Matrix Isolation Spectra and ab Initio Calculations of Isothiocyanic Acid Complexes with Carbon Monoxide

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The complexes formed by isothiocyanic acid HNCS and its deuterated analogue DNCS with carbon monoxide have been observed and characterized in argon and nitrogen matrixes. The product bands and their shifts relative to the corresponding monomer absorptions prove that the complexes are hydrogen bonded with the carbon-attached structure OC···HNCS. The structure, energetics, and vibrational properties of the complexes have been calculated by ab initio at the MP2 level. Two stable minima were localized on the potential energy surface. Both involved an almost linear hydrogen bond from the NH group of the isothiocyanic acid molecule to either the carbon or the oxygen atom of the CO molecule. The OC···HNCS and CO···HNCS complexes were found to be weakly bound by −2.84 and −1.33 kcal/mol, respectively.

Introduction

Carbon monoxide is known to form weak complexes with various proton donor molecules such as water,[1−7] methanol,[8−10] phenols,[11−13] nitric,[14,15] nitrous,[16] or sulfuric[17]acid, and others.[18−22] Accurate theoretical studies of the intermolecular potential surfaces for such systems reveal the existence of two hydrogen-bonded OC···HX and CO···HX structures. Both complexes involve a hydrogen bond from the donor group to either the carbon or the oxygen atom of the carbon monoxide molecule. The carbon-attached structures have been predicted to represent a stronger interaction than the oxygen-attached ones. Experimental findings point mostly to the OC···HX structure with a proton donor molecule interacting with the carbon atom of carbon monoxide. The OC···HX type of interaction prevails over the CO···HX type in the gas phase and in the low-temperature matrixes in those cases when components of the complex are deposited from the gas phase and the global minimum on the potential energy surface is reached. The oxygen-attached structure is formed in larger yield while the carbon monoxide−HX complex is generated directly in the matrix cage. For instance, Schatte et al.[19] reported formation of both OC···HF and CO···HF complexes by UV photofragmentation of matrix-isolated formyl fluoride. In turn, Lundell and Räsänen[5] have studied the HCOOH photodecomposition and found the CO···H_2O structure to be favored over the OC···H_2O structure in xenon matrix.

As a part of wider study of the isothiocyanic acid and its complexes in low-temperature matrixes,[23,24] we examined the interaction of HNCS with carbon monoxide. Both argon and nitrogen matrixes were used to check the influence of the more reactive N_2 environment on the studied complexes. The present work reports the results of these experimental studies supported by high level ab initio calculations.

Experimental Section

Matrix Isolation Studies. Gaseous HNCS (or DNCS) was freshly prepared in a vacuum line by the reaction of KSCN with ca. 70% H_3PO_4 (or D_3PO_4). It was collected and shortly stored at low pressure in a glass bulb. The gas mixtures of HNCS/DNCS and CO diluted in Ar or N_2 have been deposited onto a gold-coated copper mirror maintained typically at 15 or 18 K for argon or nitrogen depositions, respectively, by means of a closed-cycle helium cryostat (Air Products, Displex 202A). Infrared spectra between 4000 and 500 cm^{-1} were recorded at 11 K in a reflection mode with a resolution of 0.5 cm^{-1} by means of a Bruker 113v FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector.

Before the three component spectra were investigated, the parent molecules spectra were measured. They are in general agreement with those previously reported.[24−26] Small amounts of nitrogen and/or water impurities were present in the studied systems. The spectra were checked as to the possible bands due to complexes formed between CO, HNCS, and H_2O or N_2 according to earlier studies.[1,3,6,24]

Annealing of the samples was performed at 25 and 30 K for argon and at 25 and 28 K for nitrogen matrixes. The changes observed upon annealing speed up at higher temperature; however, matrixes with less $(HNCS)_2$ or $(DNCS)_2$ dimer are obtained after longer but gentle heating at 25 K.

Computational Details. All calculations were performed within the framework of the ab initio approach using the Gaussian 98 package of computer codes.[27] The complex properties were considered via the supermolecular Möller−Plesset perturbation theory to the second (MP2) order.[28,29] The structures of the isolated monomers, HNCS and CO, and the structures of HNCS complexes with CO were fully optimized using the 6-311++G(2d,2p) basis set. Vibrational frequencies and intensities were computed both for the monomers and for the complexes. Interaction energies were corrected by the Boys−Bernardi full counterpoise correction[30] at the MP2 level.

Results

Experimental Spectra. *Isothiocyanic Acid with CO in Argon Matrixes.* When both carbon monoxide and HNCS are co-deposited with Ar, a number of bands appear which were not

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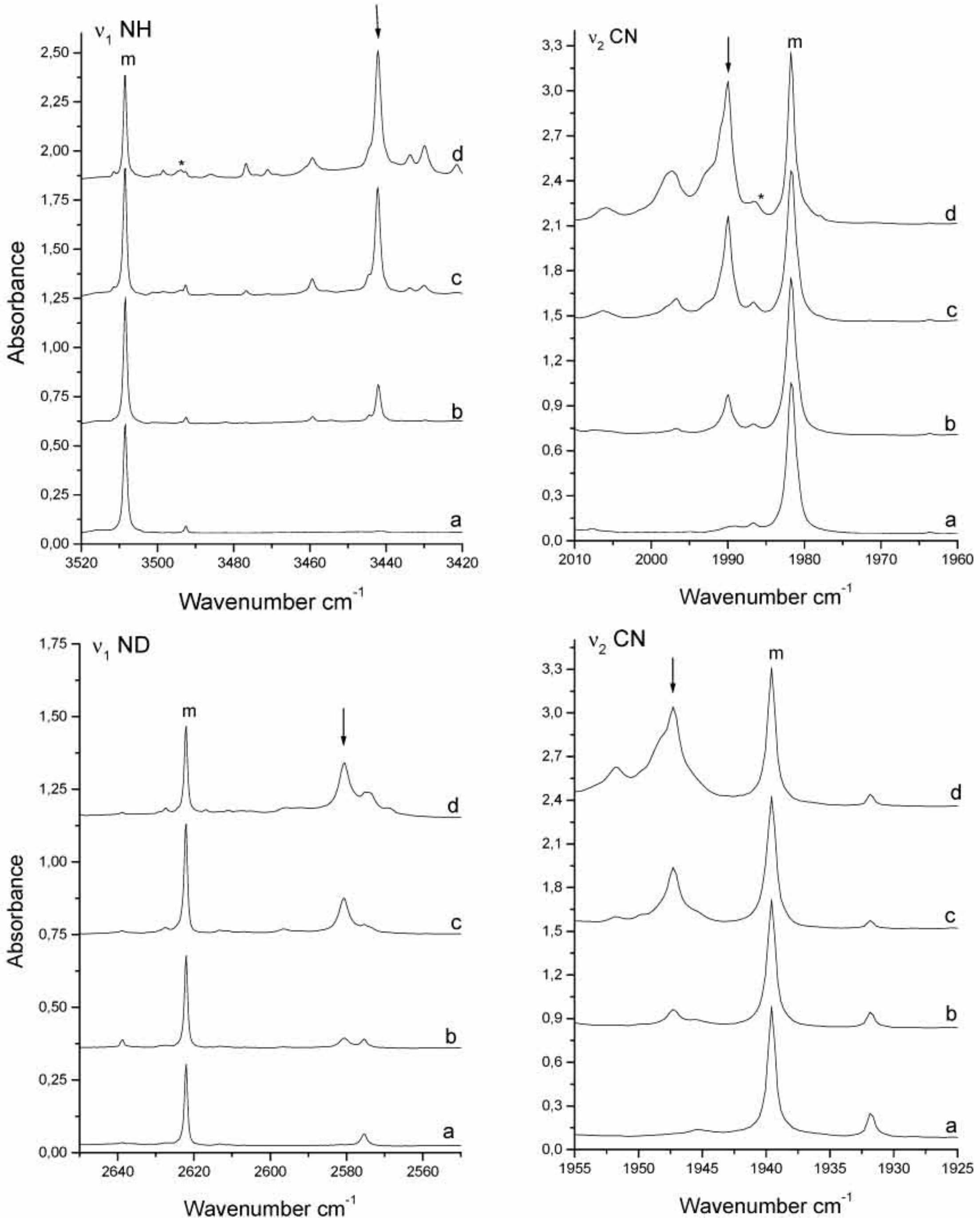

Figure 1. ν_1 NH (ν_1 ND) and ν_2 CN stretching regions of infrared spectra of matrixes. Upper: HNCS/Ar = 1/1200 (a), HNCS/CO/Ar = 1/1/1500 (b), HNCS/CO/Ar = 1/3/1500 (c), and HNCS/CO/Ar = 1/6/1500 (d). Lower: (HNCS + DNCS)/Ar = 1/1200 (a), (HNCS + DNCS)/CO/Ar = 1/1/1500 (b), (HNCS + DNCS)/CO/Ar = 1/2/1500 (c), and (HNCS + DNCS)/CO/Ar = 1/6/1500 (d). The letter "m" denotes isothiocyanic monomer absorptions; asterisks indicate bands due to the HNCS−N_2 complex[24] present as an impurity.

observed in the parent molecule spectra. Figure 1 presents the ν_1 NH and ν_2 CN stretching regions in the spectra of HNCS/CO/Ar matrixes and the corresponding regions in the spectra of the deuterated sample. A set of bands at 3442.1, 1990.0, 852.6, and 631.6 cm^{-1} is situated close to the ν_1 NH, ν_2 CN, ν_3 CS, and ν_4 NCS fundamentals of the HNCS monomer, respectively. A new band blue shifted with respect to the CO monomer absorption (at 2138.2 cm^{-1}) is also present at 2154.1 cm^{-1} as shown in Figure 2. The relative intensities of these absorptions are independent of the matrix concentration and are equal to $I(3442.1)/I(1990.0)/I(852.6)/I(631.6)/I(2154.1) = 1/1/0.01/0.25/0.1$. Several experiments have been conducted with partly deuterated isothiocyanic acid. Three new features close to the ν_1 ND, ν_2 CN, and ν CO absorptions of the corresponding monomer species are observed at 2580.7, 1947.3, and 2154.6 cm^{-1}.

In the spectra of matrixes containing a higher excess of CO (1/3 and 1/6), additional weak absorptions appear in both ν_1 NH and ν_2 CN regions at 3433.6, 3429.8 cm^{-1} and 2005.9, 1997.3 cm^{-1}, respectively. The relative intensities of these bands increase with respect to the corresponding 1:1 complex bands at higher CO concentrations. They are assigned to higher order aggregates $(CO)_n$HNCS. Annealing of the matrixes leads to increase of the intensity of all product bands. New bands appearing in the spectra of HNCS(DNCS)/CO/Ar matrixes are given in Table 1.

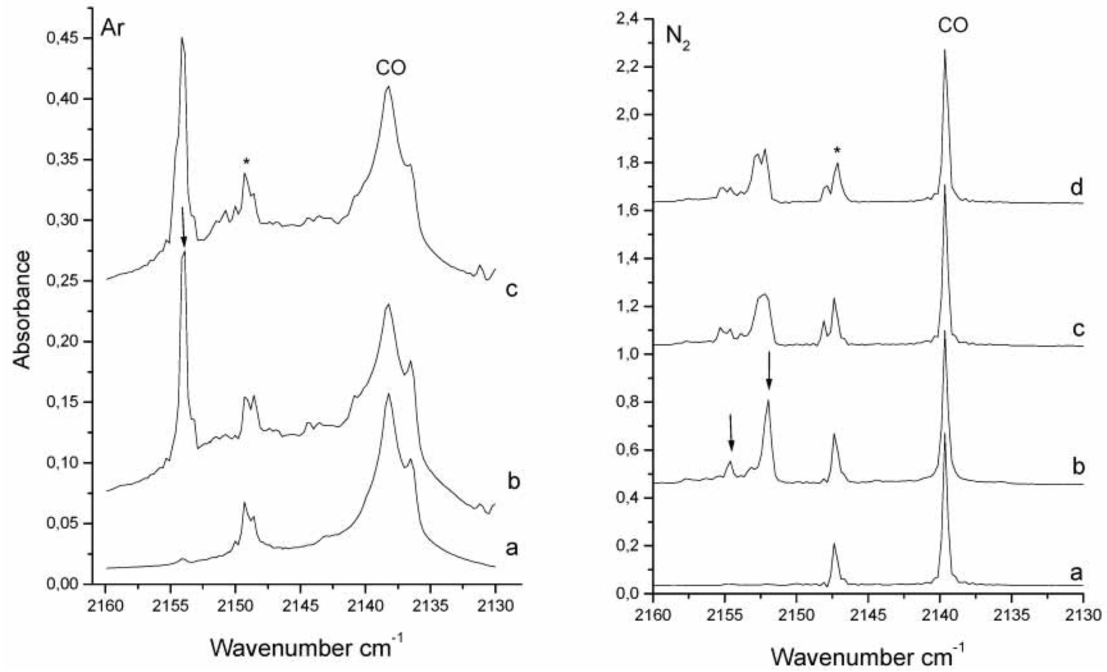

Figure 2. ν CO stretching region of infrared spectra recorded for matrixes. Ar: CO/Ar = 1/500 (a), HNCS/CO/Ar = 1/3/1500 (b), and (HNCS + DNCS)/CO/Ar = 1/3/1500 (c). N_2: CO/N_2 = 1/1000 (a), HNCS/CO/N_2 = 1/3/1800 (b), (HNCS + DNCS)/CO/N_2 = 1/3/1800 measured at 11 K (c), and (HNCS + DNCS)/CO/N_2 = 1/3/1800 measured at 18 K (d). Asterisks denote bands due to CO⋯H_2O complex at 2149.3, 2148.6 cm^{-1} (Ar)[6] and at 2147.4 cm^{-1} (N_2) present as an impurity.

TABLE 1: Band Positions and Wavenumber Shifts (cm^{-1}) for HNCS/DNCS Complexes with Carbon Monoxide in Argon and Nitrogen Matrixes

HNCS/CO		DNCS/CO		mode	
ν	$\Delta\nu$	ν	$\Delta\nu$		
		Argon Matrix			
3459.4	−49.1	2596.5	−25.7	ν_1 NH/ν_1 ND	1:1
3442.1	−66.4	2580.7	−41.5		1:1
3433.6	−74.9	2574.4 sh	−47.8		1:*n*
3429.8	−78.7				1:*n*
2005.9	+24.1			ν_2 CN	1:*n*
1997.3	+15.5				1:*n*
1996.7	+14.9	1951.8	+12.2		1:1
1990.0	+8.2	1947.3	+7.7		1:1
852.6	+2.6			ν_3 CS	1:1
631.6	+53.6			ν_4 NCS	1:1
2154.1	+15.9	2154.6	+16.4	ν CO	1:1
		Nitrogen Matrix			
3480.2	−17.2			ν_1 NH/ν_1 ND	nnn
3457.0	−40.4	2593.4	−25.7		1:1
3448.4	−49.0	2587.7	−31.4		1:1
3431.8	−65.6	2576.4	−42.7		1:*n*?
2012.2	+15.7	1961.0	+8.7	ν_2 CN	1:*n*?
2002.3	+5.8	1956.2	+3.9		1:1
2000.2	+3.7	1954.7	+2.4		1:1
2154.6	+14.9	2155.3	+15.6	ν CO	1:1
2152.0	+12.3	2152.7	+13.0		1:1

Isothiocyanic Acid with CO in Nitrogen Matrixes. Spectra of nitrogen matrixes containing both isothiocyanic acid and CO showed in addition to the monomer bands several new features in the ν_1 NH, ν_2 CN, and ν CO regions. The corresponding portions of the spectra are presented in Figures 2 and 3. Four product absorptions are observed in the ν_1 NH region of the spectra measured after matrix deposition. They are situated at 3480.2, 3457.0 (with a shoulder at 3454.1), 3448.4, and 3431.8 cm^{-1}, all red shifted with respect to the ν_1 NH stretch of the HNCS monomer (3497.4 cm^{-1}). The relative intensities of these bands do not depend on matrix concentration, and the ratio *I*(3480.2)/*I*(3457.0)/*I*(3448.4)/*I*(3431.8) is equal to 0.64/0.56/1/0.19. Upon annealing of the matrix, the most intense absorption at 3448.4 cm^{-1} moves slightly to higher wavenumbers (3449.6 cm^{-1}) and its intensity increases as compared to other product bands. The absorption at 3457.0 cm^{-1} loses its intensity on heating and simultaneously, the intensity of the weak shoulder observed in the initial spectrum at 3454.1 cm^{-1} increases. Two other product bands observed in the ν_1 NH region at 3480.2 and 3431.8 cm^{-1} lose their intensity on heating as compared with the most intense band at 3448.4 cm^{-1}. These changes are rather slow since after 1 h annealing at 25 K both 3457.0 and 3454.1 cm^{-1} absorptions are present (see Figure 3c′).

Three new features are observed in the ν_2 CN region: a doublet at 2002.3, 2000.2 cm^{-1} and a weaker band at 2012.2 cm^{-1}, all blue shifted compared to the corresponding mode of the acid monomer (1996.5 cm^{-1}). The relative intensities of these absorptions with respect to each other and to the product bands observed in the ν_1 NH region do not depend on CO concentration in the matrix. The ratio *I*(3448.4)/*I*(2012.2)/*I* (2002.3, 2000.2) is equal to 1/0.7/1.8. Upon annealing, the doublet at 2002.3, 2000.2 cm^{-1} is replaced gradually by an absorption of the intermediate wavenumber at 2001.1 cm^{-1}. The band at 2012.2 cm^{-1} moved slightly to the red (to 2011.3 cm^{-1}). There is also a $(HNCS)_2$ dimer band growing in its vicinity at 2012.5 cm^{-1}.

In the ν CO region two product absorptions are present in the initial HNCS/CO/N_2 spectra: a weak band at 2154.6 and a stronger one at 2152.0 cm^{-1}, both blue shifted compared to the ν CO monomer mode (2139.7 cm^{-1}). Upon annealing, the band at 2152.0 cm^{-1} loses a part of its intensity and a new component appears at 2153.2 cm^{-1}. In turn, the absorption at 2154.6 cm^{-1} increases relative to the 2152.0 cm^{-1} band.

The corresponding absorptions as in HNCS/CO/N_2 spectra were localized for the deuterated sample with the only exception of the 3480.2 cm^{-1} band for which no counterpart was found in the ν_1 ND region. Three new bands in the ν_1 ND stretching region red shifted compared to the ν_1 ND mode of the DNCS monomer (2619.1 cm^{-1}) are situated at 2593.4, 2587.7, and

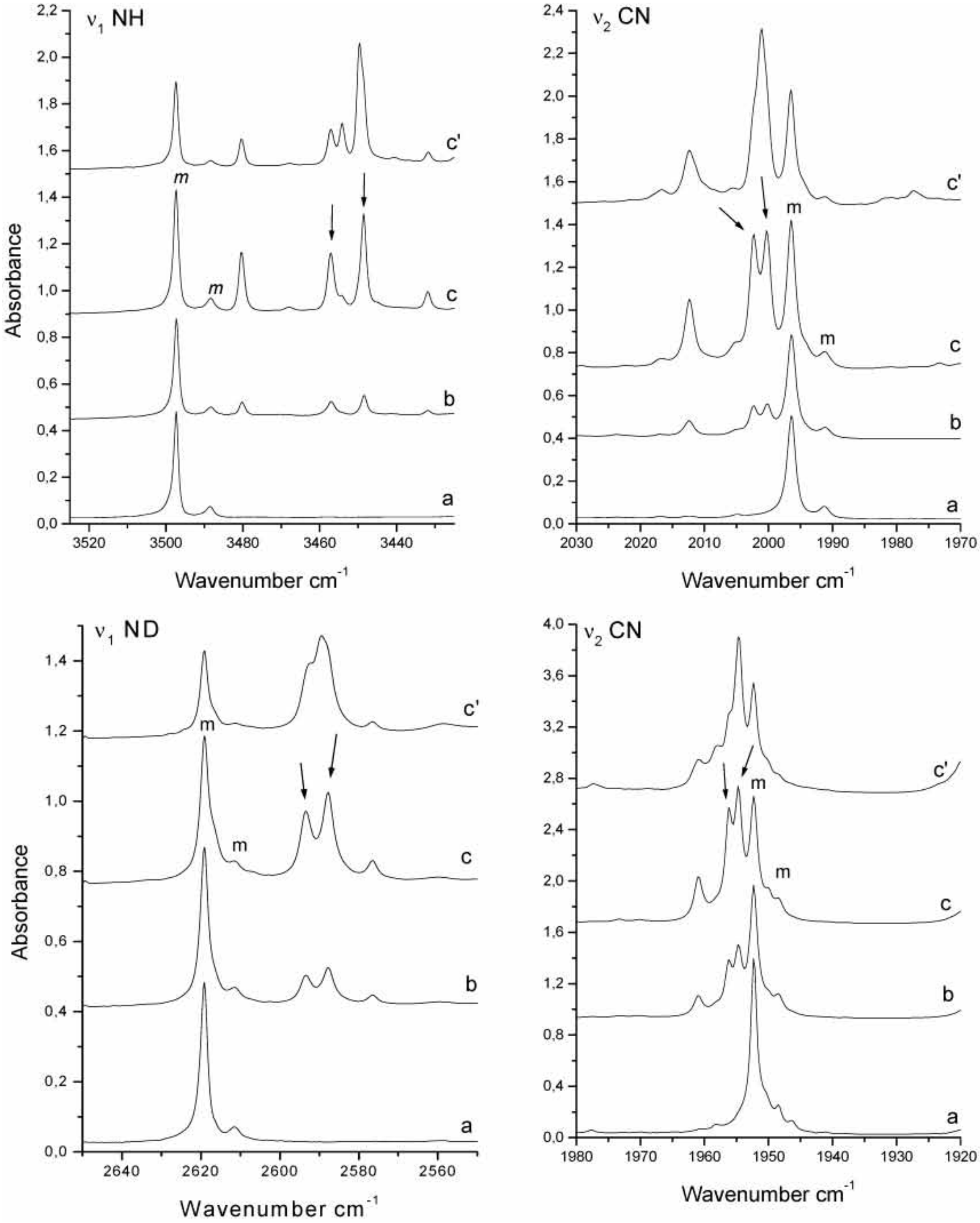

Figure 3. ν_1 NH (ν_1 ND) and ν_2 CN stretching regions of infrared spectra recorded for matrixes. Upper: HNCS/N_2 = 1/1500 (a), HNCS/CO/N_2 = 1/1/1500 (b), and HNCS/CO/N_2 = 1/2/1500, after deposition at 18 K (c) and after 60 min annealing to 25K (c′), both measured at 11 K. Lower: (HNCS + DNCS)/N_2 = 1/1500 (a), (HNCS + DNCS)/CO/N_2 = 1/1/1500 (b), and (HNCS + DNCS)/CO/N_2 = 1/2/1500, after deposition at 18 K (c) and after 60 min annealing to 25 K (c′), both measured at 11 K.

2576.4 cm^{-1}. They correspond to those at 3457.0, 3448.4, and 3431.8 cm^{-1} in the ν_1 NH, respectively. The annealing of the matrix leads to intensity changes within the observed set of bands similar to those for HNCS/CO/N_2. The maximum situated at 2587.7 cm^{-1} moves slightly to higher wavenumbers and grows in intensity, and finally a broader absorption is present at 2589.6 cm^{-1} with a shoulder at 2593.4 cm^{-1}. Absorption at 2576.4 cm^{-1} decreases in a manner similar to that of its counterpart at 3431.8 cm^{-1}.

Three product bands corresponding to those found for the nondeuterated sample are present in the ν_2 CN stretching region of the DNCS/CO/N_2 spectra. They are situated at 1961.0, 1956.2, and 1954.7 cm^{-1}. The band at 1954.7 cm^{-1} gains its intensity on annealing, while that at 1956.2 cm^{-1} becomes weaker. Absorption at 1961.0 cm^{-1} corresponding to the 2012.2 cm^{-1} band in the spectrum of nondeuterated sample loses its intensity on heating. An additional feature is also growing in this region at 1958.0 cm^{-1} due to the $(DNCS)_2$ dimer.

For (HNCS + DNCS)/CO/N_2 matrixes containing ca. 50% of the deuterated acid, two doublets in the ν CO region were apparent in the spectra taken during deposition at 18 K (trace d in Figure 2) at 2154.6, 2155.3 cm^{-1} and 2152.0, 2152.7 cm^{-1}. In the spectra measured at 11 K these doublets are hardly resolved (trace c in Figure 2). All new bands appearing in the spectra of HNCS(DNCS)/CO/N_2 matrixes are gathered in the right side of Table 1.

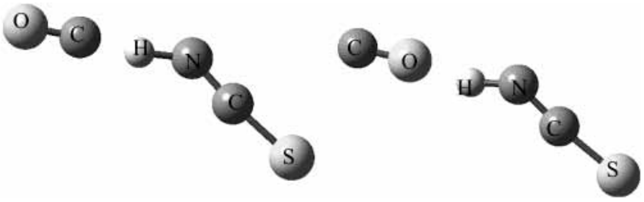

Figure 4. MP2/6-311++G(2d,2p) calculated structures of HNCS complexes with carbon monoxide.

TABLE 2: Calculated Geometry of the HNCS and CO Monomers and HNCS···CO and HNCS···OC Complexes at MP2 Level with the 6-311++G(2d,2p) Basis Set[a]

parameter	HNCS, CO monomers	OC···HNCS	CO···HNCS
r(HN)	1.0029	1.0071	1.0032
r(N=C)	1.2108	1.2065	1.2093
r(C=S)	1.5736	1.5781	1.5752
r(C≡O)	1.1370	1.1359	1.1390
θ(HNC)	132.5	135.8	134.0
θ(NCS)	173.3	173.9	173.4
R(H···C)		2.2100	
R(H···O)			2.2405
θ(C···HN)		177.9	
θ(O···HN)			168.1
ΔE^{CP}		−2.84	−1.33

[a] Bond lengths are in angstroms, angles in degrees, and interaction energies in kilocalories per mole.

Computational Results. Two stationary points were found on the PES for the isothiocyanic acid−carbon monoxide interaction at the MP2/6-311++G(2d,2p) level of theory. The corresponding structures are presented in Figure 4. Both of them are planar involving an almost linear hydrogen bond with N−H group of isothiocyanic acid directed toward either the carbon or the oxygen end of the CO molecule. The results of geometry optimization of the monomers and HNCS complexes with CO are collected in Table 2. The calculated vibrational frequencies for both HNCS and DNCS complexes are gathered in Table 3. In addition, relative intensities and frequency shifts with respect to the calculated monomer values are presented. For comparison purposes the corresponding spectral shifts observed for OC···HNCS and OC···DNCS complexes in solid argon and nitrogen are included.

Discussion

Carbon Monoxide−Isothiocyanic Acid 1:1 Complexes. The set of bands at 3442.1, 1990.0, 852.6, 631.6, and 2154.1 cm^{-1} observed in the spectra of HNCS/CO/Ar matrixes independently of the concentration used can be assigned with confidence to the 1:1 complex of isothiocyanic acid with carbon monoxide. The deuterium counterparts of the 3442.1 and 1990.0 cm^{-1} modes were found at 2580.7 (ν_1 ND) and 1947.3 cm^{-1} (ν_2 CN). The observed red shift of the NH and ND stretching modes with respect to the corresponding monomer vibrations are equal to 66.4 and 41.5 cm^{-1}, respectively, and indicate formation of a hydrogen bond between the interacting molecules. Blue shifts observed for the CN stretching modes in hydrogen and deuterium complexes (+8.2, +7.7 cm^{-1}, respectively) confirm this conclusion. The CO stretching mode in HNCS and DNCS complexes is shifted by 15.9 and 16.4 cm^{-1} to higher wavenumbers, respectively, with regard to the corresponding CO monomer value.

The presented experimental shifts of the fundamental modes in the studied system point to the structure of OC···HNCS type with the N−H group attached to the C atom of the carbon monoxide molecule. The most conclusive evidence for the carbon-attached complex is the blue shift of the product band found in the CO stretching region due to the bond strengthening as a consequence of the complex formation.[18,19] The presence of the OC···HNCS structure is confirmed by the results of ab initio calculations gathered in Tables 2 and 3. The OC···HNCS complex (Figure 4) is predicted to be more stable by 1.51 kcal/mol than the oxygen-attached CO···HNCS complex. In addition, the frequency shifts calculated for the carbon-attached complex are in accordance with the observed ones.

As presented in Table 2, calculations show that complexation with carbon monoxide influences slightly the geometry of the HNCS molecule. The N−H bond shows a small elongation of 0.004 Å, while the N=C bond becomes shorter by 0.004 Å. These changes are in agreement with the observed spectral shifts, namely a red shift of the ν_1 NH mode and a blue shift of the ν_2 CN mode.

A slightly larger blue shift of the ν CO in DNCS complex (16.4 cm^{-1}) than in the HNCS one (15.9 cm^{-1}) is not surprising. A similar small increase of the ν CO frequency was also observed for CO complexes with hydrogen fluoride[18,19] and water[5] after deuteration. An explanation for a slightly higher ν CO frequency in the OC−DNCS complex than in the OC−HNCS one is given by the performed ab initio calculations. The calculated difference in zero point vibrational energies (ΔZPE) between the complex and its subunits is equal to 1.11 and 0.95 kcal/mol for OC···HNCS and OC···DNCS complexes, respectively. Consequently, the binding energy ($E_{\mathrm{bind}} = E_{\mathrm{int}} + \Delta\mathrm{ZPE}$) is responsible for higher stabilization of OC···DNCS than OC···HNCS and for a slightly stronger hydrogen bond in the former complex.

The higher energy CO···HNCS form with the N−H group directed toward the oxygen atom of the CO molecule is not identified in the studied spectra. According to both experimental and theoretical findings,[5,16−19,22] the C≡O stretch is red shifted in this complex. There is no new absorption observed in the studied spectra downward shifted with regard to the CO monomer band, and hence formation of a CO···HNCS complex is ruled out.

The spectra of HNCS/CO/N_2 and DNCS/CO/N_2 matrixes recorded at 11 K showed a relatively complicated set of bands. The bands observed at 3448.4; 3457.0, 2002.3; 2000.2 and 2154.6; and 2152.0 cm^{-1} in the spectra taken after deposition (indicated with arrows in Figures 2 and 3) are attributed to the ν_1 NH, ν_2 CN, and ν CO modes in the 1:1 OC···HNCS complex isolated in two different trapping sites. Such assignment is justified, first by the small separation between the two site bands (2−10 cm^{-1}) which is typical for the multiple trapping site (mts) effect. Second, the annealing of the matrixes causes the reorganization of the intensity within the doublets and leads to the appearance of new components in very close vicinity of the initial absorptions, which is also a characteristic feature of the mts effect. Moreover, in the isotopic experiment the OC···DNCS spectra show a similar set of product bands at 2593.4; 2587.7, 1956.2; 1954.7 and 2155.3; and 2152.7 cm^{-1} exhibiting analogous changes upon annealing.

The origin of two other as yet unassigned bands at 3431.8 and 2012.2 cm^{-1} and their counterparts in the spectra of the deuterated sample at 2576.4 and 1961.0 cm^{-1} is not clear. Their shifts with respect to the corresponding monomer modes are higher than those found for the 1:1 complex. On the basis of this observation the obvious assignment would be $(CO)_n$HNCS or $(CO)_n$DNCS species; especially those absorptions at similar wavenumbers due to higher aggregates are present in the spectra

TABLE 3: Calculated Frequencies and Frequency Shifts (cm^{-1}) and Relative Intensities for CO Complexes with HNCS and DNCS

OC···HNCS			CO···HNCS			OC···HNCS		
ν	I/I_{NH}	$\Delta\nu$	ν	I/I_{NH}	$\Delta\nu$	$\Delta\nu_{exp}$[Ar]	$\Delta\nu_{exp}$[N_2]	assignment
3633	1.000	−90	3717	1.000	−6	−66.4	−49.0	ν_1 NH
2023	0.715	+15	2014	1.277	+6	+8.2	+4.7	ν_2 C=N
876	0.004	−4	879	0.005	−1	+2.6		ν_3 C=S
702	0.477	+48	663	0.745	+9	+53.6		ν_4 NCS
494	0.006	+12	491	0.025	+9			ν_6 NCS
520	0.037	+58	476	0.056	+14			ν_5 NH
2131	0.035	+17	2109	0.057	−5	+15.9	+12.3	ν C≡O
OC···DNCS			CO···DNCS			OC···DNCS		
ν	I/I_{ND}	$\Delta\nu$	ν	I/I_{ND}	$\Delta\nu$	$\Delta\nu_{exp}$[Ar]	$\Delta\nu_{exp}$[N_2]	assignment
2695	1.000	−58	2750	1.000	−3	−41.5	−28.5	ν_1 ND
1978	0.771	+9	1973	1.317	+4	+7.7	+3.1	ν_2 C=N
867	0.008	−6	871	0.006	−2			ν_3 C=S
559	0.251	−6	557	0.319	−8			ν_4 NCS
475	0.001	+7	472	0.004	+4			ν_6 NCS
451	0.088	+59	412	0.239	+20			ν_5 ND
2130	0.046	+16	2108	0.123	−6	+16.4	+13.0	ν C≡O

TABLE 4: Wavenumbers of the ν XH and ν CO Stretching Vibrations (cm^{-1}) and Their Relative Shifts Observed for OC−HX Complexes Isolated in Argon Matrixes

proton donor XH	ν XH in monomer	ν HX in HX···CO	rel shift (%)	ν CO in HX···CO	rel shift[a] (%)	PA(X^-)[b]	ref
H_2O (ν_3)	3734.3	3723.4	0.292	2149.4	0.523		6, 7
HBr	2559.6	2520.1	1.543	2152.4	0.664	1354	18
HNCS	3508.5	3442.1	1.892	2154.2	0.748	1361	this work
HCl	2870.6	2815.2	1.930	2154.3	0.753	1395	18
trans-HONO	3570.5[c]	3498.9	2.005	2161.8	1.104	1423	16
HCOOH	3550.4	3470.2	2.259	2158.7	0.959	1445	20
HF	3919.5	3789.3	3.322	2162.4	1.132	1554	18, 19
HNO_3	3522	3399	3.492	2164	1.207	1358	15
H_2SO_4	3566.7	3371.1	5.484	2167.1	1.352	1282	17

[a] ν CO monomer position in argon matrix is equal to 2138.2 cm^{-1}. [b] Proton affinity PA(X^-) is defined as negative enthalpy of the $X^- + H^+ \rightarrow HX$ reaction, values in kJ/mol. [c] The average of the two site bands is given.

of argon matrixes. However, rather unusual behavior of the bands in question, namely their intensity decrease upon annealing, makes this suggestion doubtful. Since nitrogen forms rather active matrixes, the OC···HNCS complex may not be simply solvated in solid nitrogen but a specific interaction is possible between the complex and one of the N_2 molecules from the matrix cage.[22]

The 3480.2 cm^{-1} absorption is attributed to the nonnearest neighbor interaction on the basis of its small red shift and intensity decrease on annealing.

It is worth noting that the shifts observed for the OC···HNCS complex in nitrogen matrix ($\Delta\nu$ NH = −40.4 and −49.0 cm^{-1} for two sites, respectively) are smaller than those in argon matrix ($\Delta\nu$ NH = −66.4 cm^{-1}). A similar situation occurs for the OC···HCl complex, where the shifts of the ν HCl stretching mode relative to the HCl monomer value are equal to −43.8[31] and −55 cm^{-1} [32] for nitrogen and argon matrixes, respectively. In turn, the opposite situation was reported for OC···Cl_2 and OC···Br_2 complexes.[33]

It is known that the strength of interaction between subunits in the matrix-isolated complex is usually different in different matrixes. For very strong hydrogen-bonded complexes of the amine−HX type, the extent of proton transfer from hydrogen halide to the amine is increased in nitrogen as compared to the complex isolated in rare gas matrixes as demonstrated by a large difference of the spectra of these systems.[34] For weaker hydrogen-bonded and van der Waals complexes in some cases the shifts observed in the spectra of nitrogen matrixes are weaker than those observed for argon matrix; however, in other cases the opposite situation is true.[32] A strengthening of the interaction between polar subunits in argon compared to more active nitrogen may be explained by electrostatic interaction between N_2 and parent molecules;[35] however, the steric hindrance effect may not be neglected.[36]

Comparisons. It is interesting to compare spectral characteristics and energies of the OC···HNCS complex with various carbon monoxide complexes studied earlier. In Table 4 the positions of the ν XH and ν CO stretching modes and their relative shifts with respect to the corresponding monomer values are compared for different OC···HX complexes isolated in solid argon. The proton affinity values of acid anions PA(X^-) are also given. The higher the PA of X^- is, the stronger the interaction for the B···HX complexes with a particular base should be. It is often true for complexes of hydrogen halides with strong bases, but the opposite was found for most weak and medium bases.[32] Complexes of various acids with CO gathered in Table 4, with the exceptions of OC···HNO_3 and OC···H_2SO_4 systems, also follow the latter trend.

A comparison of the calculated energies ΔE^{CP} for N_2–HNCS[24] and OC−HNCS complexes which are equal to −1.64 and −2.84 kcal/mol, respectively, reveals a stronger interaction in the latter system. Stronger interaction is accompanied by the larger changes of the geometric parameters of the two subunits after complex formation. For instance, elongation of the N−H bond upon complex formation is equal to 0.004 Å in OC···HNCS while it is equal to 0.001 Å in HNCS complex with nitrogen. In turn, the C=N distance is shortened by 0.004 and 0.003 Å, respectively, in OC−HNCS and N_2–HNCS complexes.

It is interesting to compare various carbon monoxide complexes studied earlier. The OC···HNCS complex is found to be 1.51 kcal/mol more stable than the CO···HNCS structure. A similar energy difference was reported for the OC···HOOH and CO···HOOH systems (1.50 kcal/mol).[22] In turn, the carbon-attached complex between nitrous acid and carbon monoxide was predicted to be 2.04 kcal/mol more stable than the oxygen-attached complex.[16] The interaction energy calculated for the OC···H_2S complex is 0.89 kcal/mol lower than that predicted for the CO···H_2S structure.[37]

Summary

Complexes between isothiocyanic acid (HNCS, DNCS) and carbon monoxide have been studied with the use of matrix-isolation Fourier Transform infrared technique and ab initio calculations at the MP2/6-311++G(2d,2p) level. Computationally, two stable structures for the 1:1 complex were found with HNCS attached to carbon or oxygen atoms of carbon monoxide. The lower energy form—the carbon-attached OC···HNCS complex—was predicted to be 1.51 kcal/mol more stable than the oxygen-attached CO···HNCS complex. Only the OC···HNCS isomer with isothiocyanic acid bonded to the carbon atom of CO was identified and characterized in both argon and nitrogen matrixes. The studied system was found to be sensitive to the matrix environment. In nitrogen matrixes the complex is trapped in several sites which could be reorganized at higher temperature to form energetically more favorable positions.

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