD and confirmed the correctness of their assignment.

The appearance of the absorptions at 2252 and 2251 cm<sup>-1</sup>, red-shifted with respect to the  $\nu_{as}$ NCO mode of the HNCO monomer band (2259 cm<sup>-1</sup>), suggests that at least one of the other two structures, 1b or 1c, is also formed in the matrix after its irradiation. The calculations indicate that in both structures, 1b and 1c, the  $\nu_{as}$ NCO wavenumber is shifted toward lower wavenumbers with respect to the HNCO monomer (-1.5 and -6 cm<sup>-1</sup>, respectively). The additional bands are identified in the region of the  $\delta$ HNC mode of HNCO (825.2 cm<sup>-1</sup>) and of the  $\nu$ CO vibration of methanol (1052.7 cm<sup>-1</sup>) and in the region of the OH and NH vibrations (3590 cm<sup>-1</sup>). The comparison of the experimental and calculated shifts (Table 2) suggests that the additional bands belong to the 1b structure.

 $H_2O\cdots CH_3NCO$ . Figure 6 presents two structures corresponding to two stationary points calculated for the methyl isocyanate complexes with water. In structure 2a ( $\Delta E^{CP} = -19.42$  kJ mol<sup>-1</sup>) the OH group of water acts as a weak proton donor toward oxygen atom, and in slightly less stable structure 2b ( $\Delta E^{CP} = -16.87$  kJ mol<sup>-1</sup>), toward nitrogen atom of CH<sub>3</sub>NCO. In addition, both structures are stabilized by weak interaction



Figure 6. MP2/aug-cc-pVTZ optimized structures of the H<sub>2</sub>O… CH<sub>3</sub>NCO complex. The selected bond distances (Å) and interaction energies  $\Delta E^{CP}$  (kJ mol<sup>-1</sup>) are given.

between oxygen atom of  $H_2O$  and one of the hydrogen atoms of  $CH_3NCO$ .

In Table 3 the wavenumber shifts of the bands identified for the two structures of the CH<sub>3</sub>NCO complex are compared with the theoretical ones. The CH<sub>3</sub>NCO monomer wavenumbers were taken from ref 34 in which the spectra of the species isolated in the nitrogen matrix were reported. The strongest absorption of the CH<sub>3</sub>NCO monomer is also identified in our spectra, in the argon matrices, as a shoulder at 2289 cm<sup>-1</sup>, this wavenumber is very close to the 2288.9 cm<sup>-1</sup> one for CH<sub>3</sub>NCO in the nitrogen matrix. The spectra of water trapped in solid argon have been extensively studied.<sup>38–41</sup> The geometrical parameters of the optimized structures 2a and 2b and the full set of calculated vibrational wavenumbers are given in Tables S4 and S5.

In the region of the NCO asymmetric stretching vibration two bands grow after matrix irradiation (2290, 2284 cm<sup>-1</sup>) which suggests formation of both optimized structures, 2a and 2b, in the irradiated matrices. The suggestion is supported by appearance of two bands for the  $\delta$ CH<sub>3</sub> of CH<sub>3</sub>NCO (1416, 1414 cm<sup>-1</sup>) and for the  $\nu_3$  H<sub>2</sub>O vibration (3717.5, 3709 cm<sup>-1</sup>). As one can see in Table 3, the experimental shifts are in accord

Table 3. Wavenumbers  $(cm^{-1})$  of the Bands Identified for the 2a and 2b Structures of the H<sub>2</sub>O····CH<sub>3</sub>NCO Complexes and for the 3a and 3b Configurations of the CH<sub>3</sub>CNO····H<sub>2</sub>O Ones<sup>*a*</sup>

s	structure 2a	ι	:					
	$H_2O/D_2O$							
$\nu_{\rm exp}$	$ \nu_{\rm exp} \qquad \Delta \nu_{\rm exp}^{\ b} \qquad \Delta \nu_{\rm theor}$			$\Delta  u_{ m exp}$	$\Delta  u_{ m theor}$	assign.		
3717.5	-18	-29	3709	-26	-37	$\nu_3 \text{ OH}$		
2759	-12	-21	2748	-23	-31	$\nu_3 OD$		
		-38	3571	-67	-79	$\nu_1 \text{ OH}$		
		-20	2623	-35	-51	$\nu_1 OD$		
1597	+7	+3				$\nu_2 \text{ OH}$		
1179.5	+3	+2				$\nu_2 OD$		
st	ructure 2a		structure 2b					
(	CH <sub>3</sub> NCO		(	CH <sub>3</sub> NCO				
$\nu_{\rm exp}$	$\frac{CH_3NCO}{\Delta \nu_{exp}}^{b}$	$\Delta  u_{ m theor}$	ν <sub>exp</sub>	$\frac{CH_3NCO}{\Delta \nu_{exp}}$	$\Delta  u_{ m theor}$	assign.		
ν <sub>exp</sub> 2290	$\frac{\Delta \nu_{exp}}{+1}^{b}$	$\Delta \nu_{\rm theor}$ +4	ν <sub>exp</sub> 2284	$\frac{\Delta \nu_{\rm exp}}{-5}$	$\Delta \nu_{ m theor}$ -14	assign. $ u_{as}NCO $		
ν <sub>exp</sub> 2290 1416	$\frac{\Delta \nu_{exp}}{\Delta \nu_{exp}} + 1$ $-3.8$	$\Delta \nu_{\rm theor}$ +4 -8	ν <sub>exp</sub> 2284 1414	$\frac{\Delta \nu_{exp}}{-5}$	$\Delta \nu_{ m theor}$ -14 -17	assign. $ u_{as}NCO $ $ \delta CH_3 $		
ν <sub>exp</sub> 2290 1416 1133.7	$\frac{\Delta \nu_{exp}^{b}}{-3.8}$	$\frac{\Delta\nu_{\text{theor}}}{+4}$ $-8$ $-1$	ν <sub>exp</sub> 2284 1414 1136.5	$\frac{\Delta \nu_{exp}}{-5}$ $-5.8$ $+2.8$	$\frac{\Delta\nu_{\text{theor}}}{-14}$ $-17$ $+8$	assign. $\nu_{as}NCO$ $\delta CH_3$ $\rho CH_3$		
ν <sub>exp</sub> 2290 1416 1133.7 859.5	$\frac{\Delta \nu_{exp}}{\Delta \nu_{exp}} + 1$ $-3.8$ $+1.5$	$ \frac{\Delta\nu_{\text{theor}}}{+4} \\ -8 \\ -1 \\ 0 $	ν <sub>exp</sub> 2284 1414 1136.5 859.5	$\frac{\Delta \nu_{exp}}{-5}$ $-5$ $-5.8$ $+2.8$ $+2$	$\frac{\Delta\nu_{\text{theor}}}{-14}$ $-17$ $+8$ $0$	assign. $\nu_{as}NCO$ $\delta CH_3$ $\rho CH_3$ $\nu C-N$		
ν <sub>exp</sub> 2290 1416 1133.7 859.5	$\begin{array}{c} \text{CH}_3\text{NCO}\\ \hline \Delta\nu_{\text{exp}} \\ +1\\ -3.8\\ +1.5\\ \text{tructure 3a} \end{array}$		ν <sub>esp</sub> 2284 1414 1136.5 859.5	$\frac{\Delta \nu_{exp}}{-5}$ $-5$ $+2.8$ $+2$ ructure 3b	$\frac{\Delta\nu_{\text{theor}}}{-14}$ $-17$ $+8$ $0$	assign. $\nu_{as}NCO$ $\delta CH_3$ $\rho CH_3$ $\nu C-N$		
$     \frac{\nu_{exp}}{2290} $ 1416 1133.7 859.5 st	$\frac{CH_3NCO}{\Delta \nu_{exp}}$ +1 -3.8 +1.5 tructure 3a $CH_3CNO$	$\frac{\Delta\nu_{\text{theor}}}{+4}$ $-8$ $-1$ $0$	ν <sub>esp</sub> 2284 1414 1136.5 859.5 st	$\frac{\Delta \nu_{exp}}{-5}$ $-5$ $-5.8$ $+2.8$ $+2$ ructure 3b CH <sub>3</sub> CNO	$\frac{\Delta\nu_{\text{theor}}}{-14}$ $-17$ $+8$ $0$	assign. $\nu_{as}NCO$ $\delta CH_3$ $\rho CH_3$ $\nu C-N$		
$     \frac{\nu_{exp}}{2290} $ 1416 1133.7 859.5 st $     \frac{\nu_{exp}}{\nu_{exp}} $	$CH_{3}NCO$ $\Delta \nu_{exp}^{\ b}$ +1 -3.8 +1.5 tructure 3a $CH_{3}CNO$ $\Delta \nu_{exp}$	$\frac{\Delta\nu_{\text{theor}}}{+4}$ $-8$ $-1$ $0$ $\Delta\nu_{\text{theor}}$	$     \frac{\nu_{exp}}{2284} $ 1414 1136.5 859.5 st $     \frac{\nu_{exp}}{\nu_{exp}} $	$\frac{\Delta \nu_{exp}}{\Delta \nu_{exp}}$ $-5$ $-5.8$ $+2.8$ $+2$ ructure 3b CH <sub>3</sub> CNO $\Delta \nu_{exp}$	$\Delta  u_{ m theor}$ -14 -17 +8 0	assign. $\nu_{as}NCO$ $\delta CH_3$ $\rho CH_3$ $\nu C-N$ assign.		

<sup>*a*</sup>Comparison of the experimental wavenumber shifts,  $\Delta \nu_{exp}$ , with the theoretical ones,  $\Delta \nu_{theor}$ , for every structure is also presented. <sup>*b*</sup>The experimental wavenumbers for the H<sub>2</sub>O/D<sub>2</sub>O, CH<sub>3</sub>NCO and CH<sub>3</sub>CNO monomers in solid argon were taken from refs 38–40, 34 and 36.

with the theoretical ones both for methyl isocyanate and for the hydrogenated and deuterated water molecules.

 $H_2O\cdots CH_3CNO$ . Two local minima calculated for the acetonitrile N-oxide-water complexes are shown in Figure 7.



Figure 7. MP2/aug-cc-pVTZ optimized structures of the H<sub>2</sub>O··· CH<sub>3</sub>CNO complex. The selected bond distances (Å) and interaction energies  $\Delta E^{CP}$  (kJ mol<sup>-1</sup>) are given.

The global minimum ( $\Delta E^{CP} = -20.9 \text{ kJ mol}^{-1}$ ) corresponds to the structure stabilized by the O–H···O bonding between the OH group of water and the oxygen atom of CH<sub>3</sub>CNO and, additionally, by van der Waals interaction between one of the hydrogen atoms of the CH<sub>3</sub> group and the oxygen atom of H<sub>2</sub>O. The less stable structure ( $\Delta E^{CP} = -8.37 \text{ kJ mol}^{-1}$ ) is maintained by interaction between methyl group and the oxygen atom of H<sub>2</sub>O. The corresponding distances between the sites of interaction are equal to  $R(C\cdots O) = 3.16 \text{ Å}$  and  $R(C\cdots$ H) = 2.76, 3.06, and 3.06 Å.

Two bands at 2311.5 and 2305.0 cm<sup>-1</sup> were identified for the  $\nu_{\rm as}$ CNO stretching vibration of the perturbed acetonitrile *N*-oxide, the first band is blue-shifted ( $\Delta \nu_{\rm exp} = +2.5 \text{ cm}^{-1}$ ) and the

second one is red-shifted ( $\Delta \nu_{exp} = -4$ ) with respect to the corresponding absorption of the CH<sub>3</sub>CNO monomer isolated in an argon matrix.<sup>36</sup> In our spectra  $\nu_{as}$ CNO of the CH<sub>3</sub>CNO monomer occurs as a shoulder at 2309 cm<sup>-1</sup> on the 2311.5 cm<sup>-1</sup> absorption. The observed shifts of the two bands suggest that both structures, 3a and 3b, are formed in the matrix, the 2311.5 cm<sup>-1</sup> band corresponding to the less stable 3a structure  $(\Delta \nu_{\text{theor}} = +3 \text{ cm}^{-1})$  and the 2305.0 cm<sup>-1</sup> absorption to the 3b configuration ( $\Delta \nu_{\text{theor}} = -2 \text{ cm}^{-1}$ ). No other band due to this complex was identified, which is possibly due to its small concentration in the matrix. The identified  $\nu_{as}$ CNO band ( $I_{theor}$ = 710 km mol<sup>-1</sup>) is calculated to be ca. 4 times more intense than the  $\delta CH_3 + \nu NO$  one  $(I = 165 \text{ km mol}^{-1})$  and ca. 10 times more intense then the  $\nu_{as}H_2O_1 \delta H_2O$  water vibrations (I = 81, 73 km mol<sup>-1</sup>, respectively). In Table 3, the identified wavenumbers of the CH<sub>3</sub>CNO-H<sub>2</sub>O complexes are presented; the geometrical parameters of the optimized structures 3a, 3b and their full sets of vibrational wavenumbers are presented in Tables S6 and S7.

 $CO \cdots CH_3 NHOH$ . As demonstrated in Figure 8, the calculations result in four stable minima, 4a, 4b, 4c, and 4d,



Figure 8. MP2/aug-cc-pVTZ optimized structures of the CO··· CH<sub>3</sub>NHOH complex. The selected bond distances (Å) and interaction energies  $\Delta E^{CP}$  (kJ mol<sup>-1</sup>) are given.

for the CO-*N*-methylhydroxylamine (MeHy) system. Two minima, 4a, 4b ( $\Delta E^{\rm CP} = -10.88$  kJ mol<sup>-1</sup>, -5.90 kJ mol<sup>-1</sup>) correspond to the structures in which the carbon or oxygen atom of CO interacts with the hydroxyl group of MeHy, forming an O–H…C or O–H…O bonding. In turn, the other two minima, 4c, 4d ( $\Delta E^{\rm CP} = -7.95$ , -5.02 kJ mol<sup>-1</sup>), correspond to the configurations in which the carbon atom of CO interacts with the NH group of MeHy forming N–H…C bonding. In 4c the arrangement of CO with respect to MeHy favors the N–H…C bonding. In 4d the orientation of CO with respect to MeHy is not optimal for the N–H…C interaction; however, it enables additional interaction between the carbon atom and methyl group of MeHy.

The most informative on the structure of the CO···  $CH_3NHOH$  complexes formed in the matrix is the region of carbon monoxide. As stated earlier, the bands due to the perturbed CO occur on the high- (2143.7, 2142.4, 2140.3 cm<sup>-1</sup>) and low-wavenumber sides (2136.8, 2132.3 cm<sup>-1</sup>) of the CO monomer absorption at 2138.7 cm<sup>-1</sup>. The relative intensities of the perturbed CO bands depend on the

monomers		structure 4a		structure 4b		structure 4c		4d	
СО		СО							ſ
$\nu_{\rm exp}$	$\Delta  u_{ m theor}$	$\nu_{\rm exp}/\Delta \nu_{\rm exp}$	$\Delta  u_{ m theor}$	$\nu_{\rm exp}/\Delta \nu_{\rm exp}$	$\Delta  u_{ m theor}$	$\nu_{\rm exp}/\Delta\nu_{\rm exp}$	$\Delta  u_{ m theor}$	$\Delta  u_{ m theor}$	assign.
2138.7		2143.7		2132.3		2142.4			νCO
		+5	+11.5	-6.4	-7.5	+3.6	+6	+2	
						2140.3			νCO
						+1.6			
monomers		structur	re 4a	structure 4b		structure 4c		4d	
CH <sub>3</sub> NHOH				CH <sub>3</sub> NHOH/C	H <sub>3</sub> NDOD				
$ u_{ m theor}^{ m anh}$	$ u^{ m h}_{ m theor}$	$ u_{\rm exp}$	$\Delta \nu_{\mathrm{theor}}^{b}$	$ u_{\mathrm{exp}}$	$\Delta  u_{ m theor}$	$ u_{\mathrm{exp}}$	$\Delta  u_{ m theor}$	$\Delta  u_{ m theor}$	assign.
3640	3827	3576.0	-65	3636.0	-15	3621.5	-1	0	$\nu OH$
		2647.5	-47	2686.5	-12	2676	-1	0	$\nu OD$
3338	3510		0		+2		-2	0	$\nu \rm NH$
1430	1484		+4		0		+10	-3	$\delta NH$
1310	1359	1343.5	+34		+10	1335.9	-4	0	$\delta OH$
1196	1233		-1	1201.1	-1	1193.7	+5	0	$\rho CH_3$
1128	1159	1127.5	+3	1127.5	+1	1127.5	-1	0	$\rho CH_3$
1036	1072	1037.0	+5	1034.5	+2	1032.5	-2	-3	$\nu_{\rm as} {\rm CNO}$
959	980	950.0	0	946.3	-1	953.7	+7.5	+6	$\gamma \rm NH$

Table 4. Wavenumbers  $(cm^{-1})$  of the Bands Identified for the 4a, 4b and 4c Structures of the CO···CH<sub>3</sub>NHOH Complex<sup>*a*</sup>

<sup>a</sup>The theoretical wavenumber shifts corresponding to the identified bands of the specific structure are presented; for CO the experimental wavenumbers shifts are also shown. The theoretical anharmonic and harmonic wavenumbers of MeHy are displayed. <sup>b</sup>Only the harmonic wavenumbers for the 4a, 4b, 4c, and 4d structures were calculated, and the  $\Delta \nu_{\text{theor}}$  values for the MeHy vibrations are calculated with respect to the harmonic wavenumbers of MeHy.

wavelength(s) of matrix irradiation. In the spectra of the matrices exposed to  $\lambda = 225$  nm radiation emitted by the OPO, the 2132.3  $\text{cm}^{-1}$  band is the strongest one among the six bands which is not the case when the matrix is irradiated with the broad output of the Xe lamp (Figure 3). Irradiation of the matrix at  $\lambda = 243$  nm enhances even more, than 225 nm radiation, the relative intensity of the 2132.3 cm<sup>-1</sup> absorption (as well as the 2136.8  $cm^{-1}$  one) with respect to the other CO bands. The different response of the spectra to the wavelength(s) of irradiation helped us to assign the bands in the whole region to the particular MeHy-CO structure. The relative intensities of the bands assigned to the specific structure were constant (within experimental error) in all experiments performed. The 2136.8 cm<sup>-1</sup> band did not match the absorptions of any of the three specific structures of CO---CH<sub>3</sub>NHOH, and is also assigned to the CO monomer in accord with earlier reported work.<sup>42</sup> In Table 4, the identified wavenumbers of the CO…CH<sub>3</sub>NHOH complexes are presented; the geometrical parameters of all optimized structures and their full sets of vibrational wavenumbers are presented in Tables S8 and S9.

The 2143.7 band, due to the perturbed CO stretch, is assigned to the most stable structure 4a, its relative intensity shows small sensitivity to the wavelength of irradiation. The band is +5 cm<sup>-1</sup> blue-shifted with respect to the CO monomer absorption, which is in reasonable agreement with the theoretical value for the 4a structure (+11.5 cm<sup>-1</sup>). The experimental spectra of MeHy have not been reported so far, and the  $\Delta \nu_{exp}$  values for CH<sub>3</sub>NHOH could not be estimated. As the calculated anharmonic wavenumbers for hydroxylamine show very good agreement with the experimental ones (3650, 3635 cm<sup>-1</sup> for  $\nu$ OH and 1351, 1342 cm<sup>-1</sup> for  $\delta$ NOH, respectively, Table S10), the same may be expected for MeHy, the theoretical anharmonic wavenumbers of MeHy are presented in Table 4. The criterion of the constant relative intensities of the perturbed MeHy bands with respect to the 2143.7 cm<sup>-1</sup> CO band helped us to identify the MeHy vibrations in the 4a, MeHy–CO structure, as well as in the other ones. In addition to the CO stretch, the following bands were attributed to the 4a configuration: 3576.0 cm<sup>-1</sup>,  $\nu$ OH; 1343.5 cm<sup>-1</sup>,  $\delta$ NOH; 1127.5 cm<sup>-1</sup>,  $\rho$ CH<sub>3</sub>; 1037.0 cm<sup>-1</sup>,  $\nu_{as}$ CNO; 950.0 cm<sup>-1</sup>,  $\gamma$ NH. The  $\rho$ CH<sub>3</sub> vibration is characterized by almost identical wavenumbers in all four structures; so, the band at 1127.5 cm<sup>-1</sup> may correspond to 4a, 4b, and 4c. The 3576.0 cm<sup>-1</sup> band is 65 cm<sup>-1</sup> red-shifted and the 1343.5 cm<sup>-1</sup> is 34 cm<sup>-1</sup> blue-shifted with respect to the corresponding theoretical anharmonic wavenumbers which evidence that OH group of MeHy forms weak O–H…C bonding with the carbon atom of CO.

The band at 2132.3 cm<sup>-1</sup> is assigned with confidence to the 4b structure in which the oxygen atom of CO is attached to the hydroxyl group of MeHy. This band exhibits a -6.4 cm<sup>-1</sup> red shift with respect to the CO monomer one in accord with the theoretical value (-7.5 cm<sup>-1</sup>) for this structure. The fact that the 2132.3 cm<sup>-1</sup> band considerably gained in intensity with respect to the other CO bands, in the spectra of matrices irradiated at  $\lambda = 225$  nm and even more in the spectra of matrices exposed to  $\lambda = 243$  nm radiation (as compared to irradiation with the full output of Xe lamp, Figure 3), helped us to identify the other perturbed MeHy bands due to the 4b structure. They were found at 3636.0, 1201.1, 1127.5, 1034.5, and 946.3 cm<sup>-1</sup>.

The bands observed in the CO stretching region at 2142.4 and 2140.3 cm<sup>-1</sup> show 3.6 and 1.6 cm<sup>-1</sup> shifts, respectively, toward higher wavenumbers, with respect to the CO monomer band, which suggests that they may correspond to the 4c, 4d structures ( $\Delta \nu_{\text{theor}} = +6$ , +2 cm<sup>-1</sup> for 4c, 4d, respectively). In the more stable 4c structure ( $\Delta E^{\text{CP}} = -7.95$  kJ mol<sup>-1</sup>) the carbon atom of CO interacts with the NH group. In the 4d configuration ( $\Delta E^{\text{CP}} = -5.02$  kJ mol<sup>-1</sup>) CO is arranged in such a way with respect to MeHy that the carbon atom interacts

simultaneously with the NH group and presumably with one of the hydrogen atoms of  $CH_3$ . The  $R(C \cdots HN)$  distance is noticeably longer in 4d than in 4c (2.86, 2.58 Å respectively). The 4c and 4d structures exhibit very similar configurations, which results in very similar sets of wavenumbers (compare  $\Delta \nu_{\text{theor}}$  for 4c and 4d in Table 4). Only one vibration, namely,  $\delta$ NH, is characterized by distinctly different wavenumbers in 4c and 4d complexes ( $\Delta \nu_{\mathrm{theor}}$  = +10, -3 cm<sup>-1</sup> for 4c, 4d, respectively); however, the corresponding band was not identified. We assigned the following set of bands: 2142.4, 2140.3, 3621.5, 1335.9, 1193.7, 1127.5, 1032.5, and 953.7 cm<sup>-1</sup> to the more stable 4c structure (taking into account the criterion of constant relative intensity of the bands with respect to the 2140.3  $\text{cm}^{-1}$  absorption). However, it has to be underlined that the assignment of the bands to 4c structure is only tentative.

**Probable Mechanisms to Different Photoproducts.** The 225 nm radiation has enough energy (532 kJ mol<sup>-1</sup>) to induce the transition of AHA to the S<sub>1</sub> state (according to our calculations the S<sub>1</sub> state is ca. 536 kJ mol<sup>-1</sup> above S<sub>0</sub>). The recorded spectra evidence that the exposure of the 1*Z* isomer of AHA to the UV radiation leads either to rotamerization reaction  $1Z \rightarrow 1E$  or to 1Z dissociation into four pairs of coproducts, namely

 $CH_3CONHOH \rightarrow CH_3OH + HNCO$  (1)

$$CH_3CONHOH \rightarrow H_2O + CH_3NCO$$
 (2)

$$CH_3CONHOH \rightarrow H_2O + CH_3CNO$$
 (3)

$$CH_3CONHOH \rightarrow CO + CH_3NHOH$$
 (4)

The coproducts of each pair, being trapped in the same cage, form molecular complexes as discussed above. However, small amounts of the formed species stay as monomers in the matrix. The plot presented in Figure 1 shows that the 1*E* isomer also photodissociates, however, much more slowly than the 1*Z* one. No additional photoproducts were detected after prolonged photolysis time, which indicates that both 1*Z* and 1*E* isomers of acetohydroxamic acid decompose into the same products. The 2*Z* AHA isomer present in a small amount in the deposited matrices was not affected by the irradiation. This is expected as 2*Z* does not involve the  $n \rightarrow \pi^*$  transition, which is responsible for the observed photochemistry.

It is well documented that photoirradiation of hydroxamic acids may lead to initial photolytic scission of the N–O bond.<sup>23</sup> The literature data on photodissociation of hydroxamic acids and our earlier study on formohydroxamic acid allow us to conclude that the first step in formation of the CH<sub>3</sub>OH + HNCO pair (1) is the fission of the N–O bond. Furthermore, the reported theoretical study on isomerization processes of CH<sub>3</sub>CNO, CH<sub>3</sub>OCN, CH<sub>3</sub>CNO, and CH<sub>3</sub>ONC species<sup>43</sup> leads to the hypothesis that the N–O bond scission acts also as a first step in formation of the CH<sub>3</sub>NCO + H<sub>2</sub>O (2) and CH<sub>3</sub>CNO + H<sub>2</sub>O (3) pairs as discussed below.

There is no theoretical study toward understanding the mechanistic photochemistry of hydroxamic acids, even the simple ones. However, the fact that fission of the N–O bond is the main photodissociation channel of hydroxamic acids, has been well documented by a number of experimental data. The cleavage of the N–O bond of AHA leads to formation of the CH<sub>3</sub>CONH and OH radicals:

$$CH_3CONHOH \rightarrow CH_3CONH + OH$$

The N–O bond is a weak bond, the dissociation energy,  $E_{\rm dis}({\rm HO-NO})$ , is reported as 206.4 kJ mol<sup>-144</sup> and  $E_{\rm dis}({\rm O-N})$  in AHA might be expected to have similar values. As the AHA molecule excited by the 225 nm laser line gains an excess energy of ca. 532 kJ mol<sup>-1</sup>, the internal energy of the two formed hot radicals may be relatively high (above 300 kJ mol<sup>-1</sup>), so they can undergo further reactions. The recorded spectra suggest that two processes may occur.

First, the  $CH_3CONH$  radical (on which most of the energy is concentrated) can further dissociate into  $CH_3$  radical and isocyanic acid, HNCO. Next, the  $CH_3$  radical recombines with OH to form  $CH_3OH$ . The isocyanic acid and methanol molecules, being trapped in the same cage form a hydrogenbonded complex:

 $CH_3CONH \rightarrow CH_3 + HNCO$  $CH_3 + OH \rightarrow CH_3OH$ 

 $CH_3OH + HNCO \rightarrow CH_3OH \cdots HNCO$ 

This reaction channel is analogous to that observed in photolysis of formohydroxamic acid.  $^{\rm 24}$ 

The second possibility is the dissociation of the CH<sub>3</sub>CONH radical into H atom (dissociation of the N–H bond) and into CH<sub>3</sub>NCO, methyl isocyanate, or CH<sub>3</sub>CNO, acetonitrile N-oxide. The average N–H bond energy is about 335 kJ mol<sup>-1,44</sup> which is close to an excess of energy that may have the CH<sub>3</sub>CONH radical. The H atom will react immediately with OH, entrapped in the same cage, to give H<sub>2</sub>O:

$$CH_3CONH \rightarrow H + [CH_3C(O)N]^* \rightarrow H + CH_3NCO$$

or

$$CH_2CONH \rightarrow H + [CH_2C(O)N]^* \rightarrow H + CH_2CNO$$

and

$$H + OH \rightarrow H_2O$$

Then  $CH_3NCO$  or  $CH_3CNO$  trapped with  $H_2O$  in one cage form the hydrogen-bonded complexes:

$$H_2O + CH_3NCO \rightarrow CH_3NCO \cdots H_2O$$

 $H_2O + CH_3CNO \rightarrow CH_3CNO \cdots H_2O$ 

The hypothesis for this reaction channel is based on the calculations for the isomerization reactions between CH<sub>3</sub>NCO, CH<sub>3</sub>OCN, CH<sub>3</sub>CNO, and CH<sub>3</sub>ONC.<sup>43</sup> The transition state, TS ( $[CH_3C(O)N]^*$ ), joining the CH<sub>3</sub>NCO, methyl isocyanate, and a cyclic, three-membered CH3CON isomers has the CH<sub>3</sub>CON configuration resembling the configuration that might have had an intermediate formed after removal of the NH hydrogen atom from the CH<sub>3</sub>CONH radical. The calculations showed that the transition state, TS, is ca. 360 kJ mol<sup>-1</sup> above CH<sub>3</sub>NCO and 92 kJ mol<sup>-1</sup> above the cyclic CH<sub>3</sub>CON configuration; the cyclic CH<sub>3</sub>CON isomer converts to CH<sub>3</sub>CNO by crossing a barrier of ca. 222 kJ mol<sup>-1</sup>. So, removal of the hydrogen atom from CH<sub>3</sub>CONH might lead directly to CH<sub>3</sub>NCO or to the cyclic isomer. The latter one might rearrange to CH<sub>3</sub>CNO by traversing the 222 kJ mol<sup>-1</sup> barrier. The barrier is relatively high; however, the cyclic isomer should be born with some excess of energy (ca. 92 kJ mol<sup>-1</sup>). Moreover, in the same cage the strongly exotermic H + OH  $\rightarrow$ H<sub>2</sub>O reaction occurs, and the cyclic isomer may gain some of the excess energy of  $H_2O$ .

Acetohydroxamic acid is the acetamide molecule where one of the NH<sub>2</sub> hydrogen is substituted by the OH group. The photolytical behavior of the simple amides (formamide, *N*-methylformamide, *N*,*N*-dimethylformamide, acetamide) have been extensively studied both experimentally and theoretically.<sup>45–52</sup> The C–N bond cleavage was evidenced to be an important photolytic channel in all amides investigated. For CH<sub>3</sub>CONH<sub>2</sub>, apart from the C–N bond cleavage, the C–C bond fission was also proposed as the primary photodissociation channel:<sup>50</sup>

$$\begin{array}{l} \mathrm{CH_3CONH_2} \rightarrow \mathrm{CH_3CO} + \mathrm{NH_2} \\ \\ \rightarrow \mathrm{CH_3} + \mathrm{CONH_2} \end{array}$$

In addition to the radical reactions, direct molecular formation of  $CH_3CN + H_2O$  and  $CH_3NH_2 + CO$  was reported in the studies of acetamide photolysis in the gas phase and in solution.<sup>45,47</sup>

The theoretical work focused on the mechanistic photochemistry of acetamide shed some light on the possible dissociation channels of this molecule.50 Three routes of deactivation were found for the acetamide molecule photoexcited to the S<sub>1</sub> state: internal conversion to the ground state, intersystem crossing to the lowest triplet state, and direct dissociation along the S1 surface. The specific route of deactivation was found to depend on the excess energy of the molecule in the  $S_1$  state. When the  $S_1$  excess energy is ca. 16–42 kJ mol<sup>-1</sup> above the S<sub>1</sub> origin, the intersystem crossing S<sub>1</sub>  $\rightarrow$  T<sub>1</sub> is a dominant path. The CH<sub>3</sub>CONH<sub>2</sub> molecule relaxed to the T<sub>1</sub> state has enough energy to overcome the barriers for the C-N and C-C bond cleavages. However, the T<sub>1</sub> C-N bond fission is much more probable than the C-C bond rupture (the barrier heights of the T1 C-C and C-N bonds fissions are 59.4-51.1, 35.6, and 14.2 kJ mol<sup>-1</sup>, respectively, dependent on the method of calculations). The CH<sub>3</sub>CO radicals formed by C-N bond cleavage in the T1 state can further dissociate into CO and CH<sub>3</sub>. The authors also found the same photodissociation mechanisms for formamide and N-methylformamide.<sup>51</sup> Our obtained spectral and calculated data for acetohydroxamic acid strongly indicate that a similar mechanism of photodissociation occurs in AHA leading to the formation of N-methylhydroxylamine and carbon monoxide,  $CO + CH_3NHOH$  (4). We calculated the energy of the three excited single states  $(S_1, S_2, S_3)$  and three triplet ones  $(T_1, T_2, S_3)$ T<sub>3</sub>) corresponding to the n  $\rightarrow \pi^*$  transitions in AHA. According to our calculations, the  $S_1$  level (537.5 kJ mol<sup>-1</sup>) is ca. 9.2 kJ mol<sup>-1</sup> above T<sub>3</sub> (528.3 kJ mol<sup>-1</sup>), ca. 14.2 kJ mol<sup>-1</sup> above  $T_2$  (523.3 kJ mol<sup>-1</sup>) and 93.8 kJ mol<sup>-1</sup> above  $T_1$  (443.7 kJ mol<sup>-1</sup>). So, the calculations predict that three lowest triplet states are below the first excited singlet state,  $S_1$  (Table S11). This fact suggests that one of the photodissociation channels of AHA is similar to that occurring in acetamide, and the following scheme of reaction can be proposed:

 $CH_3CONHOH \rightarrow CH_3CO + NHOH$  $\rightarrow CO + CH_3 + NHOH$  $\rightarrow CO + CH_3NHOH$ 

The first step is the cleavage of the C–N bond and formation of the CH<sub>3</sub>CO and NHOH radicals, in the next step the CH<sub>3</sub>CO radical dissociates into CH<sub>3</sub> radical and CO. Finally, the CH<sub>3</sub> and NHOH radicals recombine to create CH<sub>3</sub>NHOH. Most of the CH<sub>3</sub>NHOH and CO molecules form molecular complexes; however, some stay in monomeric form. The fact that most of the coproducts formed in the same cage create complexes but some stay as monomers was discussed widely in our earlier papers.<sup>24,25</sup>

## 4. CONCLUSIONS

Analysis of the spectra of the CH<sub>3</sub>CONHOH/Ar matrices exposed to a 225 nm laser line or to the full output of Xe arc lamp indicated the existence of two simultaneous photochemical processes: rotamerization reaction of the 1Z AHA isomer into 1E one  $(1Z \rightarrow 1E)$  and AHA photodissociation reaction. The high yield of the isomerization reaction enabled identification of most of the 1E AHA wavenumbers in accord with the MP2/aug-cc-pVTZ calculated spectrum.

The identified products of the AHA photolysis reaction evidence existence of four reaction channels leading to the formation of the CH<sub>3</sub>OH···HNCO (1), H<sub>2</sub>O···CH<sub>3</sub>NCO (2), H<sub>2</sub>O···CH<sub>3</sub>CNO (3), and CO···CH<sub>3</sub>NHOH (4) molecular complexes. Small amounts of the monomers forming each complex are also observed. The spectral and theoretical data obtained in this work for AHA and literature data on photodissociation of simple amides and hydroxamic acids allow us to conclude that the first step in formation of the complexes (1), (2), and (3) and their corresponding monomers is the fission of the N–O bond. In turn, a first step in formation of the complex (4) and its corresponding monomers is the cleavage of the C–N bond. The possible full mechanisms of the formation of the four pairs of coproducts are proposed.

The structures of each of the four complexes formed during AHA photodissociation were optimized in two steps using the MP2 computational level with the 6-311++G(2d,2p) and augcc-pVTZ basis sets. The calculations resulted in three stable structures for the CH<sub>3</sub>OH···HNCO complex, in two configurations for the H<sub>2</sub>O···CH<sub>3</sub>NCO and H<sub>2</sub>O···CH<sub>3</sub>CNO pairs and in four stable isomers for the CO···CH<sub>3</sub>NHOH complex. The spectra evidenced that during AHA photodissociation the configurations corresponding to the global minimum as well as those due to the local minima are formed. The performed study demonstrate that photolysis of a proper precursor entrapped in a rare-gas matrix is a powerful method of producing molecular complexes that may be difficult to obtain in a traditional way.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b09461.

Full citation for ref 26, the optimized structures of the 1*Z*, 1*E*, 2*Z*, and 2*E* isomers of acetohydroxamic acid, the spectra of CH<sub>3</sub>CONHOH/Ar and CH<sub>3</sub>CONDOD/Ar matrices after deposition and after irradiation, the tables of the computed structural parameters and wavenumbers of all optimized structures of the CH<sub>3</sub>OH···HOCN, CH<sub>3</sub>OH···HNCO, H<sub>2</sub>O···CH<sub>3</sub>NCO, H<sub>2</sub>O···CH<sub>3</sub>CNO, and CO···CH<sub>3</sub>NHOH complexes and energies of vertical excitations ( $\Delta E$ ) of AHA (PDF)

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#### Notes

The authors declare no competing financial interest.

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