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# Infrared matrix isolation and theoretical studies of the hydrogen bonded complexes between nitrous acid and 1,1-dichloroethylene

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#### Abstract

The complexes formed between *trans* and *cis* isomers of nitrous acid and 1,1-dichloroethylene (1,1-DCE) in argon matrixes have been identified and characterized by help of FTIR spectroscopy. The experimental spectra evidenced that *trans*- and *cis*-HONO isomers form two types of complexes with different structures.

The optimization and spectral characteristics of the studied systems were carried out at the MP2 level of theory with 6-311++G(2d,2p) basis set. The performed calculations resulted in five stationary points on the PES for both *trans* and *cis*-HONO complexes. Two complexes are stabilized by the O-H··· $\pi$  bond, the other two by the O-H···Cl bond and one complex by the bifurcated, asymmetric Cl···H···Cl interaction. In one of the two complexes stabilized by the O-H···Cl hydrogen bond an additional C-H···O (for *cis*-HONO) or C-H···N (for *trans*-HONO) hydrogen bond also exists. The topological analysis of the distribution of the charge density by help of AIM theory confirmed the asymmetry of the Cl···H···Cl bifurcated hydrogen bond and the double O-H···Cl and C-H···O(N) interaction in one of the five structures. The values of the  $\rho_b$  and  $\nabla^2 \rho_b$  indicate that the Cl···H···Cl bond is more asymmetric in the *cis*-HONO complex than in the *trans*-HONO one. The comparison of the experimental frequencies with the calculated ones for the five structures indicates that the *trans*-HONO complexes trapped in the matrixes correspond to the structures stabilized by the O-H··· $\pi$  bond or by the O-H···Cl bond.

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# 1. Introduction

Unsaturated hydrocarbons and their halogenated derivatives are the major constituents of polluted urban environments. Vinylidene chloride  $(1,1-C_2H_2Cl_2)$  is used industrially for the production of poly(vinyl dichloroethylene) – PVDC and is classified as human carcinogen and hepatotoxicant that exerts acute toxicity. Nitrous acid (HONO) acts in atmosphere as a main source of hydroxyl radicals (OH). The reaction of OH and  $(NO)_x$  radicals with hydrocarbons and organochlorines are of critical importance in the Earth's troposphere. Molecular complexes formed between HONO and  $1,1-C_2H_2Cl_2$  (1,1-DCE) are of interest as they may affect the overall kinetics of photoaddition reaction of OH radicals to relevant species in the atmosphere.

On the other hand, the weak hydrogen-bonded complexes involving  $XH \cdots \pi$  interaction are still the subject of interest of present-day research [1]. They are usually considered to be the initial stage of an electrophilic addition to alkene or alkyne, with an H-X orientation that is perpendicular to the CC multiple bond. Such systems were studied with Fourier transform microwave [2–6] and IR spectroscopy in the gaseous state [7–11] by IR matrix isolation spectroscopy [12–15] cryo-spectroscopy [16–18] or by X-ray scattering in the crystal [19]. Theoretical ab initio calculations have also been reported for these type of complexes [20–23]. In the complexes of ethylene or acetylene with OH proton donors such as water [24–26], nitric acid

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[27] and nitrous acid [28] the presence of the OH  $\cdots \pi$  hydrogen bond has been also evidenced. In spite of huge amount of studies devoted to this subject. less attention has been paid on the halogenated derivatives of unsaturated hydrocarbons and on the influence of the substituent on the overall complex properties. More than twenty years ago, Andrews et al. [29] reported the results of the matrix isolation studies on  $C_2HX$  complexes with HX (where X = Cl, F). The authors concluded that the substitution of acetylene molecule decreases the proton-acceptor ability of CC bond. These observations are in agreement with recent theoretical calculations performed by Li et al. [30] for the complexes of ethylene and its fluorine derivatives with HF. The authors predicted ca. 25% and 50% decrease of the interaction strength for single  $(C_2H_3F)$  and double  $(1,1-C_2H_2F_2)$ substituted ethylene, respectively.

In this paper we present the results of combined theoretical and infrared matrix isolation studies of the complexes formed between nitrous acid and 1,1-dichloroethylene. The bonding interactions in the studied complexes are determined and classified with help of Atoms in Molecules theory.

# 2. Experimental details

#### 2.1. Matrix isolation studies

Crystalline ammonium nitrite,  $NH_4NO_2$ , was employed as a source of gaseous HONO ( $NH_4NO_2 \iff HONO +$  $NH_3$ ) and  $ND_4NO_2$  was used as a source of DONO. HONO/Ar and DONO/Ar mixtures were prepared in the same way as previously described [31]. The liquid 1,1dichloroethylene (1,1-DCE) was obtained from Fluka with specified purity 99.5%. The sample was degassed through 4 freeze-thaw cycles using liquid nitrogen followed by cryogenic distillation.

HONO/Ar or DONO/Ar and 1,1-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>/Ar gas mixtures were codeposited simultaneously through two separate spray-on lines. The gas mixtures were sprayed onto a gold-plated copper mirror held at 11 K by a closed cycle helium refrigerator, Air Products, Displex 202. The approximate HONO/Ar and DONO/Ar ratio was 1/800, whereas the concentration of 1,1-DCE/Ar was varied in the range 1/150 to 1/450. The deposition was monitored by infrared spectrum of the matrix. After the infrared spectra of the initial deposit have been recorded the sample was subjected to the filtered radiation of a 200 W medium pressure mercury arc (Philips CS200W2).

The spectra were registered at  $0.5 \text{ cm}^{-1}$  resolution in reflection mode, with a Bruker 113v FTIR Spectrometer.

#### 2.2. Computational details

The ab initio calculations were carried out using the GAUSSIAN-03 package of computer codes [32]. The structures of the *trans*-HONO, *cis*-HONO and  $1,1-C_2H_2Cl_2$  monomers and their binary complexes were fully optimised

at MP2 level using the split-valence 6-311++G(2d,2p) basis set augmented with diffuse and polarisation functions. Vibrational frequencies and intensities for the monomers and for the binary complexes were also obtained at the MP2 level of theory. All interaction energies were corrected for basis set superposition error (BSSE) by the Boys–Bernardi [33] counterpoise correction scheme.

The topological analysis was performed to calculate the charge density  $(\rho)$  and its second derivative Laplacian of charge density  $(\nabla^2 \rho)$  for bonds using Bader's AIM theory [34].

# 3. Results

# 3.1. Experimental spectra

The spectra of the parent molecules are in agreement with those previously reported [31,35,36]. Infrared spectra of HONO/1,1-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>/Ar show a number of prominent new absorptions as compared to the spectra of HONO and 1,1-DCE monomers isolated in argon matrices.

Fig. 1a presents the spectra of the  $1,1-C_2H_2Cl_2/HONO/$ Ar in the region of the OH stretching vibrations. As one can see, three new strong bands marked as A or B appeared at 3515.4, 3506.2 and  $3494.5 \text{ cm}^{-1}$  in the vicinity of the v(OH) stretching vibration of *trans*-HONO. The relative intensities of these three bands are independent on matrix concentration which suggests that they are due to the 1:1 HONO...1,1-DCE complexes. After matrix annealing the band at  $3515.4 \text{ cm}^{-1}$  (B) slightly decreased with respect to the bands observed at 3506.2 and 3494.5  $\text{cm}^{-1}$  (A), which did not show noticeable changes. When the matrix was irradiated with the medium-pressure Hg lamp using  $\lambda > 320$  nm radiation, the photolysis of the studied complexes was observed. The bands marked as A decreased apparently faster than those labelled as B. The subsequent annealing of the photolysed matrixes led to partial recovering of A bands.

The comparison of the spectra recorded directly after matrix deposition with the spectra recorded after matrix annealing and after matrix photolysis allowed us to identify the B and A bands in other spectral regions. The bands attributed to group A occurred at 3506.2, 3494.5, 1682.0, 1301.0, 1298.5, 818.5 and  $631.5 \text{ cm}^{-1}$  and the B bands were identified at 3515.4, 1679.0, 1274.5, 1272.5, 813.5, 626.5,  $615.0 \text{ cm}^{-1}$ . All above absorptions appeared in the neighbourhood of the trans-HONO fundamentals and were assigned to the perturbed trans-HONO vibrations in the studied complexes. The bands belonging to groups A or B were also identified in the vicinity of cis-HONO fundamentals. The A bands appeared at 3361.0, 1628.5 and  $678.5 \text{ cm}^{-1}$ , while the B absorptions were observed at 3376.5 and 1626.4  $\text{cm}^{-1}$ . All these bands were assigned to the perturbed cis-HONO vibrations in cis-HONO...1,1-DCE complex. Only one absorption was identified for the bonded 1,1-C<sub>2</sub>Cl<sub>2</sub>H<sub>2</sub> molecule. The absorption observed at 843.7  $\text{cm}^{-1}$  that belongs to group A is attributed to the perturbed  $\delta_{op}(CH_2)$  mode of 1,1-dichloroethylene in the



Fig. 1. The v(OH) (a) and v(OD) (b) regions in the spectra of the HONO(DONO)/1,1-DCE/Ar matrices of approximate concentration 1/1/200 (B, C, D): (B) spectra recorded after matrix deposition, (C) spectra recorded after matrix annealing, (D) spectra recorded after 30 min irradiation at  $\lambda > 320$  nm. For comparison the spectra of HONO(DONO)/Ar matrices of 1/800 concentration are given (A).

2640

2620

2600

Wavenumber (cm<sup>-1</sup>)

complex with nitrous acid. The band is tentatively assigned to complex with *trans*-HONO isomer, since the concentration of the *trans* complexes in the studied matrixes is higher than the concentration of the *cis* ones [31].

3560

3600 3580

3540 3520 3500 3480 3460 3440

Wavenumber (cm<sup>-1</sup>)

а

Absorbance Units

Most of the above absorptions have their counterparts in the spectra of  $1,1-C_2H_2Cl_2/DONO/Ar$  matrix. The bands exhibit the same structure pattern and behaviour as A and B bands detected in the spectra of non-deuterated system. Fig. 1b presents the infrared spectra of the 1,1- $C_2H_2Cl_2/DONO/Ar$  matrix in the region of the v(OD)stretching vibration of *trans*-DONO isomer. The band attributed to B group appears at 2598.0 cm<sup>-1</sup>, while the A group bands are observed at 2591.4 and 2582.3 cm<sup>-1</sup>. In other spectral regions the perturbed *trans*-DONO vibrations attributed to A group appeared at 2591.4, 2582.3, 1674.0, 1033.0, 1031.5 and 623.0 cm<sup>-1</sup> and the bands due to B group were observed at 2598.0, 1671.0, 1017.5 and 764.5 cm<sup>-1</sup>, respectively. Only three bands were identified for the perturbed *cis*-DONO vibrations in complexes with 1,1-DCE; they appeared at 2500.0 and 830.0 cm<sup>-1</sup> (B group) and at 2489.0 cm<sup>-1</sup> (A group).

2580

2560

All frequencies identified for the HONO complexes with 1,1-DCE and attributed to groups A and B are collected in Table 1.

Table 1

The frequencies (cm<sup>-1</sup>) observed for trans- and cis-HONO subunits in the complexes with 1,1-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> isolated in solid argon

trans-HONO				cis-HON0	Assignmen			
HONO	C2H2Cl2-HONO	DONO	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> -DONO	HONO	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> -HONO	DONO	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> -DONO	
3572.6	3515.4 B	2635.0	2598.0 B	3412.4	3376.5 B	2524.0	2500.0 B	
3568.5	3506.2 A	2638.1	2591.4 A	3410.7	3361.0 A	2522.6	2489.0 A	vOH
	3494.5 A		2582.3 A					
1689.1	1682.0 A	1682.6	1674.0 A	1634.0	1628.5 A	1622.0	_	vN=O
1688.0	1679.0 B	1681.6	1671.0 B	1632.8	1626.4 B	1621.1		
1265.8	1301.0 A	1013.9	1033.0 A	_	_	_	_	$\delta NOH$
1263.9	1298.5 A	1011.4	1031.5 A					
	1274.5 B		1017.5 B					
	1272.5 B							
800.4	818.5 A	748.9	764.5 B	853.2	_	815.0	830.0 B	vN–O
796.6	813.5 B	744.3		850.4		811.5		
608.7	631.5 A	602.4	623.0 A	_	_	_	_	$\delta ONO$
	626.5 B	601.5						
549.4	615.0 B	-		638.4	678.5 A	-		τOH
1,1-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> -HONO							
8/3.8	843.7 A	_	_	_	_	_	_	$\partial_{op}CH_2$

## 3.2. Ab initio calculations

The calculated geometrical parameters for the *trans*- and *cis*-HONO complexes with 1,1-DCE are reported in Tables 2 and 3. In Tables 4 and 5 the harmonic vibrational frequencies computed for the optimized structures are presented.

Five stationary points that were found for both *trans*and *cis*-HONO complexes with 1,1-dichloroethylene are presented in Figs. 2 and 3. In all structures the OH group of the acid acts as a proton donor toward 1,1-DCE molecule.

Two T-shaped structures that are stabilized by the  $OH \cdots \pi$  interaction differ with the orientation of the HONO plane with respect to the 1,1-DCE plane. The AI structure is characterised by nearly perpendicular orientation of the HONO plane to the 1,1-DCE plane; the  $\Psi$  $(C_1C_2NO_1)$  dihedral angle is equal to 99° and 85° for *trans*and cis-HONO complexes, respectively. In the AII complex the HONO molecule lies in the bisecting plane of the 1,1-DCE leading to a parallel arrangement of the N-O<sub>1</sub> and  $C_1 = C_2$  bonds; the  $\Psi(C_1 C_2 N O_1)$  angle is equal to 0.9° for trans- and 2.1° for cis-HONO complexes, respectively. Both in the AI and AII complexes the OH bond does not point to the centre of the C=C bond making the  $OH \cdots \pi$ interaction asymmetric. The  $H_1 \cdots C_2$  distance is shorter than the  $H_1 \cdots C_1$  one by 0.116 Å, 0.166 Å and by 0.085, 0.165 Å for the AI, AII structures of trans and cis-HONO complexes, respectively. The OH bond direction intersects

the C=C bond at the point deviated by 0.21, 0.30 Å from the centre of C=C toward  $C_2(H_2)$  atom in the AI, AII *trans*-HONO complexes and by 0.16, 0.31 Å in the AI, AII complexes of *cis*-HONO.

In the second type of complexes denoted as B (see Table 2 and Figs. 2 and 3) the OH group interacts with one or two chlorine atoms of the 1,1-dichloroethylene molecule forming  $O-H_1 \cdots Cl_1$  bond in BI, BII complexes and three-centred, bifurcated  $Cl_1 \cdots H_1 \cdots Cl_2$  bond in BIII complex. In BI complexes the acid plane is perpendicular to the 1.1-DCE plane with the  $\Psi(C_1Cl_1H_1O_1)$  dihedral angle of 88° and 89° for trans- and cis-HONO complexes, respectively. The arrangement of trans- and cis-HONO subunits with respect to 1,1-dichloroethylene in BI structure suggests that, apart from the  $OH_1 \cdots Cl_1$  interaction, there is an additional, weak interaction between the C<sub>2</sub>-H<sub>2</sub> group and N or O<sub>2</sub> atoms, which probably contributes to the stabilisation energy of the complex. The  $H_2 \cdots N(\text{or } O_2)$  distances are calculated to amount to 3.03 Å or 3.21 Å for trans- or cis-HONO complexes, respectively. In the BII complexes the nitrous acid is nearly coplanar with 1,1-DCE; the deviation from the coplanarity is equal to 16° for *trans*- and 17° for *cis*-HONO complex. The  $H_1 \cdots Cl_1$ distance in BII trans-HONO complex is slightly longer (by ca. 0.011 Å) and in BII cis-HONO complex is slightly shorter (by ca. 0.022 Å) than in the corresponding BI transand cis-HONO complexes. The third stable structure, BIII, involves three-centered, "bifurcated"  $Cl_1 \cdots H_1 \cdots Cl_2$  interaction. The two interacting molecules are coplanar, the tor-

Table 2

The properties	of the trans-HONC	···1,1-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> complexes	calculated at MP2/6-3	311++G(2d,2p) level
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Property	Monomer	AI	AII	BI	BII	BIII
$r(H_1O_1)$	0.967	0.972	0.972	0.971	0.971	0.969
$r(O_1N)$	1.440	1.425	1.431	1.421	1.431	1.424
$r(NO_2)$	1.178	1.182	1.181	1.184	1.181	1.183
$r(C_1C_2)$	1.330	1.334	1.335	1.329	1.329	1.329
$r(C_1Cl_1)$	1.733	1.729	1.729	1.743	1.743	1.734
$r(C_1Cl_2)$	1.733	1.731	1.729	1.728	1.728	1.737
$r(C_2H_2)$	1.076	1.077	1.077	1.077	1.077	1.076
$R(H_1 \cdots C_1)$	-	2.459	2.490	-	_	_
$R(H_1 \cdots C_2)$	_	2.343	2.324	_	_	_
$R(H_1 \cdots Cl_1)$	_	_	_	2.400	2.411	2.590
$R(H_1 \cdots Cl_2)$	_	_	_	_	_	2.822
$R(H_2 \cdots N)$	-	_	_	3.029	_	_
$\theta(H_1O_1N)$	101.43	101.03	101.20	101.52	101.68	101.59
$\theta(O_1 N O_2)$	110.88	111.20	111.09	111.19	111.06	111.12
$\theta$ (Cl <sub>1</sub> C <sub>1</sub> Cl <sub>2</sub> )	114.72	114.96	115.03	114.49	114.39	114.25
$\Theta(O_1H_1\cdots C_1)$	_	160.54	176.31	_	_	_
$\Theta(O_1H_1\cdots C_2)$	_	156.22	151.61	_	_	_
$\Theta(O_1H_1\cdots Cl_1)$	_	_	_	166.78	159.69	156.08
$\Theta(O_1H_1\cdots Cl_2)$	-	-	_	-	_	138.91
$\Theta(C_2H_2\cdots N)$	_	_	_	105.14	_	_
$\Psi(C_1C_2NO_1)$	-	99.02	0.90	-	_	_
$\Psi(C_1Cl_1H_1O_1)$	_	_	_	88.00	164.00	
$\Psi(C_1Cl_1NO_1)$						0.10
$\Delta E^{\rm CP}$	-	-2.25	-2.22	-2.33	-2.09	-2.14
$\Delta E_{\text{ZPE}}^{\text{CP}}$	_	-1.57	-1.63	-1.63	-1.53	-1.64

<sup>a</sup> Bond lengths in Å, angles in deg, energy in kcal/mol.

Table 3 The properties<sup>a</sup> of the *cis*-HONO···1,1-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> complexes calculated at MP2/6-311++G(2d,2p) level

Property	Monomer	AI	AII	BI	BII	BIII
$r(H_1O_1)$	0.976	0.980	0.981	0.979	0.979	0.980
$r(O_1N)$	1.398	1.392	1.396	1.391	1.397	1.373
$r(NO_2)$	1.193	1.196	1.195	1.196	1.194	1.191
$r(C_1C_2)$	1.330	1.334	1.334	1.328	1.329	1.330
$r(C_1Cl_1)$	1.733	1.729	1.728	1.729	1.729	1.715
$r(C_1Cl_2)$	1.733	1.730	1.729	1.740	1.742	1.720
$r(C_2H_2)$	1.076	1.077	1.077	1.076	1.077	1.078
$R(H_1 \cdots C_1)$	_	2.488	2.546	_	_	_
$R(H_1 \cdots C_2)$	_	2.403	2.381	_	_	_
$R(H_1 \cdots Cl_1)$	_	_	_	2.507	2.485	2.576
$R(H_1 \cdots Cl_2)$	_	_	_	_	_	2.930
$R(H_2 \cdots O_2)$	_	_	_	3.210	_	_
$\theta(H_1O_1N)$	104.67	103.72	105.32	105.31	105.24	105.60
$\theta(O_1 N O_2)$	113.41	113.52	113.46	113.50	113.43	113.52
$\theta$ (Cl <sub>1</sub> C <sub>1</sub> Cl <sub>2</sub> )	114.72	114.97	114.99	114.43	114.44	114.19
$\Theta(O_1H_1\cdots C_1)$	_	177.66	169.71	_	_	_
$\Theta(O_1H_1\cdots C_2)$	_	147.41	158.70	_	_	_
$\Theta(O_1H_1\cdots Cl_1)$	_	_	_	177.71	151.63	179.86
$\Theta(O_1H_1\cdots Cl_2)$	_	_	_	_	_	117.37
$\Theta(C_2H_2\cdots O_2)$	_	119.46	_	149	_	_
$\Psi(C_1C_1NO_1)$	_	85.00	2.10	_	_	_
$\Psi(C_1Cl_1H_1O_1)$	_	_	_	89.00	163.00	_
$\Psi(C_1Cl_1NO_1)$	_	_	_	_	_	3.50
$\Delta E^{\mathrm{CP}}$	_	-1.99	-2.07	-2.11	-1.90	-1.70
$\Delta E_{ m ZPE}^{ m CP}$	_	-1.41	-1.53	-1.54	-1.42	-1.24

<sup>a</sup> Bond lengths in Å, angles in deg, energy in kcal/mol.

Table 4

The frequencies, frequency shifts (cm <sup>-1</sup> ) an	and intensities (km/mol) of trans-HONO complexes	s with 1,1-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> calculated at MP2/6-311++G(2d,2p) level
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AI		AII		BI		BII		BIII		Assignment
v	$\Delta v$									
3691(388)	-98	3687(364)	-102	3711(320)	-78	3714(359)	-75	3744(327)	-35	vOH
1627(142)	-17	1633(145)	-11	1626(101)	-18	1635(107)	-9	1628(124)	-16	vN=O
1331(118)	+42	1329(89)	+40	1329(117)	+40	1321(268)	+32	1303(181)	+14	$\delta$ HON
812(118)	+21	804(168)	+13	823(149)	+32	807(277)	+16	816(150)	+25	vN–O
614(160)	+34	601(155)	+21	624(149)	+44	601(223)	+21	615(161)	+35	$\delta ONO$
672(44)	+91	659(38)	+78	625(82)	+44	658(60)	+77	639(63)	+58	$\tau OH$
3314(2)	-17	3313(2)	-17	3321(2)	0	3318(2)	-3	3321(1)	0	$v_{as}CH_2$
3201(5)	-9	3201(5)	-9	3209(4)	-2	3208(5)	-3	3210(4)	-1	$v_{s}CH_{2}$
1635(55)	-13	1630(45)	-18	1648(65)	0	1648(62)	0	1650(72)	+2	vC=C
1421(2)	-2	1419(1)	-5	1426(0)	+3	1428(0)	+5	1423(0)	0	$\delta CH_2$
1117(87)	+2	1117(95)	+2	1112(92)	-3	1112(107)	+3	1111(68)	+2	rCH <sub>2</sub>
890(59)	+13	869(58)	-8	893(52)	+16	889(44)	+12	886(47)	+9	$\delta_{\rm op} CH_2$
816(177)	+3	818(87)	+5	808(115)	-5	813(30)	0	809(141)	-4	vasCCl <sub>2</sub>
721(1)	+17	729(8)	+25	706(0)	+2	705(0)	+1	705(0)	+1	twist CH <sub>2</sub>
608(14)	0	610(30)	+2	603(4)	-5	604(57)	-3	604(27)	-3	v <sub>s</sub> CCl <sub>2</sub>
485(8)	+14	479(8)	+8	471(5)	0	472(6)	-1	469(5)	-4	$\delta_{\rm op} {\rm CCl}_2$

sional  $\Psi(C_1Cl_1NO_1)$  angle being 0.9° and 3.5° for *trans*and *cis*-HONO complexes, respectively. The  $Cl_1 \cdots H_1$  and  $H_1 \cdots Cl_2$  distances in both *trans*- and *cis*-HONO complexes slightly differ which indicates that the  $Cl_1 \cdots H_1 \cdots Cl_2$  interaction exhibits some asymmetry. In *trans*-HONO complex the difference between  $Cl_1 \cdots H_1$  and  $H_1 \cdots Cl_2$  distances equals to 0.232 Å and in the *cis*-HONO one it equals to 0.354 Å, respectively.

For all optimized structures the calculated lengths of the hydrogen bonds are slightly shorter in *trans*-HONO com-

plexes than in the corresponding structures of *cis*-HONO ones which suggests higher stability of *trans*-HONO complexes as compared with those formed by the *cis*-HONO isomer.

In all calculated structures the geometrical parameters of the two complex subunits are only slightly perturbed by the complex formation. It is interesting to note that the elongation of the  $O_1$ -H<sub>1</sub> bond is very similar (0.002– 0.005 Å) both in AI, AII and BI, BII, BIII complexes. This fact suggests similar strength of interaction in A and B type

Table 5	
The frequencies, frequency shifts $(cm^{-1})$ a	nd intensities (km/mol) of <i>cis</i> -HONO complexes with 1,1-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> calculated at MP2/6-311++G(2d,2p) level

AI		AII		BI		BII		BIII		Assignment
v	$\Delta v$									
3550(243)	-115	3550(247)	-115	3581(184)	-54	3580(190)	-53	3595(207)	-38	vOH
1586(110)	-10	1584(65)	-12	1585(100)	-11	1590(166)	-16	1588(136)	-14	vN=O
1349(13)	+21	1345(22)	+17	1347(10)	+19	1341(22)	+13	1339(16)	+11	$\delta$ HON
889(294)	+21	890(117)	+22	892(302)	+24	870(441)	+2	888(385)	+20	vN–O
634(41)	+14	626(53)	+6	635(39)	+15	625(53)	+5	634(39)	+14	δΟΝΟ
740(61)	+59	754(31)	+73	725(62)	+44	727(64)	+46	719(69)	+38	τOH
3315(2)	-6	3314(2)	-7	3321(1)	0	3320(2)	-1	3321(1)	0	$v_{as}CH_2$
3202(5)	-8	3201(5)	-9	3210(4)	0	3209(5)	-1	3210(4)	0	vsCH2
1634(69)	-14	1635(87)	-13	1651(66)	+3	1648(61)	0	1649(71)	+1	vC=C
1421(1)	$^{-2}$	1420(0)	-3	1423(0)	0	1427(0)	+4	1423(0)	0	$\delta CH_2$
1117(96)	+2	1117(96)	+2	1110(87)	-5	1113(97)	$^{-2}$	1113(91)	-2	rCH <sub>2</sub>
884(105)	+7	860(219)	-17	885(40)	+8	892(40)	+15	884(46)	+7	$\delta_{\rm op} CH_2$
816(56)	+3	818(94)	+5	810(81)	-3	811(107)	$^{-2}$	809(51)	-3	$v_{as}CCl_2$
716(4)	+12	702(12)	$^{-2}$	703(0)	-1	704(6)	0	704(1)	0	twist CH <sub>2</sub>
609(11)	+2	610(8)	+3	604(11)	-3	604(10)	-3	605(15)	-2	vsCCl2
485(7)	+14	480(7)	+9	468(4)	-3	472(6)	0	468(5)	-3	$\delta_{op}CCl_2$



Fig. 2. The optimized structures of the 1,1-dichloroethylene complexes with trans-HONO.

of complexes. The additional interaction in BI complex is reflected in larger perturbation of the N–O<sub>1</sub> distances as compared with the other optimized structures; shortening of the N–O<sub>1</sub> distance by 0.019 Å and 0.007 Å is calculated for *trans*- and *cis*-HONO BI complexes, respectively. As one can see in Tables 2 and 3 the N–O<sub>1</sub> bond length is the most sensitive structural parameter to complex formation in all optimized structures; it is shortened by 0.009–0.019 Å in *trans*-HONO and by 0.001–0.006 Å in *cis*-HONO upon complex formation. The other geometrical parameters of the two complex subunits show negligible perturbations in the complex as compared to their monomers values. Tables 2 and 3 present the MP2 calculated binding energies of the studied complexes including the BSSE and ZPVE corrections. As one can see, all complexes show comparable strength of interaction, which indicates that all may be present in the matrixes. According to MP2 calculated binding energies,  $\Delta E_{ZPE}^{CP}$ , the complexes formed by *trans* isomer of nitrous acid are stronger than their *cis*-HONO counterparts by 0.1–0.16 kcal/mol. Only for BIII structures the difference in stability of *trans*-HONO and *cis*-HONO complexes is larger amounting to 0.40 kcal/ mol, which is probably due to the higher asymmetry of  $Cl_1 \cdots H_1 \cdots Cl_2$  interaction in the *cis*-HONO complex than in the *trans*-HONO one (see Figs. 2 and 3).



Fig. 3. The optimized structures of the 1,1-dichloroethylene complexes with *cis*-HONO.

In Table 6 the topological properties of the electronic charge density at BCPs found for all studied complexes are collected. Positive  $\nabla^2 \rho_b$  and small values of the electron density at the BCP of  $O_1H_1\cdots\pi$ ,  $O_1H_1\cdots Cl$  and  $Cl_1\cdots H_1\cdots Cl_2$  bonds confirm that only closed shell interactions are responsible for the presence and stability of optimized structures. The analysis of BCPs confirms the existence of  $O_1H_1\cdots\pi$  bonds in all A-type complexes,  $O_1H_1\cdots Cl_1$  bonds in BI, BII structures and  $Cl_1\cdots H_1\cdots Cl_2$  interaction in BIII structure. Additionally, the  $C_2H_2\cdots NO_2$  (for *trans*-HONO complex) and the  $C_2-H_2\cdots O_2-N$  (for *cis*-HONO complex) interaction is predicted in BI structures, which agrees well with the results of the geometrical parameters analysis. The additional weak interaction in

Table 6

The values of electron density ( $\rho_{BCP}$ ) and Laplacian ( $\nabla^2 \rho_{BCP}$ ) calculated for the complexes of *trans*- and *cis*-HONO with 1,1-C<sub>2</sub>Cl<sub>2</sub>H<sub>2</sub>

1		, 2 .	
Complexes	Bond type	$ ho_{ m b}/10^{-2}$	$\nabla^2 \rho_{\rm b}/10^{-2}$
trans-HONO			
AI	$O{-}H{\cdots}\pi$	1.4994	3.929
AII	$O{-}H{\cdots}\pi$	1.5052	3.888
BI	$O{-}H{\cdot}{\cdot}{\cdot}Cl_1$	1.5378	4.733
	$C-H \cdot \cdot \cdot N = O_2$	0.3530	1.376
BII	$O{-}H{\cdot}{\cdot}{\cdot}Cl_1$	1.5016	4.705
BIII	$O-H \cdot \cdot \cdot Cl_1$	1.0222	3.436
	$O{-}H{\cdots}Cl_2$	0.6191	2.319
cis-HONO			
AI	$O{-}H{\cdots}\pi$	1.3581	3.5500
AII	$O-H\cdots\pi$	1.3476	3.483
BI	$O-H \cdot \cdot \cdot Cl_1$	1.2252	3.782
	$C-H \cdot \cdot \cdot O_2 = N$	0.5614	2.070
BII	$O-H \cdot \cdot \cdot Cl_1$	1.2909	4.193
BIII	$O{-}H{\cdot}{\cdot}{\cdot}Cl_1$	1.0575	3.466
	$O{-}H{\cdot}{\cdot}{\cdot}Cl_2$	0.4681	1.692

BI complex is probably responsible for slightly larger stability of this structure with respect to the BII and BIII structures (see Tables 2 and 3).

# 4. Discussion

The product bands observed in the spectra of the 1,1-DCE/HONO/Ar and 1,1-DCE/DONO/Ar matrixes, in the vicinity of the *trans*-HONO(DONO) and *cis*-HONO-(DONO) absorptions, are assigned with confidence to the 1:1 *trans*-HONO···1,1-DCE and *cis*-HONO···1,1-DCE complexes, respectively.

The A and B band sets may be due to the multiple trapping site effects or to the presence of complexes of different structures. The most reliable way of distinguishing isomeric splitting from multiple trapping site effects is to vary the matrix. However this test is not definitive as the structures of weak complexes characterized by flat potential surface near the minimum may be matrix dependent [37– 39]. The preliminary experiments that we performed for  $C_2H_2Cl_2\cdots$ HONO in solid nitrogen suggests that this is the case for the complexes that are the subject of our studies. The studies in nitrogen matrixes did not allow us to distinguish site splitting from isomeric splitting. However on the basis of the arguments presented below we assigned the A and B band sets observed in the spectra of 1,1- $C_2H_2Cl_2/HONO/Ar$  matrixes to the complexes of different structures. First, the frequency difference between the A and B components in the v(OH) region is relatively large suggesting that the two bands sets are not due to the site splitting but to isomeric complexes. The difference between the B absorption and the lower component of the A doublet observed in the v(OH) region is equal to  $20.9 \text{ cm}^{-1}$ .

HONO complexes Among the studied so far [28,31,35,40,41] the largest site splitting of the v(OH) absorption was observed for the *trans*-HONO-SO<sub>2</sub> system and was equal to  $8.4 \text{ cm}^{-1}$ . On the other hand the difference between the v(OH) frequencies of the two HON-O···allene isomeric complexes [41] was found to be equal to 19.1 cm<sup>-1</sup>, so, was comparable with the 20.9 cm<sup>-1</sup> value. Second, in the spectra of all cis-HONO complexes studied so far, the OH stretching vibration was observed as a single band only. The appearance, in the spectra of the cis-HONO complexes with 1,1-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>, two OH stretching absorptions with slightly smaller frequency difference  $(15.5 \text{ cm}^{-1})$  than that observed for *trans*-HONO complexes also supports the assignment of the A and B band sets to two isomeric complexes. Moreover, the bands belonging to groups A and B exhibit different shifts with respect to monomer bands in various spectral regions. In the region of the v(N=O) mode the A bands of trans- and cis-HONO exhibit smaller shifts than B bands whereas in all other regions (v(OH),  $\delta(HON)$ , v(N-O) and  $\delta(ONO)$ ) larger shifts are observed for the A bands than for their B counterparts. The A and B bands sets show also different response to UV irradiation [42]. The A bands decrease significantly after 10 min of irradiation, while B absorptions are only slightly affected. Annealing of the photolysed matrices leads to partial recovery of A bands. The photolvsis of matrix with broad band irradiation should not lead to such a different response of the complex of the same structure trapped in two different sites. The site-selective behaviour is usually observed after narrow-band (usually IR) irradiation. On the other hand there are reported numerous examples of different rates of the photolysis or isomerization processes for the isomers or conformers being irradiated with broad band irradiation. All the above facts led us to the conclusion that the A, B band sets are due to complexes of different structures.

As discussed earlier, ab initio calculations predict stability of two T-shaped complexes with  $O_1 - H_1 \cdots \pi$  interaction (AI, AII), two with  $O_1$ - $H_1$ ··· $Cl_1$  bond (BI, BII) and one complex with bifurcated  $Cl_1 \cdots H_1 \cdots Cl_2$  bond (BIII). The calculations show that the perturbation of the OH stretching vibrations complex formation  $(\Delta v(OH) = v_{comp} - v_{mon})$ upon decreases in the order:  $AI \approx AII > BI \approx BII > BIII$ . For trans-HONO complexes the calculated  $\Delta v(OH)$  values are equal to -98,  $-102 \text{ cm}^{-1}$  for the AI, AII structures; to -78, -75 cm<sup>-1</sup> for the BI, BII ones and to -35 cm<sup>-1</sup> for the BIII structure. The comparison of the calculated frequency shifts with those observed for the B and A bands in the OH stretching region of the matrix spectra suggests, that the 3515.4 cm<sup>-1</sup> band (B) of *trans*-HONO complex corresponds to one of the BI, BII complexes and the 3506.2,  $3494.5 \text{ cm}^{-1}$  doublet (A) to one of the AI, AII ones. The two components of A doublet are 76, 64 cm<sup>-1</sup> and the B band is 55 cm<sup>-1</sup> red shifted with respect to the OH stretch of *trans*-HONO monomer [43] in accord with the predicted order of the OH stretch perturbation in A and B complexes. The observed frequency difference between the A doublet components and B band (20 and 9 cm<sup>-1</sup> for the two components) is also in accord with the calculated value (ca. 20 cm<sup>-1</sup>). The computed v(OH) frequency shifts for the A and B types of complexes are overestimated which can be due to neglecting anharmonicity in calculations and/or to relatively strong influence of environment on the HONO···1,1-DCE complex and, particularly, on the polar 1,1-dichloroethylene molecule. The frequency shift predicted for the OH stretching vibration in the BIII structure (35 cm<sup>-1</sup>) is quite smaller than those observed for A and B bands and allows us to exclude the presence of BIII in the matrix; the matrix environment should not favour the formation of this complex.

The A and B bands due to the perturbed OH stretching vibrations of *cis*-HONO complexes show similar shifts pattern as the corresponding bands of *trans*-HONO complexes. The A band exhibits larger shift with respect to the corresponding band of HONO monomer  $(50.6 \text{ cm}^{-1})$  than the B band  $(35.1 \text{ cm}^{-1})$  and the bands are assigned to A and B type of complexes, respectively.

The other perturbed HONO vibrations provide little information on the structures of the complexes present in matrixes; the calculations predict (Tables 4 and 5) small frequency shift of the particular mode in the same direction (toward higher or lower frequencies) for all optimized structures. Some information on the complex structure provides the identified out of plane CH<sub>2</sub> vibration of 1,1-DCE that occurs at 843.7 cm<sup>-1</sup> and is assigned to A complex. The 843.7  $\text{cm}^{-1}$  band is ca. 30  $\text{cm}^{-1}$  shifted toward lower frequencies with respect to the corresponding band of the 1,1-DCE monomer. For all optimized structures, except AII, the calculations predict the shift of the out of plane CH<sub>2</sub> vibration toward higher frequencies upon complex formation and only for AII the low frequency shift is predicted. The observed shift of the out of plane CH<sub>2</sub> bending mode toward low frequencies suggests that the A group of bands is due to AII complex although the presence of the AI structure cannot be excluded. So, the comparison of the calculated and experimental frequencies allows us to conclude that two types of complexes are trapped in the matrixes, one type involves the O–H $\cdots\pi$  bond and has most probably the AII structure and the second type involves O-H···Cl bond and is characterized by BI or BII structure. However the existence of the AI complexes in the studied matrixes cannot be excluded.

The calculations predicted five stable *trans-* and *cis*-HONO complexes with comparable binding energies but we identified in the matrixes only two types of complexes for each isomer. The existence of the other structures in the matrixes cannot be completely excluded. We identified the complexes on the basis of the perturbed HONO vibrations mainly. The calculations show that the HONO vibrations in all five complexes show similar perturbations (the frequencies are shifted in the same direction). So, the absorptions due to different structures may overlap obscuring the presence of the other structures. On the other hand it is known that the weak complexes with comparable stabilization energy and flat Potential Energy Surface near the minimum are very sensitive to external factors. Different matrixes may stabilize different structures of these types of complexes. Ab initio calculations reported here indicate the shallowness of the PES near the minima both for the *trans*- and *cis*-HONO complexes. So, different matrix environments may constrain one or more favourite structures. The preliminary studies of the complexes in solid nitrogen seem to confirm this suggestion.

The comparison of the studied complexes with that formed by ethylene with HONO shows that substitution of H atoms by Cl atoms weakens the  $O-H\cdots\pi$  interaction. As already discussed, the v(OH) vibration in the T-shaped complex between *trans*-HONO and 1,1-DCE is ca. 70 cm<sup>-1</sup> red shifted from the corresponding HONO monomer mode while in the analogous complex with C<sub>2</sub>H<sub>4</sub> the red shift increases up to 137 cm<sup>-1</sup> indicating stronger hydrogen bond in the latter complex [28]. Similar effect was observed by Andrews et al. for the complexes of acetylene and chloroacetylene with HF. The shift of the v(HF) stretching frequency increases by  $18 \text{ cm}^{-1}$  when going from  $HF \cdots C_2 HCl$  complex to  $HF \cdots C_2 H_2$  one [13]. On the other hand, the accumulation of the double bonds strengthens the OH··· $\pi$  interaction. The  $\Delta v$ (OH) of *trans*-HONO in complex with allene is equal to  $-164 \text{ cm}^{-1}$  [41].

Recently Li et al. [30] have studied theoretically the F substituent effect on the  $H \cdots \pi$  bond in T-shaped complexes between HF and  $C_2H_{4-n}F_n$  (n = 0, 1, 2). According to their calculations the interaction energies change in the order -4.18, -3.07 and -2.46 kcal/mol for the C<sub>2</sub>H<sub>4</sub>···HF,  $C_2H_3F_{\cdots}HF$  and  $1,1-C_2H_2F_2\cdots HF$  complexes, respectively. The authors also predicted that in  $1,1-C_2H_2F_2\cdots HF$ complex, the intersection point between HF axis and C=C double bond deviates from the middle point of C=C by about 0.3 Å toward the unsubstituted carbon atom direction, making the interaction asymmetric. This result is in accord with our calculations for the AI, AII complexes between HONO and 1,1-DCE. For AI complexes the deviation is predicted to be equal 0.21 and 0.31 Å, for transand cis-HONO complexes, respectively. The reason of the asymmetry is the p- $\pi$  conjugate effect (p electrons of X atom transfer to carbon-carbon double bond) in the 1,1- $C_2H_2F_2[30]$  or 1,1- $C_2H_2Cl_2$  subunit. The p- $\pi$  conjugation in 1,1-DCE effects the OH  $\cdots \pi$  hydrogen bond parameters in two ways. First,  $\pi$ -electrons cloud is pushed to the C<sub>2</sub> atom and  $OH \cdots \pi$  bond is also shifted in the same direction. Second, the small deviation (5° and 9° for the trans and cis-HONO AI complex, respectively) of HONO and 1,1-DCE planes from the perpendicular mutual orientation can be considered as effect of the small deviation of the two lobes of  $\pi$  electron cloud from the molecular vertical plane passing through C=C bond.

As discussed above, the theoretical data, particularly the analysis of geometrical parameters, indicate that BI complex is stabilized by relatively strong  $OH \cdots CI$  interaction and very weak  $C-H \cdots O(N)$  interaction, while for AI, AII and BII structures only one type of interaction is predicted  $(OH \cdots \pi \text{ or } OH \cdots CI, \text{ respectively})$ . The AIM analysis of

the studied complexes confirmed the additional interaction in BI complex (see Table 6). The calculations demonstrate that the Bond Critical Point appeared between H<sub>2</sub> atom and acceptor atom (O<sub>2</sub> or N). The charge density and the Laplacian at the BCPs are equal to 0.0059 au and 0.0192 au, respectively, for *trans*-HONO complex and 0.0056 au or 0.02070 au, respectively, for *cis*-HONO structure. Both values are in the range required for hydrogen bond (0.002–0.04 au for  $\rho_b$  and 0.15–0.02 au for  $\nabla^2 \rho_b$ ) [44].

The application of Atoms in Molecule theory confirmed the unequivalency of Cl atoms in  $Cl_1 \cdots H_1 \cdots Cl_2$  bridge predicted for BIII complex. As discussed earlier, the analvsis of the geometrical parameters indicated shorter distance between  $H_1$  and  $Cl_1$  atoms than between  $H_1$  and Cl<sub>2</sub>. The corresponding values are equal to 2.590, 2.822 Å for trans-HONO complex and 2.576, 2.930 Å for cis-HONO system. These parameters correlate well with the  $\rho_{\rm b}$  and  $\nabla^2 \rho_{\rm b}$  values. The charge density calculated for the shorter  $(H_1 \cdots Cl_1)$  and longer  $(H_1 \cdots Cl_2)$  bond path amounts to 0.0102 and 0.0062 au, respectively for trans-HONO complex. Analogically, the Laplacians at the discussed BCPs are equal to 0.0344 au (for  $H_1 \cdots Cl_1$ ) and 0.0232 au (for  $H_1 \cdots Cl_2$ ). In turn, for *cis*-HONO BIII complex the  $\rho_b$  value is predicted to be 0.0106 au for  $H_1 \cdots Cl_1$ and 0.0047 au for  $H_1 \cdots Cl_2$  while the  $\nabla^2 \rho_b$  values amount to 0.0347 au and 0.0169 au for  $H_1 \cdots Cl_1$  and  $H_1 \cdots Cl_2$ bonds, respectively. The comparison of  $\rho_{\rm b}$  and  $\nabla^2 \rho_{\rm b}$  calculated for discussed BCPs in trans- and cis-HONO complexes confirmed larger asymmetry of  $Cl_1 \cdots H_1 \cdots Cl_2$  in cis-HONO complex than in trans-HONO one.

# 5. Conclusions

The ab initio calculations, performed at MP2 level, indicate that both trans- and cis-HONO isomers form with 1,1-dichloroethylene three types of hydrogen bonded complexes; one involving  $OH \cdots \pi$  bond, the second one being stabilized by OH...Cl interaction and the third type of complexes with three centred, bifurcated  $Cl \cdots H \cdots Cl$  bond. For the complexes with  $OH \cdots \pi$  interaction two stationary points are predicted, which are characterised by perpendicular (AI) or parallel (AII) orientation of HONO plane with respect to the 1,1-DCE plane. For  $O-H \cdots Cl$  complexes two stationary points were found that correspond to the planar (BI) or non-planar (BII) geometry. The binding energies corrected for BSSE and ZPVE have similar values for all complexes and vary in the range 1.53–1.64 kcal/mol for trans-HONO complexes and 1.24-1.54 kcal/mol for cis-HONO ones. The geometrical parameters analysis suggests that in BI structure an additional interaction exists between the C-H bond of 1,1-DCE and the N or O atoms (in *trans*- and *cis*-HONO complexes, respectively) of the acid molecule which additionally stabilizes this complex. The topological analysis of the charge density performed by help of the AIM theory confirms this suggestion and shows that the C–H···O, C–H···N interactions in the BI complexes are of hydrogen bond nature.

The FTIR matrix isolation studies indicate that two types of complexes are stabilized in the matrixes: the complex involving  $OH \cdots \pi$  interaction (most probably A1) structure) and the complex stabilized by OH···Cl bond (BII or BIII structure). The perturbations of the HON group vibrations in the HONO complexes with 1,1-DCE molecule indicate that the trans-HONO isomer forms slightly stronger complexes than the cis-HONO one. The ab initio calculations predict ca. 0.1 kcal/mol lower binding energy for trans-HONO complexes than for cis-HONO ones; the exception is the BIII complex, for which the calculated difference in binding energies between trans- and cis-HONO complexes amounts to 0.4 kcal/mol. This results probably from the higher asymmetry of  $Cl \cdots H \cdots Cl$ interaction in cis-HONO complex as compared with the complex formed by trans-HONO. According to the topological analysis of the charge densities and the Laplacians, in cis-HONO complex BIII the interaction of OH group with one Cl atom is twice as strong as with the other Cl atom whereas in the corresponding *trans*-HONO structure the discrepancy between these values does not exceed 40%.

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