Infrared Spectra of the Nitric Acid−Ethylene Complex in Solid Argon. UV Irradiation Effects

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The hydrogen-bonded complexes between C_2H_4 and HNO_3, and their deuterated analogs, have been isolated and characterized in argon matrices. The concentration studies, matrix annealing, and UV irradiation effects prove formation of stable 1/1 π-electron hydrogen-bonded complexes isolated in two trapping sites. Eight perturbed HNO_3 vibrations and three perturbed C_2H_4 vibrations were identified for this complex. The spectra also indicate the existence of a less stable 1/1 π-electron hydrogen-bonded complex for which one perturbed frequency due to the OH stretching mode was identified. Photochemistry of the complexes was also studied with the 266 nm laser line and with a medium-pressure mercury lamp. The photolysis products of HNO_3, OH and NO_2 radicals, recombine in the matrix cage to form nitric acid, and peroxynitrous acid which are the main reaction products. The new major product of photolysis of the C_2H_4−HNO_3 complex is ethylene glycol nitrite formed in double-addition reaction of OH and NO_2 radicals to the C═C bond of the ethylene molecule.

1. Introduction

Nitric acid, formed via the reaction of OH with NO_2, is an important species in the atmosphere. In the stratosphere, it is a temporary reservoir of odd nitrogen and a constituent of polar stratospheric clouds. In urban air it is a major component of photochemical smog,[1,2] and it contributes to acid deposition and to nitrate-containing aerosol formation. Due to its importance, during the past decade, considerable attention has been directed toward its reaction with OH radical [3] and its photodissociation in the gas phase[4−6] and in matrices.[7,8] Nitric acid is a strong proton donor, and the knowledge of the photochemistry of molecular complexes formed between HNO_3 and other atmospheric species is of great interest for understanding the chemistry that occurs in the polluted troposphere. However there is very little information in this area. Thirty years ago the complexes of nitric acid with a series of ethers in the gas phase were reported.[9,10] Recently Barnes studied nitric acid complexes with N_2, CO, H_2O, and NH_3 by means of infrared spectroscopy and matrix isolation techniques.[11] The infrared spectra of the complexes between nitric acid and ethylene have not been studied so far.

Ethylene and propylene are the main alkenes observed in the troposhere near large urban sources of hydrocarbon emission. It is well-known that ethylene is a π-electron donor and some work was focused on the hydrogen bond formed between ethylene and hydrogen halides[12,13] or water.[14]

As an extension of our previous study on the nitric acid−methane complex,[15] this paper presents the results of matrix isolation studies of the nitric acid−ethylene system. Infrared spectroscopic studies of the UV photolysis of the complex are also reported.

2. Experimental Section

Nitric acid was prepared by adding drop by drop concentrated (98%) sulfuric acid (or deuterated sulfuric acid) to solid potassium nitrate. In order to minimize the HNO_3 decomposition, the reaction vessel was kept at a temperature of 0 °C. The reaction product was vacuum distilled. The mixtures of C_2H_4(C_2D_4)/Ar and HNO_3(DNO_3)/Ar were prepared using standard manometric techniques. The two mixtures were simultaneously deposited onto a gold-plated copper mirror held at 20 K by a closed cycle helium refrigerator (Air Products, Displex 202A). The concentration of the studied matrices varied in the range 1/1/800 to 1/4/500. Infrared spectra were recorded with the matrix maintained at ca. 11 K. The spectra were registered at 0.5 cm^{-1} resolution in a reflection mode, with a Bruker 113v Fourier transform infrared spectrometer.

Two different light sources have been employed for photolysis: a medium-pressure Hg lamp (200 W) and a Nd:YAG laser (Quantel YG 781C 20), 266 nm, 20 Hz.

3. Vibrational Spectra of Parent Molecules

The spectra of the reactants, nitric acid and ethylene in argon, were recorded for comparison with the spectra of nitric acid/ethylene/argon matrices.

3.1. HNO_3/Ar Samples. The IR spectrum of HNO_3 in the gas phase was first reported by Cohn.[16] Later McGraw[9] analyzed the spectra of all HNO_3 isotopomers (H, D, ^{14}N, ^{15}N) and performed force field calculations for nitric acid molecule. More recently, a number of infrared bands (fundamentals and combinations) have been analyzed at high resolution (refs 17−19 and references therein). In particular the ν_4 mode (δ_{NOH}) was reassigned, and resonances between $3\nu_9$ (1288.9 cm^{-1}), ν_4 (1303.6 cm^{-1}), ν_3 (1326.18 cm^{-1}) and $\nu_5 + \nu_9$ (1343.65 cm^{-1}) transitions were analyzed[19] as well as those between ν_5 (879.1 cm^{-1}) and $2\nu_9$ (896.4 cm^{-1}).[18]

The IR spectra of three isotopic species of nitric acid isolated in nitrogen and argon have been reported by W. J. Chen et al.[8] Spectra of HNO_3 in argon recorded in this work are in good agreement with the literature data. Bands due to OH stretching (ν_1) and OH torsion (ν_9) appeared as doublets, the splitting was

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TABLE 1: Absorptions Observed for the Perturbed HNO_3 Modes in C_2H_4−HNO_3 Complexes and Their Isotopomers in Argon Matrices

mode	HNO_3	C_2H_4/HNO_3	C_2D_4/HNO_3	DNO_3	C_2H_4/DNO_3	C_2D_4/DNO_3	
ν_1 OH stretch	3522.3	3325.1	3321.6	2601.5	2468.5	2466.2	II
	3519.3	3320.3	3316.7	2599.1	2464.9	2462.5	III
		3307.4	3304.7		2456.2	2454.3	I_α
		3300.8	3297.8		2451.6	2449.5	I_β
		3287.7	3284.3				IV
		3280.7	3277.2				V
ν_2^{as} NO_2 stretch	1699.4	1688.8	1688.6	1678.6	1661.7	1661.5	I_α
	1696.2	1686.2	1686.1	1674.9	1659.4	1659.1	I_β
ν_3 NOH bend	1304.4	1400.8	1401.8	1013.4	1041.0	1038.0	I_β
		1394.4	1394.3	1012.2	1036.2	1035.6	I_α
ν_4^{s} NO_2 stretch	1321.4	1307.6	1307.5	1310.4	1307.3	1307.8	I_α, I_β
	1318.7						
ν_5 N−O stretch	896.9	904.7	905.7	894.2	907.9	908.5	I_β
	896.5	903.5	904.2	884.5	905.7	906.4	I_α
ν_6 NO_2 scissors	656.6			650.4			
ν_7 ONO_2 in plane	588.0	600.3	602.3	548.0			I_α, I_β
ν_8 ONO_2 out of plane	763.6	769.5	769.6	763.7	768.7	768.8	I_β
		768.6	768.5		767.8	767.7	I_α
ν_9 OHN torsion	450.3	610.6	611.6				I_β
	450.1	608.3	609.4				I_α

[a] The frequencies indicated by I_α, I_β, II correspond to the 1/1 C_2H_4−HNO_3 complexes; the frequencies indicated by III, IV, and V correspond to higher order $(C_2H_4)_nHNO_3$ complexes.

also observed for the in plane and out of plane bending modes (ν_7, ν_8, respectively) as well as for the NO_2 stretching mode (ν_2).

As previously reported in the Experimental Section, it is difficult to obtain a pure HNO_3 sample, and weak absorptions due to NO_2 traces and to the $NO_2\cdots HNO_3$ complex[11] were observed in the studied spectra.

3.2. Ethylene/Ar Samples. The infrared and Raman spectra of the ethylene monomer and dimer in an argon matrix have been previously reported.[20,21] Some modes that are IR inactive for the ethylene monomer were observed for the dimer. Both in solid argon[20,21] and in solid xenon[22] most of the ethylene monomer fundamentals appear as doublets. Our spectra are in agreement with the previous results. The vibrational spectrum of C_2D_4 in argon, not reported before, showed absorptions at 2344 cm^{-1} (ν_a CH_2), 2205.4 cm^{-1} (ν_s CH_2), 1074.7 cm^{-1} (δ CH_2), 719.2 cm^{-1} (ω CH_2), and 620 cm^{-1} (ρ CH_2).

4. Vibrational Spectra of the Nitric Acid−Ethylene Complexes

Infrared spectra of matrices obtained by codeposition of $HNO_3/Ar = 1/1000$, 1/500, 1/200, 1/100 samples and C_2H_4-$(C_2D_4)/Ar = 1/400$, 1/250, 1/100 samples have been studied. In three experiments deuterium-enriched (ca. 50%) nitric acid samples, $D(H)NO_3/Ar = 1/250$, 1/150, were codeposited with a $C_2H_4(C_2D_4)/Ar = 1/250$ sample. The obtained spectra were compared with the spectra of HNO_3, DNO_3, C_2H_4, and C_2D_4 in argon. The observed product absorptions due to the nitric acid−ethylene complexes of different isotopic composition are listed in Table 1; Figures 1−4 illustrate some spectral regions of interest.

The concentration studies and matrix annealing allowed us to identify the bands due to the 1/1 complexes between nitric acid and ethylene. The spectra of the 1/1 HNO_3−C_2H_4 complexes will be described below by considering absorptions due to the perturbed $H(D)NO_3$ and C_2H_4, C_2D_4 submolecules in the complex.

4.1. HNO_3, DNO_3 Submolecules in the Complex. *ν(OH), ν(OD) Regions.* When HNO_3 and C_2H_4 molecules were present in an argon matrix, a strong doublet appeared in the studied spectra at 3307.4, 3300.8 cm^{-1} (I_α, I_β respectively) and additional weaker bands were observed at 3325.1 cm^{-1} (II) and at 3320.3 cm^{-1} (III). The relative intensities of the four bands were approximately constant within the range of concentrations studied. Figure 1′a,b shows the bands I_α, I_β, II, and III in the spectra of the $HNO_3/C_2H_4/Ar = 1/1500$ matrix after deposition (a) and after matrix irradiation for 1 h with a 266 nm YAG laser line (b); (spectrum b is scaled in such a way that the intensity of the I_α band is the same in the spectra a and b). All product absorptions were destroyed by matrix irradiation, but the band I_β was more sensitive whereas the band II was less sensitive to irradiation than the band I_α. Figure 1′c,d demonstrates the influence of annealing on the $HNO_3/C_2H_4/Ar = 1/1/800$ matrix. The intensity of the absorption I_β slightly increased with respect to the band I_α after matrix annealing, the absorption II strongly decreased whereas the band III considerably increased, and additional weak bands occurred at 3287.7 cm^{-1} (IV) and at 3280.7 cm^{-1} (V).

A similar pattern of bands was observed in the ν(OH) region in the spectra of $HNO_3/C_2D_4/Ar$ matrices; the bands I_α, I_β, II, and III were identified at 3304.7, 3297.8, 3321.6, and 3316.7 cm^{-1}; the absorptions IV and V occurred after matrix annealing at 3284.3, 3277.2 cm^{-1}. In the spectra of $Ar/D(H)NO_3/C_2H_4$ matrices containing deuterium-enriched nitric acid the deuterium counterparts of the bands I_α, I_β, II, and III were identified in the ν(OD) region at 2456.2, 2451.6, 2468.5, and 2464.9 cm^{-1}, whereas in the spectra of $Ar/D(H)NO_3/C_2D_4$ matrices the corresponding I_α, I_β, II, and III bands appeared, respectively, at 2454.3, 2449.5, 2466.2, and 2462.5 cm^{-1}. In Figure 1″ the ν(OD) regions in the spectra of the $D(H)NO_3/C_2H_4/Ar = 1/1/500$ and $D(H)NO_3/C_2D_4/Ar = 1/1/500$ matrices are presented.

The concentration and annealing studies demonstrate that the bands I_α, I_β, and II correspond to the 1/1 $C_2H_4\cdots HNO_3$ complexes characterized by the ν(OH) stretching vibration, respectively, at 3307.4, 3300.8, and 3325.1 cm^{-1}. The concentration of the complexes characterized by the I_α and I_β bands is much higher than the concentration of the complex II, as indicated by much larger intensity of the 3307.4, 3300.8 cm^{-1} bands as compared to the 3325.1 cm^{-1} band. The bands due to the complexes I_α and I_β were identified in all regions of HNO_3 fundamentals and in the regions of the ν_7, ν_{12} vibrations of C_2H_4 molecule.

The absorption III occurs in all studied spectra as a weak band after matrix deposition and increases strongly after matrix

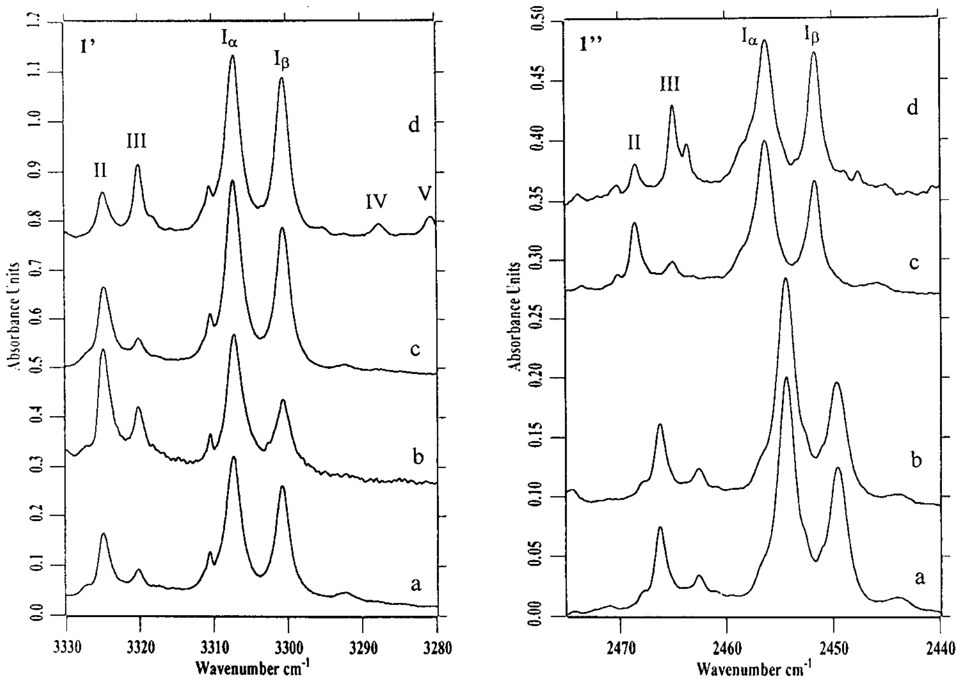


Figure 1. (1′) ν(OH) region in the spectra of $HNO_3/C_2H_4/Ar$ matrices. The spectra of the $HNO_3/C_2H_4/Ar = 1/1/500$ matrix after deposition (a) and after irradiation for 100 min with 266 nm YAG laser line (b); spectrum b is scaled by 6. The spectra of the $HNO_3/C_2H_4/Ar = 1/1/800$ matrix after deposition (c) and after matrix annealing to 33 K for 10 min (d). (1″) ν(OD) region in the spectra of $D(H)NO_3/C_2H_4(D_4)/Ar$. The spectra of the $D(H)NO_3/C_2H_4/Ar = 1/1/500$ matrix after deposition (a) and after matrix irradiation for 120 min with a medium-pressure mercury lamp (b); spectrum b is scaled by 5. The spectra of the $D(H)NO_3/C_2D_4/Ar = 1/1/500$ matrix after deposition (c) and after matrix annealing to 33 K for 10 min (d).

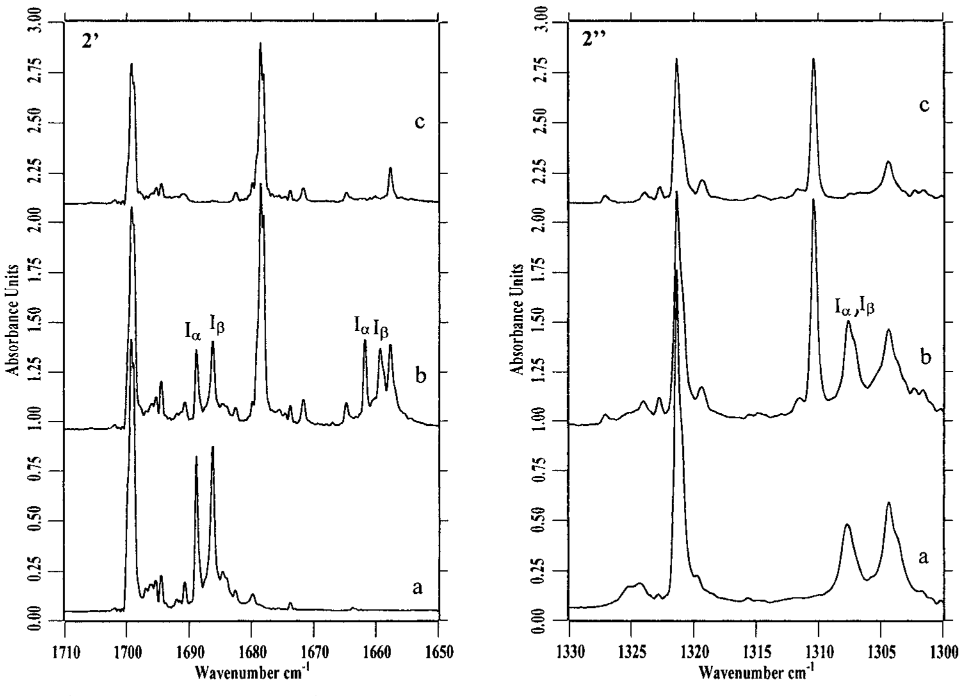


Figure 2. 1710−1650 cm^{-1} (2′) and 1330−1300 cm^{-1} (2″) regions in the spectra of $HNO_3/C_2H_4/Ar = 1/1/500$ (a), $D(H)NO_3/C_2H_4/Ar = 1/1/500$ (b), and $D(H)NO_3/Ar = 1/500$ (c) matrices.

annealing; the bands IV and V are observed only after matrix annealing. The bands III, IV, and V are tentatively assigned to higher order $HNO_3\ (C_2H_4)_n$ complexes.

1700−1250 cm^{-1} Region. Three fundamentals of the nitric acid monomer appear in the 1700−1250 cm^{-1} region: ν_2, NO_2 asymmetric stretch (1699.4, 1696.2 cm^{-1}), ν_3, NOH in plane bend, and ν_4, NO_2 symmetric stretch (1304.4 cm^{-1} and 1321.4, 1318.7 cm^{-1}, respectively, according to ref 18). In the spectra of $HNO_3/C_2H_4/Ar$ matrices the product absorptions were identified in this region at 1688.8, 1686.2, 1400.8, 1394.4, cm^{-1} and at 1307.6 cm^{-1}. The annealing and irradiation experiments demonstrate that the 1688.8, 1394.4 cm^{-1} absorptions correspond to the complex I_α, whereas the 1686.2, 1400.8 cm^{-1} bands correspond to the complex I_β. The 1688.8, 1394.4 cm^{-1} and the 1686.2, 1400.8 cm^{-1} bands are assigned to the perturbed ν_2, NO_2 asymmetric stretching and ν_3, NOH in plane bending vibrations in I_α and I_β complexes, respectively. The 1307.6 cm^{-1} band is assigned to the perturbed ν_4, NO_2 symmetric stretching vibration in I_α, I_β complexes.

In the spectra of matrices containing deuterium-enriched nitric acid, $D(H)NO_3/C_2H_4/Ar$, the perturbed ν_2, ν_3 nitric acid fundamentals were shifted to 1661.7, 1036.2 cm^{-1} and to 1659.4,

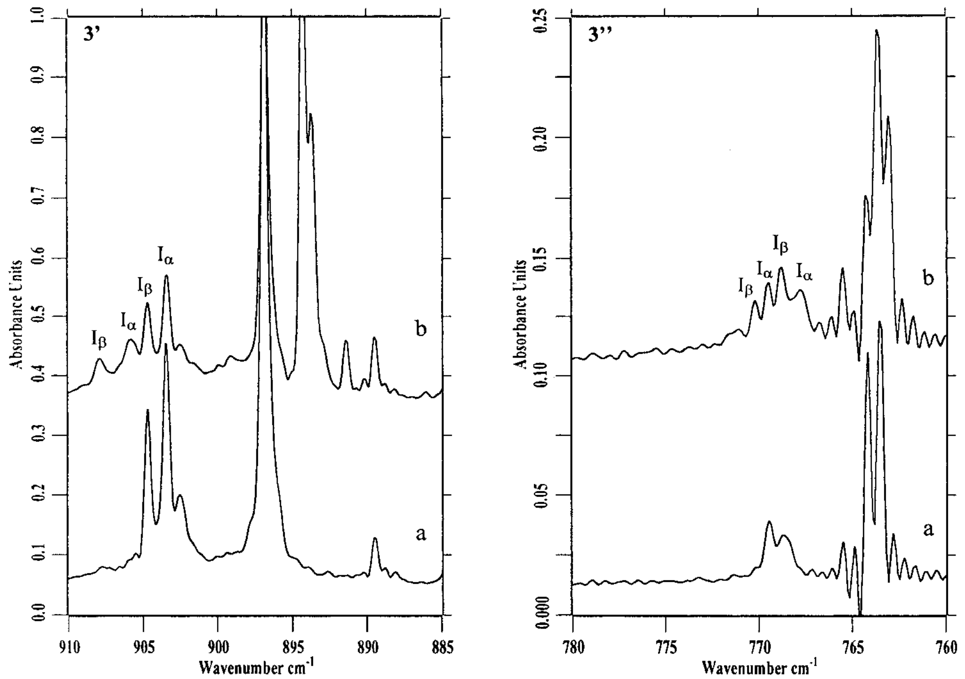


Figure 3. 910−885 cm^{-1} (3′) and 780−760 cm^{-1} (3″) regions in the spectra of $HNO_3/C_2H_4/Ar$ = 1/1/500 (a) and $D(H)NO_3/C_2H_4/Ar$ = 1/1/500 (b) matrices.

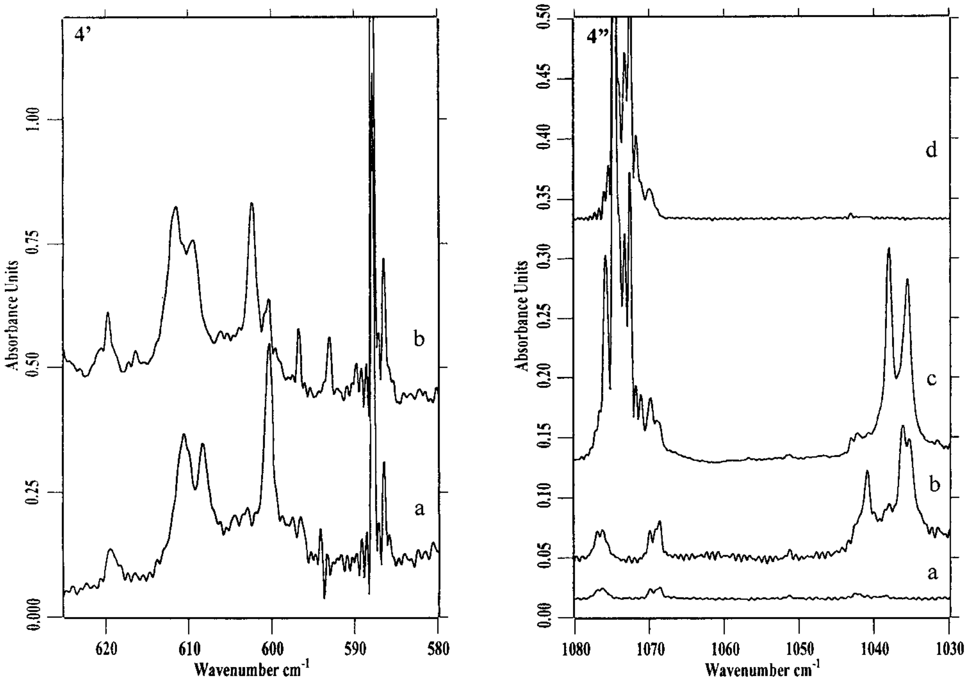


Figure 4. (4′) 625−580 cm^{-1} region in the spectra of $HNO_3/C_2H_4/Ar$ = 1/1/500 (a) and $HNO_3/C_2D_4/Ar$ = 1/1/500 (b) matrices. (4″) 1080−1030 cm^{-1} region in the spectra of $D(H)NO_3/Ar$ = 1/500 (a), $D(H)NO_3/C_2H_4/Ar$ = 1/1/500 (b), $D(H)NO_3/C_2D_4/Ar$ = 1/1/500 (c), and C_2D_4/Ar = 1/500 matrices (d).

1041.0 cm^{-1} in I_α and I_β complexes, respectively. The corresponding ν_4 mode is observed at 1307.3 cm^{-1} for both I_α and I_β complexes. Substitution of C_2H_4 with C_2D_4 only slightly affected the frequencies of the observed product absorptions; the observed shifts are less than 0.3 cm^{-1} (see Table 1).

900−700 cm^{-1} Region. In the spectra of $HNO_3/C_2H_4/Ar$ matrices the product absorptions were observed in this region at 903.5, 904.7 cm^{-1} and at 768.6, 769.5 cm^{-1}, respectively, in the vicinity of the ν_5, O−NO_2 stretching and ν_8, ONO_2 in plane bending fundamentals of the HNO_3 monomer (see Figure 3). The annealing and irradiation experiments allowed us to assign the 903.5, 768.6 cm^{-1} bands to the complex I_α and the 904.7, 769.5 cm^{-1} bands to the complex I_β. The product bands observed in this region show small shift when DNO_3 is substituted for HNO_3 or C_2D_4 is substituted for C_2H_4, as reported in Table 1.

700−400 cm^{-1} Region. When HNO_3 and C_2H_4 were present in the matrix samples, the infrared spectra showed a doublet at 610.6, 608.3 cm^{-1} and a sharp band centered at 600.3 cm^{-1} (see Figure 4′). In the spectra of matrices containing HNO_3 and C_2D_4 the doublet was slightly blue shifted to 611.6, 609.4 cm^{-1}. No additional absorptions were observed in this region in the spectra of $D(H)NO_3/C_2H_4$ and $D(H)NO_3/C_2D_4$ matrices. Assignment of the observed product bands is not straightforward. In this region are expected to appear the ν_7, ONO_2 in plane bending mode and the ν_9, OH torsion mode of the HNO_3

submolecule. The observed doublet at 608.3, 610.6 cm^{-1} is assigned to OH torsion in I_α, I_β complexes, respectively, and the absorption at 600.3 cm^{-1} to the ν_7, ONO_2 in plane bending mode of nitric acid in I_α, I_β complexes. The OH torsion mode is expected to be more sensitive to the complex type and to the complex environment than the ν_7, ONO_2 in plane bending mode.

4.2. Ethylene Submolecule in the Complex. Three product absorptions were observed in the studied spectra in the vicinity of ethylene vibrations. They include weak absorptions at 1929.0 and 1442.4 cm^{-1} assigned, respectively, to the perturbed $\nu_7+\nu_8$ combination vibration and to the ν_{12} vibration of the C_2H_4 submolecule, and a medium intensity doublet at 971.7, 972.7 cm^{-1} due to the perturbed ν_7 vibration of C_2H_4 in the complex. The concentration and annealing studies demonstrate that the 971.7, 972.7 cm^{-1} components of the doublet correspond to the I_α, I_β complexes, respectively. The frequencies of the perturbed ethylene vibrations are not sensitive to DNO_3 substitution, whereas in the C_2D_4-substituted complexes the 1929.0, 1442.4, 972.7, 971.7 cm^{-1} bands are shifted, respectively, to 1514.4, 1075.8 and 743.1, 740.0 cm^{-1}. Figure 4″ presents the region of the ν_{12}, C_2D_4 mode in the $HNO_3/C_2D_4/Ar = 1/1/500$ matrix.

5. Bonding of the Nitric Acid−Ethylene Complex

Eight perturbed HNO_3 vibrations and two perturbed C_2H_4 vibrations were identified for the $C_2H_4\cdots HNO_3$ I_α, I_β complexes. All observed I_α, I_β bands are a few wavenumbers apart, which suggests that the two complexes have the same structure, but the geometry of their matrix environment is different. The concentration of the complex I_β increases after matrix annealing, which suggests that the complex is trapped in a more stable environment than the complex I_α. The complex II is less stable and probably has different structure than the complexes I_α and I_β. Unfortunately, we observed only one band due to the complex II (the absorption due to the $\nu(OH)$ stretching vibration), which does not allow us to draw conclusions about its structure.

The shifts of the HNO_3 (DNO_3) fundamentals in I_α, I_β complexes clearly show that nitric acid is hydrogen bonded to C_2H_4. As expected, the most perturbed vibrations are the NOH group vibrations. The OH stretching fundamental is 300 cm^{-1} red shifted, whereas the OH in plane bending and OH torsion modes are ca. 100, 150 cm^{-1} blue shifted, respectively, upon complexation with C_2H_4. The magnitude of the relative shift $\Delta\nu_s/\nu_o = 0.086$ of the perturbed OH stretching frequency is a good indicator of the strength of the hydrogen bond in a complex. In a set of complexes of nitric acid with various bases the strength of interaction depends on the proton affinity of a base. Barnes[11] has correlated the relative shifts, $\Delta\nu_s/\nu_o$, of the $\nu(OH)$ stretching frequency of HNO_3 in nitric acid complexes with various bases with the proton affinities of the bases. The $\Delta\nu_s/\nu_o$ value for the nitric acid−ethylene complex correlates well with the proton affinity of C_2H_4 [160 kJ mol^{-1}]. Nitric acid is a stronger acid than HF and forms a substantially stronger complex with C_2H_4 than HF, for which the $\Delta\nu_s/\nu_o$ value is 0.056.

An interesting observation concerns the sensitivity of the perturbed OH fundamentals to the replacement of C_2H_4 by C_2D_4. The $\nu(OH)$ and $\nu(OD)$ vibrations are red shifted by 2.7 and 1.9 cm^{-1}, respectively, when C_2H_4 is substituted by C_2D_4 in the ethylene−HNO_3 complex. Due to the anharmonicity of the hydrogen bond stretching vibration or to the larger mass of C_2D_4, the average distance between HNO_3 and C_2D_4 can be somewhat shorter than the distance between HNO_3 and C_2H_4, leading to larger shift. Such a trend was already observed for the NO-HX complexes[23,24] and for the H_2O-NH_3 complexes.[14]

TABLE 2: Observed Shifts (in cm^{-1}) of the ν_7, ν_{12} Fundamentals and of the $\nu_7+\nu_8$ Combination Transition of C_2H_4 in Its Complexes with H_2O, HCl, HF, and HNO_3 Isolated in Argon Matrices

	H_2O^{14}	HCl^{12}	HF^{12}	HNO_3 (this work)
ν_7	12.2	10.1	25.5	26
ν_{12}	1.1		0	2.4
$\nu_7+\nu_8$	16.9		38	38

As summarized in Table 1, other HNO_3 fundamentals are weakly perturbed upon complexation. In particular, the ν_4, NO_2 symmetric stretching mode seems insensitive to complexation, which suggests that the NOH in plane bending coordinate does not contribute to this mode. The perturbed ν_4 mode is observed at ca. 1307 cm^{-1} in all isotopically substituted complexes ($HNO_3-C_2H_4$, $HNO_3-C_2D_4$, $DNO_3-C_2H_4$, $HNO_3-C_2D_4$) and has a frequency value close to the nonperturbed ν_4 mode in the DNO_3 monomer. Upon HNO_3 complexation or in deuterated nitric acid, DNO_3, there is decoupling between $\delta(OH)$ and $\nu_s(NO_2)$ internal coordinates, and hence $\nu_s(NO_2)$ appears at 1307 cm^{-1} in the spectra of HNO_3 and DNO_3 complexes.

Due to the relatively weak hydrogen bonding in I_α, I_β complexes, the C_2H_4 submolecule is only slightly perturbed by the nitric acid molecule. The most perturbed ethylene fundamental is the ν_7, CH_2 out of plane wagging mode, which is blue shifted by 26 cm^{-1} from the ν_7 mode of the C_2H_4 monomer; only a 2.4 cm^{-1} displacement toward higher frequencies is observed for the perturbed ν_{12}, CH_2 in plane bending mode of the ethylene molecule in the complex. The significant perturbation of the ν_7 out of plane bending mode and very weak perturbation of the ν_{12} in plane bending mode indicate that the OH group is bonded to the C_2H_4 π-electron system in an out of plane position, a situation already encountered in all ethylene complexes studied so far. The combination band, $\nu_7+\nu_8$, is 38 cm^{-1} blue shifted in the complex, suggesting ca. 12 cm^{-1} blue shift for the infrared inactive ν_8 out of plane bending of C_2H_4. In the complex formed between C_2H_4 and HF the HF molecule placed in an out of plane position to the ethylene molecule also exerts more perturbation on the ν_7 than on the ν_8 mode of C_2H_4.[12] No complex counterpartners were observed for any of the infrared forbidden bands of C_2H_4. In Table 2 the complex shifts of C_2H_4 fundamentals in ethylene complexes with nitric acid, hydracids, and water are compared.

The obtained spectra indicate that in I_α, I_β complexes the OH group of nitric acid is bonded to the C_2H_4 π-electron system in an out of plane position. The spectra do not provide information about mutual arrangement of the HNO_3 plane with respect to the C_2H_4 plane, but the most stable structure is probably the structure in which the plane of the HNO_3 molecule is perpendicular to the C_2H_4 plane and to the C=C bond of the ethylene molecule. One might expect that I_α, I_β complexes possess this kind of geometry. In the less stable complex II the plane of the HNO_3 molecule may be perpendicular to the C_2H_4 plane but parallel to the C=C bond. Unfortunately, the obtained spectra do not provide information about mutual arrangement of C_2H_4 and HNO_3 planes in the studied complexes.

6. Photolysis of the Nitric Acid−Ethylene Complex

Two kinds of photolysis experiments were carried out after deposition of $H(D)NO_3/C_2H_4(D_4)/Ar$ mixtures. In the first set of experiments the matrices were irradiated with the 266 nm laser line, whereas in the second set of experiments the full output of the mercury lamp was used. In the two cases the bands characteristic of the ethylene−nitric acid complex disappeared totally after 5 h irradiation time, whereas the absorptions due to the HNO_3 monomer decreased by 20%.

TABLE 3: Product Absorptions (cm^{-1}) Observed after Irradiation of the C_2H_4+HNO_3 System in an Argon Matrix

$C_2H_4 + HNO_3$ laser	$C_2H_4 + HNO_3$ Hg lamp	$C_2D_4 + HNO_3$ Hg lamp	$C_2D_4 + DNO_3$ Hg lamp		$C_2H_4 + HNO_3$ laser	$C_2H_4 + HNO_3$ Hg lamp	$C_2D_4 + HNO_3$ Hg lamp	$C_2D_4 + DNO_3$ Hg lamp	
3635 ↓[a]	3635	3625 ?		D	1323 ↓	1323	1323		C
3623	3623			A	1259	1259		916	A
3576					1253	1254			
3550 ↑	3550			G		1246	1246		G
3524 ↓	3524	3524		C	1194 ↓	1194			D
3448				A	1130 ?	1130 ?			G ?
	3419 ↑		2527	F	1106	1106	1103 ?		A
	3416				1096 ↓	1096	1096		D
3404.5 ↑	3404.5 ↑	3402.5	2519	F	1089	1089			
3342 ↑	3342	2475	2475	G	1076 ↑	1076			G
2826	2826	2089	2090	G					
2637.5 ↓	2637.5	2637.5		C	1036	1036			A
1841.5	1841.5	1841.5			1035	1035			
1791 ↑	1791	1791	1791	G	925 ↓	925			D
1755 ↓	1755	1742	1742	E	888 ↓	888	888		C
1724 ↑	1724	1719 ?		G	864 ↓	864	864		D
1652	1650	1632 ?		A	854				
1650					843 ↑	843		833 ?	G
1647				A	837	837		814 ?	A
1565	1565	1564		B	790 ↑	790	790		G
	1407 ↑		1145	F	616	616	616		A
	1395 ↑?		1141	F	582 ↓	582			D

[a] ↑, the band increases after matrix annealing; ↓, the band decreases after matrix annealing.

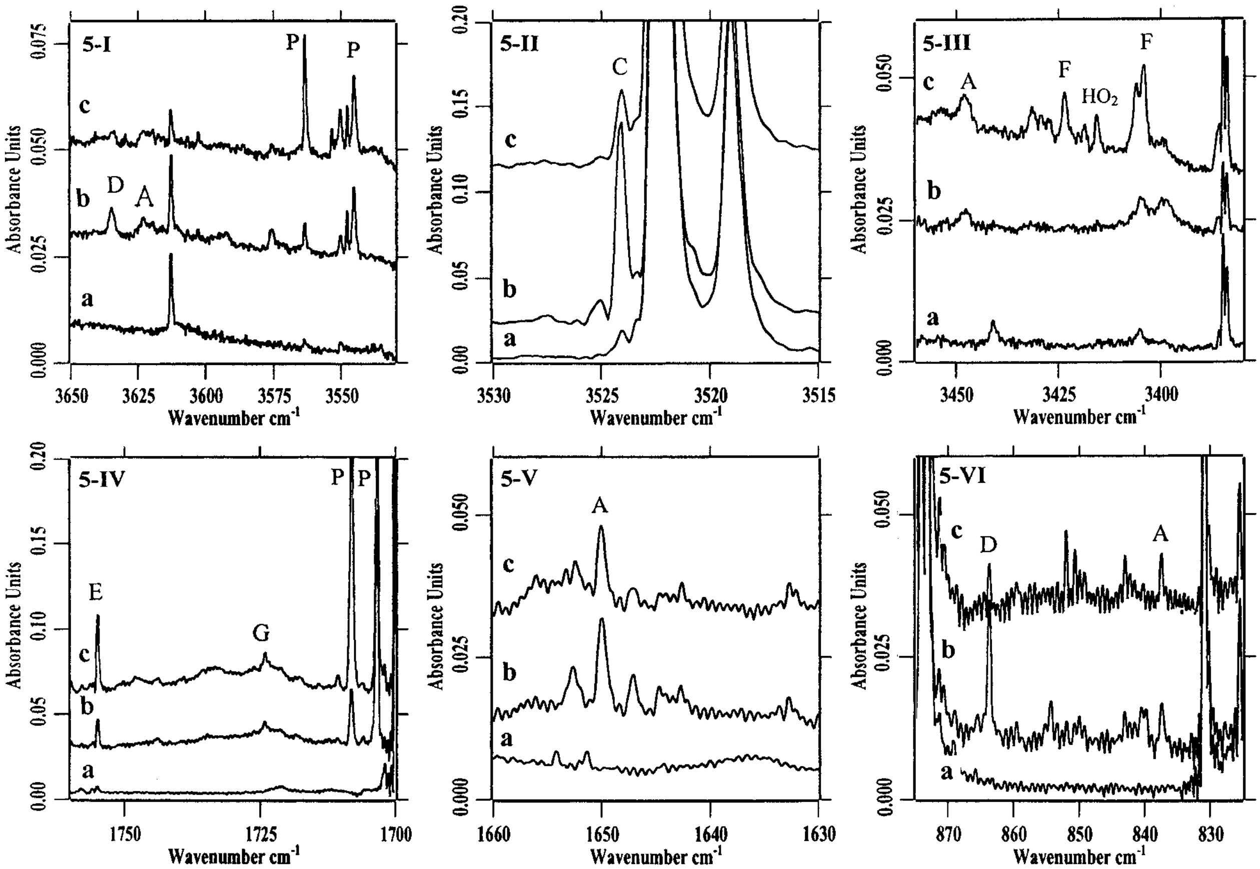


Figure 5. 3650−3530 cm^{-1} (I), 3530−3515 cm^{-1} (II), 3460−3380 cm^{-1} (III), 1760−1700 cm^{-1} (IV), 1660−1630 cm^{-1} (V) and 875−825 cm^{-1} (VI) regions in the spectra of the $HNO_3/C_2H_4/Ar$ = 1/1/500 matrix after deposition (a), after irradiation for 105 min with a 266 nm laser line (b), or after irradiation for 240 min with a Hg lamp (c).

In the gas phase the primary photolysis reaction of pure nitric acid by ultraviolet radiation proceeds via the channel $HNO_3 + h\nu \Rightarrow HO + NO_2$ with a quantum yield of 1.[25] In argon matrices the OH and NO_2 fragments recombine and form two different conformers of peroxynitrous acid HOONO.[7,8] Additional weak lines due to OH, HNO, NO, and NO_2 molecules and to the $H_2O{\cdots}NO$ complex were also identified in argon matrices.[7,8] After irradiation of $HNO_3/C_2H_4/Ar$ matrices all these bands were also observed. In addition, the bands characteristic of HO_2 and CO molecules and several bands that can be attributed to the products of the reaction of ethylene molecules with HNO_3 photofragments also appeared. Only the new product bands are reported and discussed.

Figure 5 compares the spectra obtained by irradiation of the $HNO_3/C_2H_4/Ar$ = 1/1/500 matrix with the 266 nm laser line and with the medium pressure mercury lamp. As illustrated in

Figure 5, the products formed after photolysis and their relative yields depend on the nature of the excitation source. The performed experiments allowed us to characterize seven different band sets that are formed with different yields on irradiation with a laser or mercury lamp and respond in different ways to prolonged photolysis and annealing processes. Absorptions labeled A (3623, 3448, 1650, 1647, 1259, 1106, 1036, 837, 616 cm^{-1}) and B (1565 cm^{-1}) are more intense in the laser experiment or are observed with comparable intensities in the laser and mercury lamp experiments, their intensities decrease after prolonged irradiation with the mercury lamp, and they show a small sensitivity to matrix annealing. The relative intensity of the B absorption with respect to A absorptions varies slightly in different experiments. The bands labeled C (3524, 2637.5, 1323, 888 cm^{-1}) and D (3635, 1194, 1096, 925, 864, 582 cm^{-1}) are much more intense in laser experiments than in mercury lamp experiments; the C absorptions appear as weak bands after matrix irradiation with the mercury lamp, whereas the D absorptions are still weaker or are not observed at all. Both C and D bands disappear after matrix annealing. The bands labeled E (1755 cm^{-1}), F (3419, 3404.5, 1407, 1395 cm^{-1}), and G (3550, 3342, 2826, 1791, 1724, 1246, 1130, 1076, 843, 790 cm^{-1}) appear with larger intensity in mercury lamp experiments than in the laser experiment. The 1755 cm^{-1} band is shifted after matrix annealing to 1750.5 cm^{-1}; no other product absorption was identified that had the same relative intensity with respect to the E band in all performed experiments. The intensities of the F bands decrease, whereas the intensities of the G bands increase after prolonged photolysis; both F and G bands grow in intensity after matrix annealing.

Identification of the photolysis products from the observed bands is not straightforward. First, each group of bands may correspond to one or several products formed either as primary or secondary photolysis products. Second, due to the low yield of the reaction products, only the most intense absorptions characteristic of the products formed during photolysis are observed. The possibility of formation of the complexes between photolysis products and ethylene also has to be taken into account.

The bands labeled A are tentatively assigned to HOH_2C-CH_2ONO, ethylene glycol nitrite, as is now discussed. The 3623, 3448 cm^{-1} bands are characteristic of the ν(OH) stretching vibrations. The 1259 cm^{-1} band may be attributed to the δ(COH) bending vibration; its deuterium counterpart was identified at 916 cm^{-1}, which gives an isotopic shift ratio 1259/916 = 1.37 and confirms the band assignment. The bands observed at 1650, 1647, 837, and 616 cm^{-1} demonstrate the presence of the O−N═O group in species A. In the spectra of *trans*-methyl nitrite isolated in an argon matrix the ν(N═O) and ν(N−O) stretching and δ(ONO) bending vibrations were observed, respectively, at 1666, 809, and 565 cm^{-1} and in the spectra of *cis*-methyl nitrite at 1617, 839, and 624 cm^{-1}.[26,27] The 1036 cm^{-1} absorption observed for species A may be due to the ν(C−ONO) stretching vibration; the corresponding vibrations were observed at 1043 and 987 cm^{-1} for *trans*- and *cis*−methyl nitrite isomers, respectively. The 1106 cm^{-1} band appears in the region of the ν(CCO) asymmetric stretching vibration of *trans*-ethanol (1091.7 cm^{-1}).[28] The bands observed for species A correspond to the vibrations that are characteristic for ethylene glycol nitrite and that are expected to give rise to the strongest absorptions in the spectrum of this molecule. The two bands observed in the ν(OH) stretching region may be due to different conformers of ethylene glycol nitrite, but identification of one band only in the δ(COH) and ν(N−O) regions does not support this assignment. Another possibility is that the lower frequency band at 3448 cm^{-1} is due to an intermolecular complex between A species and another photolysis product; the possibility that one of the two ν(OH) bands belongs to another species and not to ethylene glycol nitrite also cannot be excluded. The very low yield of the A product and strong sensitivity of the frequencies and intensities of the ν(OH) bands to any perturbation of the OH stretch mode make identification and assignment of the bands occurring in the OH stretch region particularly difficult. However the whole set of A bands allows us to tentatively identify ethylene glycol nitrite in the studied matrices. Ethylene glycol nitrite can be formed as the primary photolysis product in double-addition reaction of OH and ONO radicals to the C═C bond of the ethylene molecule.

The 1565 cm^{-1}, B band appears in the vicinity of the 1562 cm^{-1} ν_2(N═O) stretching vibration of the HNO radical, which suggests that the band may be due to the complexed HNO radical. In this region may appear the ν(N═O) stretching vibration of the nitrosyl group and the asymmetric stretching $\nu(NO_2)$ vibration of the nitro group. Double-addition reaction of OH and NO_2 photofragments to the C═C bond would lead to formation of 2-nitroethanol, but this is excluded on the basis of the following reasons. The spectra of the $HOH_2C-CH_2-NO_2$ molecule isolated in an argon matrix reveal two intense absorptions at 1570 and 1373.9 cm^{-1} due to the asymmetric stretch NO_2 vibration and to the coupled symmetric stretch NO_2 and COH bending vibrations.[29] The absence in our spectra of one of two most characteristic vibrations of the 2-nitroethanol molecule indicates that this molecule is not the primary photoproduct of the nitric acid−ethylene reaction.

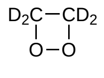
All four C bands at 3524, 2637, 1323, and 888 cm^{-1} appear, respectively, in the vicinity of the 3522.3, 2635.5, 1321.4, and 897.0 cm^{-1} HNO_3 monomer absorptions. The bands disappear after matrix annealing. So, the species can be identified with confidence as the HNO_3 monomer in an unstable site or weakly perturbed by another photolysis product.

The identification of D species is not straightforward. The D bands (3635, 1194, 1096, 925, 864, 582 cm^{-1}) appear with reasonable yield in the laser experiment and are extremely weak or are not observed at all in mercury lamp experiments, the bands are very sensitive to matrix annealing. The 3635 cm^{-1} band characteristic of the ν(OH) stretch vibration proves the presence of an OH group in the species D. The 1096, 864 cm^{-1} bands are observed at frequency values close to the absorptions corresponding to CCO asymmetric and symmetric stretching vibrations of *trans*-ethanol (1091.7, 886.7 cm^{-1}).[28] The 1194 cm^{-1} band may be due to the δ(COH) bending vibration which is expected to occur in this region of the spectrum. The absorption at 582 cm^{-1} may be attributed to a CH_2 rocking vibration; in the spectrum of the CH_2OH radical the corresponding absorption was observed at 569 cm^{-1}. No absorption characteristic of D species was identified in the 1670−1500 cm^{-1} region, which suggests an absence of the nitro, nitrite, and nitroso groups in the species D; the NO_2, O−N═O, and −N═O groups all give rise to strong absorption in this region of the spectrum. The gas phase studies of the reaction of OH with ethylene demonstrated that at low temperatures the reaction mechanism is dominated by electrophilic addition of OH to the double bond.[30] So, the species D is tentatively identified as the $HOH_2C═CH_2$ radical.

The E, F, and G species appear with higher yield when the matrices are irradiated with output of the mercury lamp. The species E is characterized by one band only observed at 1755 cm^{-1}; no other bands in the studied spectra were found to have the same relative intensity with respect to the 1755 cm^{-1} absorption in the performed experiments. The band is stronger in mercury lamp experiments but is also well-defined in laser experiments. The 1755 cm^{-1} absorption occurs in the C═O stretch region and suggests the presence of a −CHO group in species E; the C═O stretch vibrations of formaldehyde and acetaldehyde in argon matrices are observed in this region of the spectrum.[31,32] Lack of any other band accompanying the 1755 cm^{-1} absorption suggests that species E does not involve groups that give rise to characteristic, intense bands of intensity comparable to the C═O stretch absorption (like COH, NO_2, NO, ONO). In the C_2D_4/HNO_3 experiment the counterpartner of the 1755 cm^{-1} band was identified at 1742.3 cm^{-1}. The 13.7 cm^{-1} isotopic shift of the 1755 cm^{-1} absorption suggests that the band may be due to the C═O stretch vibration in a perturbed acetaldehyde molecule and rather excludes its assignment to formaldehyde. The 44.2 cm^{-1} deuterium isotopic shift was observed for the C═O stretch vibration in formaldehyde, whereas the ca. 10 cm^{-1} deuterium isotopic shift was found for the corresponding vibration in acetaldehyde.[31,32] Acetaldehyde is one of the probable decomposition products of the energized HOH_2C-CH_2 radical. The studies of the reaction of OH with ethylene in discharge flow reactors indicated the formation of the following products: $HOCH_2CH_2$, CH(OH)Me, MeCHO and H, and HCHO and Me.[33] The larger intensity of the 1755 cm^{-1} band in the mercury lamp experiment than in the laser experiment supports an identification of the acetaldehyde molecule as a decomposition product of the HOH_2C-CH_2 radical; the low yield of the radical in the mercury lamp experiment is most probably due to its photodecomposition. The acetaldehyde molecule formed in decomposition reaction of the $HOCH_2CH_2$ radical may be trapped in an unstable site, and the shift of the 1755 cm^{-1} band to 1750.5 cm^{-1} after matrix annealing may be due to the change of site geometry or to the complex formation between the acetaldehyde molecule and another molecule present in the matrix.

The species F is tentatively identified as peroxynitrous acid, HOONO, complexed with the ethylene molecule. The bands observed at 3404.5, 3419 cm^{-1} are assigned to perturbed OH stretch vibrations of *cis-perp*-HOONO (PB) and *trans-perp*-HOONO (PA) conformers; the corresponding bands are observed at 3545.5 (PB) and 3563.3 cm^{-1} (PA) for HOONO monomers. The two bands show 141 (PB), 144 (PA) cm^{-1} red shifts when the two HOONO conformers are complexed with C_2H_4. For comparison the OH stretch vibrations of HNO_3, *trans*-HONO, and *cis*-HONO are ca. 220, 137, and 103 cm^{-1} red shifted when the respective molecules are complexed to ethylene. The 3404.5 cm^{-1} band observed in C_2H_4/HNO_3 experiments is shifted to 3402.5 cm^{-1} in C_2D_4/HNO_3 experiments (the deuterium counterpartner of the 3419 cm^{-1} band was not observed), as expected for the band due to the −OH group hydrogen bonded to C_2H_4, C_2D_4 molecules. As was discussed earlier in this paper, the OH stretches of perturbed HNO_3 are observed at 3307.4, 3300.8 cm^{-1} for the $HNO_3 \cdots C_2H_4$ complex and are red shifted to 3304.7, 3297.8 cm^{-1} for the $HNO_3 \cdots C_2D_4$ complex. In the C_2D_4/DNO_3 experiment the counterpartners of the 3419, 3404.5 cm^{-1} absorptions were identified at 2527, 2519.0 cm^{-1}, respectively. The isotopic shift ratios, 3404.5/2519.0 = 1.35 and 3419/2527 = 1.35, support the assignment of the 3404.5, 3419 cm^{-1} bands. The 1407, 1395.0 cm^{-1} absorptions occurring in C_2H_4/HNO_3 experiments are tentatively assigned to perturbed HOO bending vibrations of *trans-perp* (PA) and *cis-perp* (PB) HOONO conformers bonded to the ethylene molecule. The 1407, 1395 cm^{-1} bands are 35 and 31 cm^{-1} blue shifted from the corresponding bands of HOONO monomers. In C_2H_4/DNO_3 experiments their corresponding counterpartners were identified at 1145, 1141 cm^{-1}, which leads to isotopic shift ratios (1.23, 1.22, respectively) of values similar to those characteristic of the corresponding vibrations of HOONO monomers (1364.1/1089.7 = 1.25 for PB and 1772.5/1091.7 = 1.26 for PA). Unfortunately, no perturbed ν_7 mode of the ethylene molecule was identified for the $C_2H_4 \cdots HOONO$ complex. This may be due to the possibility that the ν_7, C_2H_4 absorption for this complex is weaker than the absorptions due to the perturbed HOONO modes. In the spectra of the studied $C_2H_4 \cdots HNO_3$ complex and in the spectra of the previously reported $C_2H_4 \cdots HF$,[12] $C_2H_4 \cdots HONO$[34] complexes the band due to the ν_7 mode of bonded C_2H_4 was found to be ca. 4 times weaker than the band due to bonded OH or HF groups. The possibility that the band due to the ν_7, C_2H_4 mode of the $C_2H_4 \cdots HOONO$ complex coincides with the corresponding absorption of the $C_2H_4 \cdots HNO_3$ complex also has to be taken into account. Thus, a very low yield of the $C_2H_4 \cdots HOONO$ complex in the studied matrices, the relatively small intensity of the ν_7 C_2H_4 band as compared to the ν(OH) band, and the possibility of coincidence of the perturbed ν_7, C_2H_4 absorptions for the $C_2H_4 \cdots HOONO$, $C_2H_4 \cdots HNO_3$ complexes seem to be a reasonable explanation of the fact that we do not observe in the studied spectra the absorption due to the ν_7 mode of C_2H_4 complexed with the HOONO molecule.

The bands corresponding to G species are more intense in the mercury lamp experiment; their intensities increase with prolonged photolysis and after matrix annealing, which suggests that they are due to secondary photolysis products. They probably correspond to more than one product; due to their weak intensity, it was difficult to estimate the relative intensity of the G bands in different experiments. The 3342, 1724, 1246, 1130, 1076, and 843 cm^{-1} bands have frequency values close to the 3300, 1748.2, 1270, 1116.5, 1075, and 863.5 cm^{-1} bands observed for glycoaldehyde.[35] The hydrogen-bonded complex between glycoaldehyde and HNO could be the photolysis product of energized ethylene glycol nitrite: $[HOH_2C-CH_2ONO]^* \Rightarrow HOH_2CCHO \cdots HNO$. The relatively large shifts of the observed bands from the glycoaldehyde monomer bands may be justified by the replacement of an intramolecular hydrogen bond by an intermolecular hydrogen bond to HNO. The photolysis studies of methyl nitrite in low-temperature matrices have shown that the photodecomposition product of CH_3ONO is a hydrogen-bonded complex between H_2CO and HNO.[36] The obtained spectra suggest that the 3342 cm^{-1} band observed in the $C_2H_4+HNO_3$ experiment and tentatively assigned to the ν(OH) vibration of glycoaldehyde is shifted to 2475 cm^{-1} both in $C_2D_4+HNO_3$ and $C_2D_4+DNO_3$ experiments. This indicates a rather complex photoprocess by which $HOH_2CCHO \cdots HNO$ is formed. It is known that in the primary photodissociation reaction of CH_3ONO the CH_3O and NO radicals are formed, which may further react to form the $H_2CO \cdots HNO$ complex.[37] Thus, it is not excluded that in the primary photodissociation reaction of ethylene glycol nitrite the OHH_2CCH_2O and NO radicals are produced ($HOH_2CCH_2ONO \Rightarrow HOH_2CCH_2O + NO$ or $HOD_2CCD_2ONO \Rightarrow HOD_2CCD_2O + NO$). The shift of the 3342 cm^{-1} band observed in the $C_2H_4+HNO_3$ to 2475 cm^{-1} in $C_2D_4+HNO_3$ experiment suggests that this is the hydrogen atom of the OH group that reacts with NO to form the $DOD_2CCDO \cdots HNO$ complex. Intuitively it might be expected that in the abstraction reaction of the hydrogen atom from the HOD_2CCD_2O radical an oxygen-bridged species is formed:



Unfortunately, due to the very low yield of the G product, the above considerations are speculative.

Mechanism of Photolysis. The main products formed on photolysis of $HNO_3/C_2H_4/Ar$ matrices are peroxynitrous acid, OH, and NO_2, i.e. the products of HNO_3 photolysis in solid argon. This is confirmed by high relative intensity ratios of peroxynitrous acid absorptions with respect to the bands tentatively assigned to the products formed in reaction of HNO_3 photofragments with C_2H_4. So, most of the OH and NO_2 fragments, formed in the photodissociation process of the $HNO_3-C_2H_4$ complex and trapped in one matrix cage with the C_2H_4 molecule, recombine and form HNO_3 and HOONO. These processes explain the formation of an unstable site for the HNO_3 molecule (C species) as well as the formation of the C_2H_4-HOONO complex (F species). The HNO_3 molecule recombined from OH and NO_2 photofragments may be oriented in such a way with respect to the C_2H_4 molecule trapped in the same matrix cage that the $C_2H_4-HNO_3$ complex is reproduced. If, however, the orientation of the recombined HNO_3 molecule does not favor the hydrogen bond interaction between the two molecules, then the HNO_3 molecule is trapped in unstable geometrical arrangement (i.e. in an unstable site). In a similar way the HOONO molecule formed by recombination of OH and NO_2 may interact with the C_2H_4 molecule trapped in the same cage, forming the C_2H_4-HOONO complex.

The absorptions of the products formed in addition reactions of OH and NO_2 photofragments to the ethylene molecule allowed us to only tentatively identify the reaction products. The obtained results suggest that ethylene glycol nitrite (A species) is formed in a double-addition reaction of OH and NO_2 to the C=C bond of ethylene. The A species is not sensitive to matrix annealing and decomposes on prolonged photolysis, as expected for ethylene glycol nitrite molecules. Ethylene glycol nitrite may photolyze to glycoaldehyde and HNO; the photolysis studies of methyl nitrite in low-temperature matrices have shown that the primary photodecomposition product of CH_3ONO is the $H_2CO-HNO$ hydrogen-bonded complex.[35]

The analysis of the obtained results also suggests that in a single-addition reaction of the OH radical to the C_2H_4 molecule the HOH_2CCH_2 radical (D species) is formed. But the identification of this radical is rather tentative, as the bands assigned to the radical are very weak and the performed isotopic studies are only fragmentary. The infrared spectra of the HOH_2CCH_2 species have not been reported so far. The higher concentration of the radical in laser experiments than in mercury lamp experiments can be readily explained by the fact that the radical decomposes easily when photolyzed with broad band output of the mercury lamp. The possible product of photolytic decomposition of HOH_2CCH_2 is CH_3CHO (species E).

7. Conclusions

Infrared studies of the $HNO_3-C_2H_4$ system and its deuterated isotopomers in argon matrices indicate the existence of a stable 1/1 π-electron hydrogen-bonded $HNO_3\cdots C_2H_4$ complex in two trapping sites. Eight perturbed HNO_3 vibrations and two perturbed C_2H_4 vibrations were identified for the complexes trapped in the two sites. The spectroscopic analysis of the complexes proves that in the stable 1/1 complexes the OH group is bonded to the π-electron system in an out of plane position. The spectra also indicate an existence of a less stable 1/1 complex.

The main products of photolysis of nitric acid/ethylene/argon matrices are nitric acid and peroxynitrous acid, i.e. the same products that are formed on photolysis of nitric acid/argon matrices, which means that most of the OH and NO_2 photofragments recombine and do not react with the C_2H_4 molecule. Peroxynitrous acid forms a hydrogen-bonded complex with ethylene molecules trapped in the same matrix cage. The new major photolysis product of the $C_2H_4-HNO_3$ complex is ethylene glycol nitrite, which is formed in a double-addition reaction of OH and NO_2 photofragments to ethylene. The spectra also suggest the formation of the HOH_2CCH_2 radical in a single-addition reaction of OH to ethylene.

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