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# Photolysis of the $C_2H_4$ -HONO complex in low temperature matrices: formation of 2-nitrosoethanol

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Dedicated to Professor Achim Müller on the occasion of his 65th birthday

#### Abstract

Photochemistry of  $C_2H_4$ ...HONO complexes in argon matrices has been investigated using  $\lambda > 340$  nm radiation of a medium pressure mercury arc. IR spectra were recorded after various periods of photolysis. The photolysis reaction was found to lead to formation of 2-nitrosoethanol that was identified for the first time. Three groups of bands showing different behavior during photolysis process and after matrix annealing were assigned to three different conformers of 2-nitrosoethanol molecule. The experimental data are supported by ab initio calculations.

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#### 1. Introduction

Hydrocarbons, nitrogen oxides (NO<sub>2</sub>, NO<sub>3</sub>), nitric and nitrous acids are the major constituents of polluted urban environments. The reactions of the hydroxyl and (NO)<sub>x</sub> radicals with hydrocarbons are of critical importance in the Earth's troposphere. Consequently, there has been a huge amount of research carried out on the kinetics and mechanisms of the reactions of OH and (NO)<sub>x</sub> with a wide range of organic compunds [1]. In particular a large number of work has been devoted to the study of kinetics and mechanisms of the reactions of OH radical with hydrocarbons [2].

Matrix isolation technique is very useful method in obtaining direct spectroscopic information on the reaction intermediates. The technique was recently employed [3,4] to characterize the infrared absorption spectrum of the 2-hydroxyethyl radical, HOCH<sub>2</sub>CH<sub>2</sub> which is an intermediate product in OH + ethene reaction.

We have studied recently the complexes between ethene and nitrous acid isolated in an argon matrix [5]. It is well known that HONO photodissociates into OH and NO radicals [6]. One may expect that the photolysis of the  $C_2H_4\cdots$ HONO complex will lead to formation of the OH and NO radicals in the presence of the  $C_2H_4$  molecule. The trapping of these species in one matrix cage should favour the formation

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#### 3. Results

of the product(s) of addition of the OH and/or NO radicals to the ethene molecule. The similar studies of the photochemistry of the OC···HONO complexes have shown that both HOCO radical and HOC(O)NO molecule are the photoproducts of this reaction [7].

Herewith we report the results of the study of the photochemistry of  $C_2H_4$ ...HONO complex in argon matrices. The infrared matrix isolation studies are supported by ab initio calculation of the structure and vibrational frequencies of the formed photoproducts.

#### 2. Experimental

Two different deposition setups were used to obtain HONO/ $C_2H_4$ /Ar matrices; their detailed description is given in our earlier report [7].

The C<sub>2</sub>H<sub>4</sub>/Ar mixtures were prepared by standard manometric techniques and their concentrations varied in the range 1/800-1/100. The overall HONO/C<sub>2</sub>H<sub>4</sub>/Ar concentrations of the studied matrices were estimated to be: 1/n/800(n = 1, 2, 4), 1/1/400 and 1/1/300.

The gas mixtures were sprayed onto a goldplated copper mirror held at 20 K by a closed helium refrigerator (Air Products, Displex 202A). Infrared spectra were recorded of the matrices maintained at ca. 12 K. 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 (Philipps CS200W2). A 5 cm water filter served to reduce the amount of infrared radiation reaching the matrix and glass long wavelength pass filter (Zeiss WG 345) was applied to cut off the radiation with  $\lambda < 340$  nm.

The spectra were recorded at  $0.5 \text{ cm}^{-1}$  resolution in a reflection mode, with a Bruker 113v FTIR spectrometer equipped with a liquid N<sub>2</sub> cooled MCT detector.

 $NH_4NO_2$  was prepared from  $(NH_4)_2SO_4$  and  $KNO_2$  according to Ref. [8]. A source of DONO was  $ND_4NO_2$  which was synthesised from  $(ND_4)_2SO_4$  and  $KNO_2$ .  $(ND_4)_2SO_4$  was obtained by multiple dissolution and crystallisation of ammonium sulphate from  $D_2O$ .  $C_2H_4$  (99.5%, Aldrich Chemical Co.) and  $C_2D_4$  (99% Aldrich Chemical Co.) were used as supplied by the companies.

3.1.1. Photolysis and annealing of HONO/Ar matrices

3.1. Infrared matrix isolation studies

Before we studied photochemistry of HONO/ C<sub>2</sub>H<sub>4</sub>/Ar matrices a set of experiments had been performed with HONO/Ar matrices of concentrations varying in the range 1/800 - 1/300. The matrices were photolyzed with  $\lambda > 340 \text{ nm}$  radiation at 12 K. Similarly as in HONO/N<sub>2</sub> matrices, [7,9] also in the photolyzed HONO/Ar matrices, the OH and NO radicals were detected as the primary photolysis products. The bands, assigned to the perturbed OH radical and its complex with water, were observed at 3532.3 and 3498.5  $cm^{-1}$ , respectively. The bands due to NO and its complex with HONO were identified at 1871.5, and at 1882.5, 1880.8  $\text{cm}^{-1}$ , respectively. The observed frequencies are in accord with literature data for those two radicals [10-16]. In addition to the absorptions due to the OH and NO radicals, the bands due to trans-HONO and cis-HONO molecules trapped in unstable sites were also observed after matrix photolysis (at 3564.5, 1686.7, 1259.6, 788.7 cm<sup>-1</sup> for trans-HONO and at 843.6,  $631.8 \text{ cm}^{-1}$  for cis-HONO). The HONO molecule in unstable site is most probably formed in recombination reaction of OH and NO radicals, and is a secondary reaction product. The other secondary reaction products of HONO photolysis in an argon matrix involve H<sub>2</sub>O,  $HO_2$ ,  $NO_2$ , and  $N_2O_3$  [9] molecules. All products were identified by comparison of the studied spectra with literature data reported for H<sub>2</sub>O, [17,18] HO<sub>2</sub> [19] NO<sub>2</sub> [20,21] and N<sub>2</sub>O<sub>3</sub> [22-24].

## 3.1.2. Photolysis and annealing of $HONO/C_2H_4/Ar$ matrices

Experiments were performed for HONO/C<sub>2</sub>H<sub>4</sub>/Ar matrices of concentration varying in the range 1/1/800-1/4/800 and, in addition, for matrices of concentration 1/1/400 and 1/1/300. Three experiments were also performed for each of the isotopically substituted systems: HONO/C<sub>2</sub>D<sub>4</sub>/Ar and DONO/C<sub>2</sub>H<sub>4</sub>/Ar. The matrices were photolyzed with  $\lambda >$  340 nm at 12 K. The spectra were registered after 10, 20, 30, 60 and 90 min. of matrix irradiation. After the irradiation process was completed the samples were annealed to 30 K for 10 min, recooled to 12 K and





Fig. 1. The  $\nu$ (OH) stretching region in the spectra of the matrices HONO/C<sub>2</sub>H<sub>4</sub>/Ar  $\approx$  1/1/400: (a) the spectrum recorded directly after matrix deposition; (b) after 30 min. photolysis at  $\lambda$  > 340 nm and (c) after matrix annealing to 30 K and recooling to 12 K.

the spectra of the annealed matrices were recorded. The spectra of the studied matrices are presented in Figs. 1-4.

In the spectra recorded directly after matrix deposition the absorptions due to *trans*- and *cis*-HONO isomers, to  $C_2H_4$  monomers and dimers and to  $C_2H_4\cdots$ HONO-*trans* and  $C_2H_4\cdots$ HONO-*cis* complexes were identified on the basis of literature data and our earlier studies [5]. During photolysis the bands due to ethene complexes with nitrous acid have been diminishing rapidly, and simultaneously a set of new bands have been growing in the spectra of irradiated matrices.

The performed experiments allowed us to characterize three band sets ( $I^A$ ,  $I^B$  and II) that appear after irradiation of HONO/C<sub>2</sub>H<sub>4</sub> matrices, in the presence of C<sub>2</sub>H<sub>4</sub> only, and which respond in different ways to photolysis and annealing processes. The bands due to groups  $I^A$  and  $I^B$  appeared in the spectra with reasonable intensities after 10 min. of matrix irradiation whereas the bands due to group II were detectable only after 20 min of irradiation.



Fig. 2. The  $\nu$ (OD) region in the spectra of matrices DONO/C<sub>2</sub>H<sub>4</sub>/-Ar  $\approx 1/1/400$ : (a) the spectrum recorded directly after matrix deposition, (b) after 30 min. photolysis at  $\lambda > 340$  nm and (c) after matrix annealing.

The intensities of the bands due to group I<sup>A</sup> increased whereas the intensities of the bands due to group  $I^{B}$ decreased considerably after matrix annealing. The bands of group II were less sensitive to annealing; their intensities slightly decreased during annealing process. Figs. 1-4 present different response of the bands belonging to groups I<sup>A</sup>, I<sup>B</sup> and II on matrix annealing. The bands due to groups  $I^A$  and  $I^B$  were observed at 3639.6, 3648.0, 1561.9, 1225.6, 1040.0,  $770.0 \text{ cm}^{-1}$  and at 3657.0, 1555.4, 1048.5 cm<sup>-1</sup>, respectively, in the spectra of HONO/C2H4/Ar matrices. Their counterparts appeared at 3640.3, 3648.6, 1552.8, 1120.6, 1118.8, 1056.7, 887.9, 769.8 cm<sup>-1</sup> (I<sup>A</sup>) and at 3657.2, 1554.2, 1151.3,  $1020.2 \text{ cm}^{-1}$  (I<sup>B</sup>) in the spectra of HONO/C<sub>2</sub>D<sub>4</sub>/Ar matrices and at 2685.2, 2686.4, 1557.2, 876.8 cm<sup>-1</sup> (I<sup>A</sup>); 2703.7, 2698.5, 1555.5 and 1057.4, 905.8 cm<sup>-1</sup>  $(I^{B})$  in the spectra of DONO/C<sub>2</sub>H<sub>4</sub>/Ar matrices. The frequencies of the bands due to groups  $I^A$ ,  $I^B$  and II are collected in Table 1.

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Fig. 3. (a, b, c) The N=O stretching region in the spectra of the same matrices as presented in Fig. 1a-c. (d) The N=O stretching region in the spectrum of the same matrix as presented in Fig. 2b.

#### 3.2. Computational details and results

The full conformational search was undertaken by DFT calculations using Gaussian 98 package of computers code [25] employing the Becke, Lee, Yang and Paar density functionals (B3LYP). The structures of all conformers of 2-nitrosoethanol were fully optimized using the 6-311++G(2d,2p) basis set [26,27].

The calculations predicted eight stationary points on the potential energy surface. The conformers are identified by a scheme based upon Newman projection and described by the values of the three torsion angles,  $O_1C_1C_2N$ ,  $H_1O_1C_1C_2$  and  $O_2NC_2C_1$ , each of them denoted as *sp* (synperiplanar), *ap* (antiperiplanar), *sc* (synclinal) or *ac* (anticlinal). Table 2 lists the predicted geometrical parameters and energies of all stable conformers of 2-nitrosoethanol molecule. In Fig. 5 all stable conformers and the adopted atom numbering system are presented.

Four conformers that show the synclinal relations of the CN and CO bonds (see S1-S4 conformers in Fig. 5) are more stable than the four anticlinal



Fig. 4. The C–O stretching region in the spectra of the same matrices as presented in Fig. 3.

conformers (A1-A4). The lowest energy conformer corresponds to the S1 structure in which three torsion angles, O1C1C2N, H1O1C1C2 and O2NC2C1, are -69.86, 72.69 and  $4.2^{\circ}$  corresponding to -sc, +sc, sp arrangement. This geometry favors the formation of the hydrogen bond between the OH group and the oxygen atom of the N=O group which stabilizes the S1 conformer. The distance between H<sub>1</sub> and O<sub>2</sub> atoms is equal to 2.36 Å. The synclinal conformer, S2, is computed to be 0.44 kcal/mol less stable than the S1 one. In the S2 conformer a weak hydrogen bond is formed between the OH group and the nitrogen atom of the N=O group. The calculated distance between hydrogen atom of OH group and nitrogen atom is equal to 2.60 Å. The S3 and S4 conformers are not stabilized by the hydrogen bond and are 0.69 and 1.33 kcal/mol less stable than the S1 conformer.

The A1–A4 conformers showing antiperiplanar arrangement of the CO and CN bonds are circa 2 kcal/mol less stable than the S1 conformer. Absence of intramolecular hydrogen bond partially accounts for the higher energy of these forms. The main

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Table 1 The observed frequencies (cm<sup>-1</sup>) of the three conformers (A1, A2, S1) of 2-nitrosoethanol molecule

HONO/C <sub>2</sub> H <sub>4</sub>		DONO/C <sub>2</sub> H <sub>4</sub>		HONO/C2D4	Approximate description <sup>a</sup>
Exp.	Calc.	Exp.	Calc.	Exp.	
A1					
3639.6	3847	2685.2	2801	3640.3	<i>ν</i> (OH), <i>ν</i> (OD)
3648.0		2686.4		3648.6	
1561.9	1640	1557.2	1640	1552.8	$\nu$ (N=O)
1225.6	1249		864	1120.6	$\delta(COH), \delta(COD)$
				1118.8	
1040.0	1050		1051	1056.7	$\nu$ (C-O) + $\gamma_{\Gamma}$ (CH <sub>2</sub> ), $\nu$ (C-O)
	892	876.8	901	887.9	$\nu(CN) + \delta(CNO)$
770.0				769.8	
A2					
3657.0	3836	2703.7	2791	3657.2	<i>ν</i> (OH), <i>ν</i> (OD)
		2698.5			
1555.4	1634	1555.5	1634	1554.2	$\nu(N = O)$
		905.8	878	1151.3	$\delta(COH), \delta(COD)$
1048.5	1049	1057.4	1050	1020.2	$\nu$ (C-O) + $\gamma$ $\Gamma$ (CH <sub>2</sub> ), $\nu$ (C-O)
S1					
3580.6	3580	2654.6	2787	3581.6	$\nu(OH), \nu(OD)$
		2643.1			
1549.0	1633	1549.0	1633	1544.3	$\nu(N = O)$
1383.6	1427	1376.1	1424		$\delta(CH_2), \delta(CD_2)$
1187.1	1237	898.4(?)	844	1091.2	$\delta(\text{COH}) + \gamma_{w}(\text{CH}_{2})/\gamma(\text{CD}_{2})$
					δ(COD)
1019.6	1074		1049		$\nu(C-O)$
1017.3					

The groups of bands corresponding to the three conformers A1, A2 and S1 are denoted in text as I<sup>A</sup>, I<sup>B</sup> and II, respectively.

<sup>a</sup> The abbreviations used for description of CH<sub>2</sub> group vibrations were adopted from reference 5.

difference between the A1 and A2 conformers is the value of the  $H_1O_1C_1C_2$  torsion angle which is equal to ca. 176 and 72°, respectively, for the A1 and A2 conformers. The two conformers are characterized by very close energy values; the A1 conformer is only ca. 0.02 kcal/mol less stable than the A2 one. The difference in energy values between these two conformers grows up to 0.18 kcal/mol when zero point vibrational energy correction is taken into account.

The harmonic vibrational frequencies computed at the B3LYP levels of theory for the S1, A1 and A2 conformers of the CH<sub>2</sub>OHCH<sub>2</sub>NO and CH<sub>2</sub>ODCH<sub>2</sub>. NO molecules are presented in Table 3. The calculated IR spectra confirm the formation of intramolecular hydrogen bond in S1 and S2 conformers. The  $\nu$ (OH) stretching frequency calculated for S1 has slightly lower value than those calculated for A1, A2 conformers. However this is the frequency of the  $\tau$ (OH) vibration which is the most sensitive one to hydrogen bond formation; the calculated  $\tau$ (OH) frequency of S1 conformer is ca. 200 cm<sup>-1</sup> larger than those calculated for A1 and A2 conformers.

#### 4. Discussion

#### 4.1. Identification of the photoproduct— 2-nitrosoethanol

The most prominent bands for all three photoproducts (I<sup>A</sup>, I<sup>B</sup> and II) were identified in three spectral regions, namely in the regions of the OH and N=O stretching vibrations and in the 1250–750 cm<sup>-1</sup> spectral region in which the bands due to COH bending + C–O stretching + CH<sub>2</sub> wagging, rocking and torsion vibrations appear. In the spectra of HONO/C<sub>2</sub>H<sub>4</sub>/Ar matrices the bands due to OH

Table 2 The calculated p	roperties of the 2-ni	itrosoethanol conforme	ers					
	$\begin{array}{l} \text{S1} \\ (-\text{sc},+\text{sc},\text{sp}) \end{array}$	$\begin{array}{l} \text{S2} \\ (-\text{sc},+\text{sc},-\text{ac}) \end{array}$	$\begin{array}{l} \text{S3} \\ (+\text{sc},-\text{sc},-\text{ac}) \end{array}$	S4 (+sc, + sc, - ac)	A1 (ap, ap, + ac)	A2 (ap, + sc, + ac)	A3 (ap, + sc, - ac)	A4 (ap, $+$ sc, sp)
r (0 <sub>1</sub> H <sub>1</sub> )	0.9620	0.9624	0.9613	0.9614	0.9606	0.9611	0.9611	0.9608
r (NO <sub>2</sub> )	1.2205	1.2028	1.2034	1.2019	1.2030	1.2040	1.2036	1.2052
$r(C_1O_1)$	1.4209	1.4179	1.4199	1.4186	1.4246	1.4199	1.4202	1.4267
r (C <sub>2</sub> N)	1.4904	1.4835	1.4833	1.4858	1.4844	1.4824	1.4840	1.4862
r (C <sub>1</sub> C <sub>2</sub> )	1.5174	1.5282	1.5279	1.5280	1.5225	1.5357	1.5355	1.5221
$\theta$ (H <sub>1</sub> O <sub>1</sub> C <sub>1</sub> )	107.56	108.49	109.47	109.45	109.01	109.32	109.34	109.32
$\theta$ (O <sub>2</sub> NC <sub>2</sub> )	114.54	114.67	114.50	114.20	114.16	114.21	114.14	114.48
$\varpi(O_1C_1C_2N)$	-69.86	-65.81	72.35	68.12	168.26	169.23	-173.71	175.82
$w(H_1O_1C_1C_2)$	72.69	61.68	-74.43	64.79	175.98	71.85	74.23	74.41
$\varpi(O_2NC_2C_1)$	4.2	-138.52	-128.53	-121.86	131.44	118.16	-120.12	-0.86
E (hartree)	-284.4249965	-284.4242811	-284.4238971	-284.4228618	-284.4218233	-284.4217871	-284.4213440	-284.4210629

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2.47

2.29

2.01

1.99

1.33

0.69

0.4

 $\Delta E^{a}$  (kcal/mol)

Energies relative to the most stable form.

Bond length in Å, angles in deg

stretches of the three photoproducts appeared at  $3639.6 \text{ cm}^{-1}$  (I<sup>A</sup>),  $3657.0 \text{ cm}^{-1}$  (I<sup>B</sup>) cm<sup>-1</sup> and at 3580.6 (II)  $\text{cm}^{-1}$ . There is one additional band in this region at  $3648.0 \text{ cm}^{-1}$ , whose origin is less clear. Due to the fact that the band appears immediately after photolysis and is placed very close to the 3639.6  $\text{cm}^{-1}$ I<sup>A</sup> band it is also assigned to the photoproduct I<sup>A</sup> although it shows slightly different behavior after matrix annealing (smaller increase of intensity) than the 3639.6  $\text{cm}^{-1}$  band. No counterparts of this band were found in other spectral regions. The deuterium counterparts of the 3639.6, 3657.0 and 3580.6  $cm^{-1}$ bands are observed, respectively, at 2685.2 cm<sup>-1</sup> (I<sup>A</sup>), 2703.7, 2698.5 cm<sup>-1</sup> (I<sup>B</sup>) and at 2643.1 cm<sup>-1</sup> (II) in the spectra of DONO/C2H4/Ar matrices which proves their assignment to the OH, OD stretching vibrations.

The second prominent band of each of the three photoproducts appears in the N=O stretching region. The bands were identified at 1561.9, 1555.4 and at 1549.0 cm<sup>-1</sup>, respectively, for the I<sup>A</sup>, I<sup>B</sup> and II products in the spectra of HONO/C<sub>2</sub>H<sub>4</sub>/Ar matrices. The characteristic feature of the 1549.0 cm<sup>-1</sup> band (II) is its broadness. The three bands show little sensitivity to deuterium substitution of both nitrous acid and ethene molecule (Table 1) which suggests their assignment to the N=O stretching vibration. In the spectra of *trans-* and *cis-*nitrosomethanol molecule isolated in argon the N=O stretching vibration was identified at 1555, 1559 cm<sup>-1</sup>, respectively, and in the spectra of 1-nitrosoethanol in solid argon the N=O stretch was observed at 1552 cm<sup>-1</sup> [28,29].

The other characteristic bands of the three photoproducts appeared in the spectral region 1250–  $1000 \text{ cm}^{-1}$ . In the spectra of HONO/C<sub>2</sub>H<sub>4</sub>/Ar matrices the bands due to I<sup>A</sup> product appeared at 1225.6, 1040.1 cm<sup>-1</sup> and in addition one band was observed at 770.0 cm<sup>-1</sup>. Only one band due to I<sup>B</sup> product was identified in this region at 1048.5 cm<sup>-1</sup> and the bands due to the product II were observed at 1187.1, 1019.6, 1017.3 cm<sup>-1</sup>. As one can see in Table 1 the frequencies of the bands appearing in this region are sensitive to deuterium substitution of both C<sub>2</sub>H<sub>4</sub> and HONO molecules.

The fact that all three photoproducts  $I^A$ ,  $I^B$ , II exhibit prominent bands due to the OH and N=O stretching vibrations suggests that the main secondary product of the photolysis of  $C_2H_4\cdots$ HONO complex is 2-nitrosoethanol which is formed in double addition



Fig. 5. The optimized structures of the eight stable conformers of 2-nitrosoethanol molecule.

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 Table 3

 The calculated frequencies and intensities of the experimentally observed conformers of 2-nitrosoethanol

S1		A1		A2		Approximate description <sup>a</sup>
Freq (cm <sup>-1</sup> )	I [km/mol]	Freq (cm <sup>-1</sup> )	I [km/mol]	Freq (cm <sup>-1</sup> )	I (km/mol)	
3829	42	3847	40	3836	38	<i>ν</i> (OH)
3091	16	3150	16	3113	21	$\nu_{\rm as}  ({\rm CH}_2)^1$
3063	8	3044	24	3092	2	$\nu_{as} (CH_2)^2$
3031	7	3029	10	3031	23	$\nu_{\rm s} (\rm CH_2)^2$
3025	33	3008	38	3024	21	$\nu_{\rm s} \left( {\rm CH}_2 \right)^1$
1633	71	1640	96	1634	96	$\nu(NO)$
1494	4	1530	2	1516	2	$\delta (CH_2)^1$
1427	38	1463	8	1468	6	$\delta (CH_2)^2$
1414	25	1451	7	1407	49	$\gamma_{\rm w} ({\rm CH}_2)^1$
1390	5	1322	9	1388	4	$\gamma_{\rm t} ({\rm CH}_2)^1$
1347	15	1292	24	1315	10	$\gamma_{\rm w} (\rm CH_2)^2$
1237	41	1249	46	1259	21	$\delta$ (COH)
1183	4	1190	3	1185	11	$\gamma_{\rm t} (\rm CH_2)^2$
1074	86	1050	94	1049	167	$\nu(CO)$
1026	3	1129	7	1094	4	$\gamma_r (CH_2)^1$
940	19	992	21	984	4	$\delta(NCC)$
870	20	579	14	586	6	$\delta(ONC)$
775	13	892	15	879	37	$\nu(CN)$
658	1	816	2	817	7	$\gamma_r (CH_2)^2$
426	119	227	118	273	42	τ (OH)
407	4	413	6	407	1	$\delta(OCC)$

<sup>a</sup> Upper index 1 or 2 indicates that the coordinate of the  $(CH_2)^1$ ,  $(CH_2)^2$  groups of the C1 or C2 atoms (Fig. 5) give the main contribution to the vibration. The abbreviations used for the description of CH<sub>2</sub> group vibrations were adopted from reference 35.

reaction of the OH and NO radicals to C2H4 molecule. The presence of the bands characteristic of the three photoproducts in the COH bending and C-O stretching regions is in accord with this conclusion. The 2nitrosoethanol molecule has not been identified so far and its spectra are not known. However there is report on the infrared spectra of the cis-nitrosoethanol in solid argon (the most stable conformer of nitrosoethanol) which is formed in light induced rearrangement reaction of the nitrosooxyethane [28]. The comparison of the spectra of the three photoproducts  $I^A$ ,  $I^B$  and II with the spectra of *cis*-nitrosoethanol excludes the latter molecule as a possible product of the photolysis of the  $C_2H_4$ ···HONO complex. So, we identify the three photoproducts,  $I^A$ ,  $I^B$  and II as the three conformers of the 2-nitrosoethanol molecule. The assignment is confirmed by ab initio calculations of the geometry and vibrational frequencies of all stable isomers of the 2-nitrosoethanol molecule as will be discussed below.

## 4.2. Assignment of the observed bands in terms of 2-nitrosoethanol conformers

As discussed earlier the calculations predicted eight stable conformers of 2-nitrosoethanol molecule. The most stable one is the synclinal conformer S1 with intramolecular hydrogen bond between OH group and oxygen atom of the NO group. The next one with respect to stability is synclinal conformer S2 (with intramolecular hydrogen bond between OH group and nitrogen atom) which is calculated to be 0.44 kcal/mol less stable than the S1 conformer. The most stable antiperiplanar conformer A1 is calculated to be 1.99 kcal/mol less stable than the S1 conformer but there is very small energy difference in the stability of the four antiperiplanar conformers (Table 2).

The calculations predict six modes of every stable conformer to give rise to much more intense absorptions than all the other modes. These modes can be approximately described as the OH and N=O stretching,  $CH_2$  deformation, COH in plane bending, C–O stretching and OH torsion. There are relatively small differences between the calculated vibrational spectra of the eight conformers (compare the vibrational frequencies of the S1, A1 and A2 conformers in Table 3) which is the reason why the comparison of the calculated frequencies of the eight conformers with the experimental spectra of the three photoproducts did not allow us to draw definitive conclusions about the geometry of the three photoproducts. However, some suggestions concerning the geometries of the three photoproducts can be made on the basis of the experimental results.

First, the obtained experimental data indicate that the I<sup>A</sup>, I<sup>B</sup> and II products correspond to three different conformers and are not due to one conformer trapped in various matrix sites. The frequencies belonging to I<sup>A</sup>, I<sup>B</sup> and II products show relatively large differences in isotopic shifts after deuterium substitution of ethene or nitrous acid molecules which is not expected for a molecule trapped in sites of different geometries. For example the band due to the N=O stretching mode appears at 1561.9 (IA), 1555.4 (IB) and at 1549.5 cm<sup>-1</sup> (II) in the spectra of irradiated HONO/C2H4/Ar matrices and is shifted, respectively, 9.1, 1.2, 5.2 cm<sup>-1</sup> toward lower frequencies when  $C_2H_4$  is replaced by  $C_2D_4$  (Table 1). Site effect cannot account for such, relatively large differences, in isotopic shifts of the N=O stretching absorption. The three products exhibit also slightly different spectral pattern in the 1100-1000 cm<sup>-1</sup> region (Fig. 4, Table 1) which also indicates that they correspond to different conformers.

Some information on the conformers produced by the photochemical reaction is provided by the  $\nu$ (OH) stretching frequencies of the three species. For species II the  $\nu$ (OH) stretching frequency is equal to 3580.6 cm<sup>-1</sup> which suggests that the OH group in species II is involved in intramolecular hydrogen bond. The OH stretching frequencies of the nonbonded, free OH group in the spectra of ethanol and its derivatives occur above 3600 cm<sup>-1</sup> whereas those of the bonded OH groups may appear above or below 3600 cm<sup>-1</sup> depending on the strength of interaction. For example in the spectra of *trans* and *gauche* ethanol isolated in an argon matrix the  $\nu$ (OH) stretching vibration appears

at 3657.6,  $3662.2 \text{ cm}^{-1}$ , respectively [30]. In the spectra of 2-nitroethanol, CH<sub>2</sub>OHCH<sub>2</sub>NO<sub>2</sub>, in an argon matrix the free or *trans*  $\nu$ (OH) band is at 3660 cm<sup>-1</sup> and the bonded or gauche  $\nu$ (OH) band at  $3614 \text{ cm}^{-1}$  [31]. In turn, in the spectra of the most stable ethylene glycol conformer isolated in an argon matrix the free and bonded  $\nu(OH)$  modes occur at 3667 and 3626 cm<sup>-1</sup>, respectively. [32] The above data clearly indicate that in the species II, characterized by the 3580.6 cm<sup>-1</sup>  $\nu$ (OH) stretching frequency, the OH group is involved in the intramolecular hydrogen bond. So, we tentatively identify the species II as the most stable 2nitrosoethanol conformer with intramolecular hydrogen bond i.e. synclinal conformer S1. The  $3580.6 \text{ cm}^{-1}$  band is not sensitive to substitution of  $C_2H_4$  by  $C_2D_4$ ; in the spectra of  $CH_2ODCH_2NO$ two bands due to product II are observed at 2654.6,  $2643.1 \text{ cm}^{-1}$ . The other bands of species II are not helpful in determining its conformation. The N=O stretching vibration occurs at circa  $1549 \text{ cm}^{-1}$  in the spectra of both CH<sub>2</sub>OHCH<sub>2</sub>NO and CH<sub>2</sub> ODCH<sub>2</sub>NO and is shifted slightly toward lower frequencies, to  $1544.3 \text{ cm}^{-1}$ , in the spectra of CD<sub>2</sub>OHCD<sub>2</sub>NO. The absorption observed at  $1383.6 \text{ cm}^{-1}$  in the spectra of CH<sub>2</sub>OHCH<sub>2</sub>NO (II) is shifted to  $1376.1 \text{ cm}^{-1}$  in the spectra of CH<sub>2</sub>ODCH<sub>2</sub>NO (II) which suggests its assignment to  $CH_2$  deformation mode. The 1187.1 cm<sup>-1</sup> band characteristic for CH2OHCH2NO (II) is shifted to 1091.2, 898.4 cm<sup>-1</sup> in the spectra of CD<sub>2</sub>OHCD<sub>2</sub> NO,  $CH_2ODCH_2NO$  (II), respectively. The sensi-tivity of the 1187.1 cm<sup>-1</sup> absorption to deuterium substitution of both CH2 and OH groups indicate that the coupled CH<sub>2</sub> rocking and torsion and COH bending vibration may give rise to its intensity. The contribution of the C-O stretching cannot be excluded. The doublet observed at 1019.6,  $1017.3 \text{ cm}^{-1}$  is tentatively assigned to the CO stretching mode.

The frequency values of the OH stretches of the other two photoproducts,  $(3639.6, I^A)$  and  $3657.0 \text{ cm}^{-1}$ ,  $I^B$ ), suggest that the corresponding vibrations are due to the conformers with free, nonbonded OH groups. Additional information concerning their geometry is provided by matrix annealing; the bands due to the product  $I^A$  increase whereas the bands due to  $I^B$  product strongly

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decrease when the matrix is annealed to 30 K. Absence of intramolecular hydrogen bond suggests that the species characterized by the bands belonging to groups IA, IB have antiperiplanar structure A. The four A conformers are calculated to be within 1.99 - 2.47 kcal/mol less stable than the most stable conformer S1. It is well known that photochemical reactions carried out in low temperature matrices may lead to population of less stable reaction intermediates and products. For example the irradiation of the CH2O···HNO complex may lead either to formation of less stable trans conformer of nitrosomethanol or more stable *cis* conformer depending on the wavelength of radiation. [28] The two photoproducts  $I^{A}$  and  $I^{B}$ are tentatively assigned to two antiperiplanar conformers A1 and A2. The calculations predict very small energy difference between these two conformers which is equal to 0.18 kcal/mol when zero point vibrational energy correction is taken into account. The conformer A2 is converted into A1 by rotating OH group around C-O bond which requires small activation energy. This fact might explain why the bands due to I<sup>B</sup> conformer decrease whereas the bands due to IA increase after matrix annealing.

The  $3657.0 \text{ cm}^{-1}$  band observed for the  $CH_2$  OHCH<sub>2</sub>NO, I<sup>B</sup> molecule is not sensitive to substitution of  $C_2H_4$  by  $C_2D_4$  and is shifted to  $2698.5 \text{ cm}^{-1}$ , with isotopic shift ratio 1.35, when OH group is replaced by OD. The N=O stretching vibration is identified at  $1555.4 \text{ cm}^{-1}$  for CH<sub>2</sub> OHCH<sub>2</sub>NO and at  $1554.2 \text{ cm}^{-1}$  for CD<sub>2</sub>OHCD<sub>2</sub> NO. The counterpart of the  $1151.3 \text{ cm}^{-1}$  absorption characteristic for the CD<sub>2</sub>OHCD<sub>2</sub>NO species was found to appear at  $905.8 \text{ cm}^{-1}$  in the spectra of CH<sub>2</sub>ODCH<sub>2</sub>NO, however no counterpart of this band was found in the spectra of CH<sub>2</sub>OHCH<sub>2</sub>NO. The large sensitivity of this band to substitution of OH by OD suggests its assignment to COH bending vibration. The CH<sub>2</sub> rocking and torsion may also contribute to this mode. The  $1048.5 \text{ cm}^{-1}$ band observed in the spectra of hydrogenated molecule is shifted to 1020.2,  $1057.4 \text{ cm}^{-1}$  in the spectra of CD<sub>2</sub>OHCD<sub>2</sub>NO, CH<sub>2</sub>ODCH<sub>2</sub>NO molecules, respectively. The band appears in the region characteristic for C-O stretching vibration but its relatively strong sensitivity to deuterium substitution

of  $C_2H_4$  and OH groups indicates that  $CH_2$  group coordinates (rocking and/or torsion) and COH bending also contribute to the mode giving rise to this band.

The bands due to I<sup>A</sup> species which is identified tentatively as A1 conformer appear in the vicinity of the absorptions due to  $I^{B^{-1}}$  (except the lowest frequency band at ca. 770 cm<sup>-1</sup>) and are assigned to the same modes. So, the 3639.6, 1561.9 and  $1040.0 \text{ cm}^{-1}$  bands observed in the spectra of CH<sub>2</sub>OHCH<sub>2</sub>NO, I<sup>A</sup> are assigned, respectively, to the OH and N=O stretching and to the coupled C-O stretching and CH<sub>2</sub> deformation coordinates (rocking and/or torsion). The  $1225.6 \text{ cm}^{-1}$  band appearing in the spectra of CH2OHCH2NO has its counterparts at 1120.6, 1118.8 cm<sup>-1</sup> in the spectra of CD<sub>2</sub>OHCD<sub>2</sub>NO; no counterpart of this band was found in the spectra of CH2ODCH2NO. The 1120.6, 118.8 cm<sup>-1</sup> (I<sup>A</sup>) bands lie in the vicinity of the 1151.3  $\text{cm}^{-1}$  (I<sup>B</sup>) band and are also assigned to the COH bending mode to which may contribute CH<sub>2</sub> rocking and/or torsion coordinates. The band observed at  $887.9 \text{ cm}^{-1}$  in the spectra of CD<sub>2</sub>OH-CD<sub>2</sub>NO is tentatively assigned to the coupled C-N stretching and CNO bending coordinates.

#### 4.3. Matrix chemistry

The obtained spectra prove that exposure of the  $C_2H_4$ ...HONO complex trapped in a matrix cage to  $\lambda > 340$  nm (E < 84 kcal/mol) radiation leads to formation of 2-nitrosoethanol molecule. The priproducts photodissociation of mary the  $C_2H_4{\cdots}HONO$  complex are OH, NO radicals and C2H4 molecule. As was already discussed in our earlier paper [7] the OH and NO radicals are generated in their ground electronic states with some excess of vibrational and rotational energy. Both radicals add to the double bond of ethylene to form 2-nitrosoethanol. It is interesting to compare the photochemistry of the  $C_2H_4$ ···HONO and CO···HONO systems, the latter one have been studied recently [7]. The photolysis of the CO···HONO complex trapped in a matrix cage leads to formation of trans and cis-HOCO radicals (single addition products) and trans and cis-HOC(O)NO molecules (double addition products).

The relative yield of the HOCO radicals and HOC(O)NO molecules was dependent on the conditions of the experiment (temperature of deposition, matrix temperature during photolysis process) however both species were always detected. In contrast with the CO···HONO system after photolysis of the  $C_2H_4$ ···HONO complex only 2-nitrosoethanol molecule, which is the product of double addition reaction, was detected. The spectra of 2-hydroxyethyl radical are well known, [3,4] no band characteristic for this radical was detected in our spectra. There are two possible reasons which could explain different behavior of these two systems. First, the 2-hydroxyethyl radical, CH<sub>2</sub> OHCH<sub>2</sub>, is more reactive than hydroxy formyl radical, HOCO, so, once it is formed it reacts readily with the NO radical present in the same matrix cage to form 2-nitrosoethanol molecule. Second, one perhaps should take into account the possibility that the  $C_2H_4 \cdots HONO$  complex does not dissociate completely and as a transition state a cyclic intermediate is formed.

### 5. Conclusions

We have shown that the photolysis of the C<sub>2</sub>H<sub>4</sub>···HONO complex trapped in argon matrices with  $\lambda > 340$  nm radiation leads to the formation of 2-nitrosoethanol molecule that has been identified for the first time. Three conformers of 2nitrosoethanol molecule are formed whereas ab initio calculations predict eight stable conformers of this molecule. The conformers produced in photochemical reaction were identified tentatively as the most stable conformer with synclinal orientation of the CO and CN bonds and intramolecular hydrogen bond between OH and NO groups (S1) and two less stable conformers with antiperiplanar orientations of the CO and CN bonds (A1 and A2). The experimental results are supported by ab initio calculations of the geometries, energies and vibrational frequencies of the eight conformers. The 2-hydroxyethyl radical has not been identified in the studied spectra.

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