ELSEVIER

Chemical Physics 228 (1998) 17–29

Chemical Physics

Infrared matrix isolation and theoretical studies of SO_2–HNO_3 and SO_2–HONO systems

Maria Wierzejewska *, Zofia Mielke, Robert Wieczorek, Zdzislaw Latajka

Faculty of Chemistry, University of Wroclaw, Joliot Curie 14, 53-343 Wroclaw, Poland

Received 22 July 1997

Abstract

Argon matrix infrared spectra of sulphur dioxide complexes with nitric or nitrous acid indicate formation of hydrogen-bonded structures. The red shifts of the OH stretching modes are equal to ca. 179, 51 and 40 cm^{-1} in SO_2–HNO_3, SO_2–HONO-trans and SO_2–HONO-cis complexes, respectively. Theoretical studies of the structure and spectral characteristics of the title complexes were carried out on the electron correlation level with 6-31G(d) basis set. For all studied systems only one stable structure was found with the OH group interacting with one oxygen atom of the sulphur dioxide molecule. The calculated infrared spectra reproduce well the frequencies and the intensities of the measured spectra. © 1998 Elsevier Science B.V.

1. Introduction

Sulphur compounds play a significant role in atmospheric chemistry. They are released to the atmosphere from a variety of sources including both natural and anthropogenic emissions. Sulphur dioxide — the most important S-containing pollutant — and its complexes have received growing attention in recent years.

Infrared studies of different isotopic species of SO_2 monomer and dimer isolated in low-temperature matrices have been a subject of many investigations [1–5]. Sodeau and Lee [6] studied photooxidation of sulphur dioxide in solid argon, nitrogen and oxygen.

Complexes containing the SO_2 molecule have also been studied both by microwave [7–11] and infrared spectroscopy [12–15] revealing a majority of possible structures. Schriver et al. [14] studied SO_2–H_2O interaction in argon and nitrogen matrices. They concluded that the 1:1 SO_2–H_2O complex is of charge transfer type with SO_2 acting as an electron acceptor. This was later confirmed by microwave spectra [9]. In turn, SO_2–HF and SO_2–HCl hetrodimers appeared to form hydrogen-bonded structures with a proton directed toward one of the oxygen atoms of sulphur dioxide [7,15].

Both nitric and nitrous acids are also important atmospheric species. The infrared spectra of HNO_3 and HONO monomers were extensively studied in the gas phase and low-temperature matrices [16–19]. Recently several papers were published on HNO_3

---

* Corresponding author.

PII S0301-0104(97)00336-4

Table 1
Calculated geometry of the SO_2–HNO_3 complex and HNO_3 and SO_2 monomers at the MP2 level[a]

Parameter	SO_2–HNO_3 complex	HNO_3	SO_2
$R(O_3 \cdots O_8)$	2.908		
r(N–O)	1.394	1.412	
$r(N=O_2)$	1.230	1.226	
$r(N=O_5)$	1.218	1.216	
r(O–H)	0.990	0.983	
$r(S–O_8)$	1.484		1.477
$r(S–O_6)$	1.475		1.477
$r(O \cdots H)$	1.920		
$\Theta(O–N=O_2)$	116.6	115.8	
$\Theta(O–N=O_5)$	114.0	113.6	
$\Theta(O_2=N=O_5)$	129.3	130.6	
Θ(N–O–H)	103.7	102.1	
$\Theta(O_3–H–O_8)$	176.0		
$\Theta(H–O_8–S)$	120.1		
$\Theta(O_6–S–O_8)$	118.9		119.8
$\varphi(O_3–O_8–S–O_6)$	30.3		
ΔE_{MP2}	−17.66		

[a] Bond lengths in Å, bond angles in degrees, ΔE_{MP2} in kJ/mol.

and HONO complexes with various bases of atmospheric significance [19–24].

In this paper we report the results of a matrix isolation infrared study and ab initio calculations for sulphur dioxide complexes with nitric and nitrous acids.

2. Experimental

2.1. Matrix isolation studies

Sulphur dioxide (Matheson Gas Products) was used without further purification. The gaseous HNO_3 was prepared in a vacuum line by treating KNO_3 kept at 0°C with concentrated H_2SO_4.

NH_4NO_2 salt was used as a source of the nitrous acid. The equilibrium $NH_4NO_{2(s)} \rightleftharpoons NH_{3(g)} + HONO_{(g)}$ gives a partial pressure of NH_3 and HONO equal to 0.04 mbar at 298 K. Two different deposition setups were used to obtain matrix isolated HONO molecules. The detailed description of the first method was given elsewhere [19]. Briefly, the matrix gas mixtures were prepared by adding ~ 30 mbar of argon to a 1 l bulb containing a small amount of NH_4NO_2. The resultant concentration of the HONO/NH_3/Ar mixture was equal to 1:1:800. Such a mixture was deposited through a stainless-steel vacuum system onto a sample holder. SO_2/Ar mixtures were sprayed simultaneously through the separate inlet. In the second method HONO and NH_3 were evaporated from a small glass tube containing NH_4NO_2 maintained at room temperature placed in the vacuum vessel of the cryostat. Argon or SO_2/Ar mixtures were deposited directly into the cryostat in such a way that they mixed with HONO (NH_3)

Table 2
Calculated geometry of the SO_2–HONO-trans and SO_2–HONO-cis complexes and the monomers at the MP2 level[a]

Parameter	SO_2–HONO-trans	trans-HONO	SO_2–HONO-cis	cis-HONO	SO_2
$R(O_3 \cdots O_6)$	2.908		2.999		
$r(N–O_3)$	1.400	1.423	1.373	1.386	
$r(N=O_2)$	1.203	1.197	1.215	1.210	
$r(O_3–H)$	0.984	0.979	0.994	0.991	
$r(S–O_6)$	1.481		1.482		1.477
$r(S–O_7)$	1.474		1.474		1.477
$r(O_6 \cdots H)$	2.004		2.006		
Θ(O–N=O)	111.1	110.3	113.4	112.8	
Θ(N–O–H)	101.6	101.9	106.2	104.6	
$\Theta(O–H–O_6)$	151.7		176.9		
$\Theta(H–O_6S_5)$	120.1		120.6		
$\Theta(O_6SO_7)$	119.2		119.0		119.8
$\varphi(O_3O_6SO_7)$	50.7		−30.5		
ΔE_{MP2}	−13.6		−11.8		

[a] Bond lengths in Å, bond angles in degrees, ΔE_{MP2} in kJ/mol.

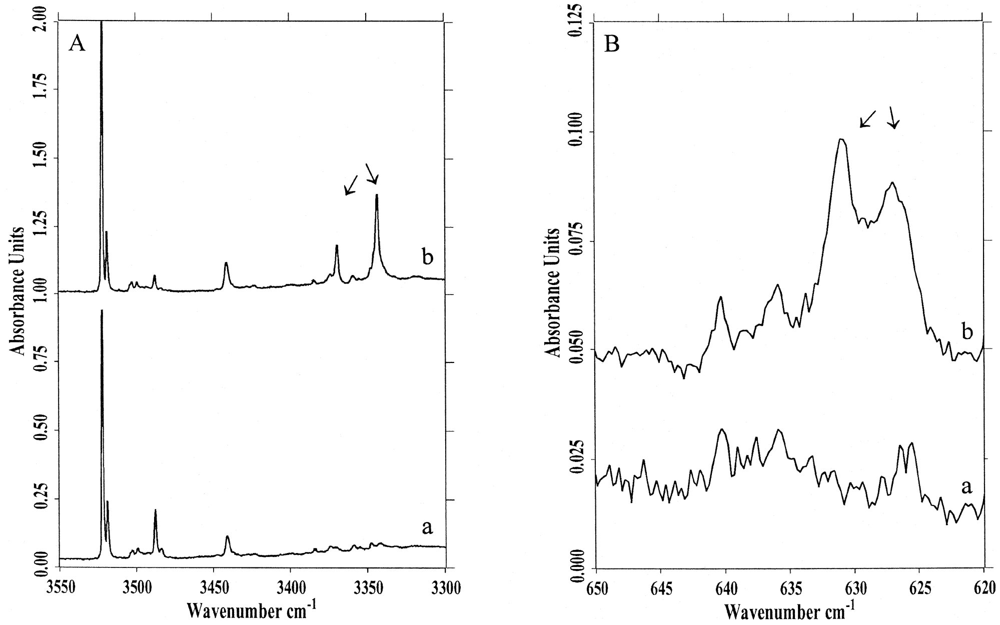

Fig. 1. The ν_1 OH stretching (A) and 650–620 cm^{-1} (B) regions in the spectra obtained for matrices: HNO_3/Ar = 1:1000 (*a*) and HNO_3/Ar = 1:1000 codeposited with SO_2/Ar = 1:250 (*b*).

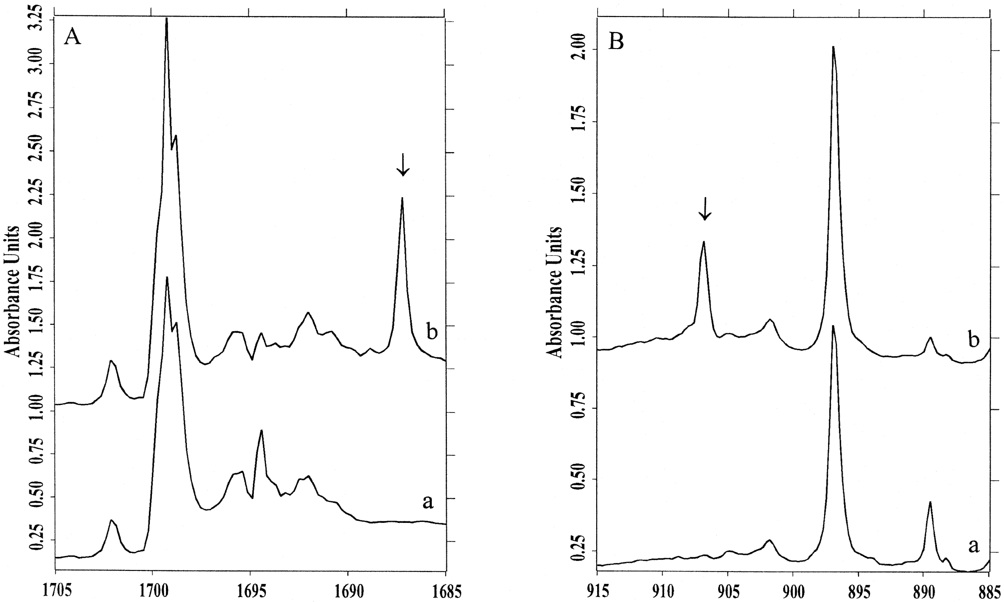

Fig. 2. The ν_2 NO_2 asymmetric stretching (A) and ν_5 N–O stretching (B) regions in the spectra of the same matrices as in Fig. 1.

vapour inside the vacuum chamber. The HONO/Ar ratio was varied by changing the flow rate of the matrix gas. As NH_3 was present as contaminant in the studied matrices several experiments have also been performed on $SO_2/NH_3/Ar$ matrices in order to identify the absorptions due to SO_2 vibrations perturbed by the NH_3 molecule.

The SO_2/Ar and HNO_3/Ar mixtures were prepared by standard manometric techniques and their concentrations ranged between 1:1500 and 1:100 and between 1:1500 and 1:500 for SO_2/Ar and HNO_3/Ar, respectively.

Gold-plated copper mirror was used as a sample holder and was maintained at 20 K (11 K for IR measurements) by means of a closed-cycle helium refrigerator (Air Products, Displex 202A). Infrared spectra were recorded in reflection mode with a resolution of 0.5 cm^{-1} by means of a Bruker 113 v FTIR spectrometer.

2.2. Computational details

Ab initio calculations were carried out using the Gaussian 94 [25] package of computer codes. The structures of all complexes and corresponding isolated monomers were fully optimized by using the second-order Möller–Plesset perturbation theory (MP2) with the 6-31G(d) basis set [26,27]. This basis set is relatively compact and literature data show that it gives quite accurate results [28–30]. Vibrational frequencies and intensities were computed for SO_2–HONO-cis, SO_2–HONO-trans and SO_2–HNO_3 complexes and for the monomers. Single-point energies were calculated at the MP2 level using the 6-311++(2d,2p) basis set [31,32]. The optimized geometries of the monomers and of the complexes are presented in Tables 1 and 2.

Interaction energies were corrected by the Boys–Bernardi full counterpoise correction [33] at both the SCF and MP2 levels.

3. Results

3.1. Experimental spectra

Blank experiments were conducted on all reagent molecules deposited separately. Their spectra agreed well with those previously reported [4,19,20].

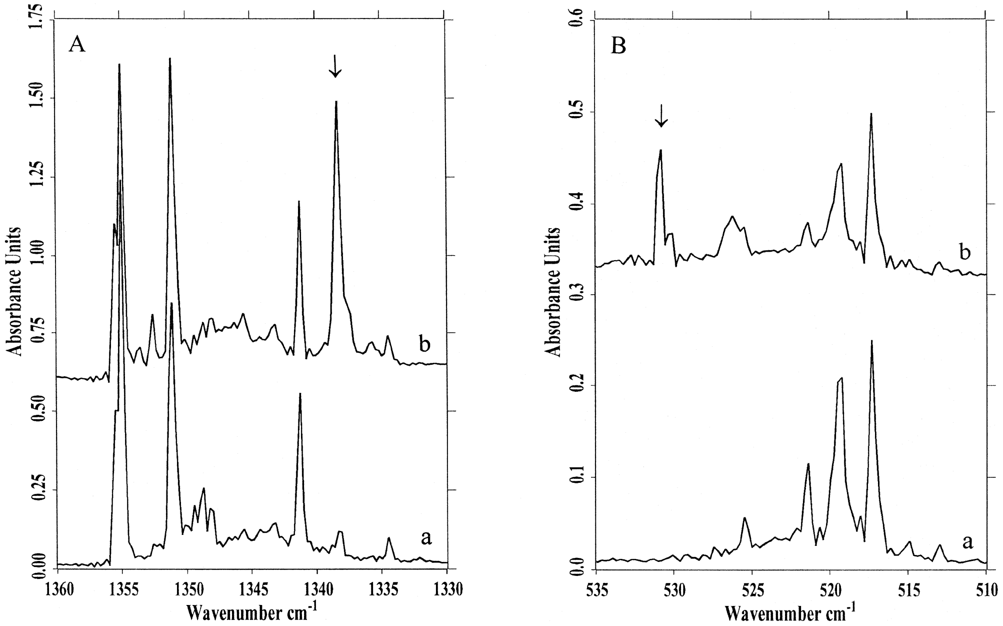

Fig. 3. The SO_2 modes: ν_3 asymmetric stretching (A) and ν_2 bending (B) regions in the spectra of matrices: SO_2/Ar = 1:500 (*a*) and HNO_3/Ar = 1:1000 codeposited with SO_2/Ar = 1:250 (*b*).

3.1.1. Nitric acid–sulphur dioxide

Codeposition of mixtures of HNO_3/Ar and SO_2/Ar revealed several new absorptions which could not be assigned to the parent molecules. Figs. 1–3 present the characteristic regions of the spectra of $HNO_3/SO_2/Ar$ matrices obtained by simultaneous deposition of the HNO_3/Ar and the SO_2/Ar mixtures of various concentrations. The product bands can be grouped into two sets: those at 3369.1, 3343.3, 1687.2, 1302.8(sh), 906.0, 631.0 and 627.1 cm^{-1} due to the perturbed HNO_3 molecule, and those at 1338.4, 1143.4, 1142.1 sh and 530.8 cm^{-1} appearing in the vicinity of the vibrations of the parent SO_2 molecule.

The above absorptions were observed for all concentrations studied. Furthermore, the intensities of all product bands grew in a similar way when the excess of SO_2 was increased. After annealing small changes

Table 3
Comparison of experimental and calculated frequencies ν (cm^{-1}) and intensities I (km mol^{-1}) for HNO_3 and SO_2 monomers and SO_2–HNO_3 complex

HNO_3 and SO_2 monomers					SO_2–HNO_3 complex					Assignment
exp.		calc.			exp.		calc.			
ν	I/I_N	ν	I[a]	I/I_N[b]	ν	I/I_N	ν	I	I/I_N	
3522.4 3519.0	1.4	3662	92	0.5	3369.1 3343.3	7.3	3543	510	3.4	ν_1 O–H stretch
1699.3 1694.5	2.4	1904	193	1.0	1687.2	2.6	1884	233	1.6	ν_2 NO_2 asym. stretch
1321.6	1.7	1372	108	0.6	1302.8 sh		1365	244	1.6	ν_3 NO_2 sym. stretch
1304.4	0.7	1352	217	1.1			1439	80	0.5	ν_4 NOH i.p. bend
897.0	1.0	909	191	1.0	906.0	1.0	941	148	1.0	ν_5 N–O stretch
764.2 763.5	0.1	755	9	0.05			763	2	0.01	ν_8 ONO_2 o.p. bend
		659	40	0.02			676	4	0.03	ν_6 NO_2 scissors
587.0	0.05	580	11	0.06			607	4	0.03	ν_7 ONO_2 i.p. bend
451.0 450.3	1.0	501	144	0.8	631.0 627.2	1.2	674	124	0.8	ν_9 NOH torsion
1355.0		1312	81		1338.4	2.2	1298	86	0.6	ν_3 SO_2 asym. stretch
1152.0		1083	13		1143.4 1142.1 sh	0.3	1084	26	0.2	ν_1 SO_2 sym. stretch
519.9		488	32		530.8	0.2	487	47	0.3	ν_2 SO_2 bend

[a] In the experimental intensities both component bands were included in the case where splitting due to the site effect was observed.
[b] I_N is the intensity of the ν_5 N–O stretching vibration.

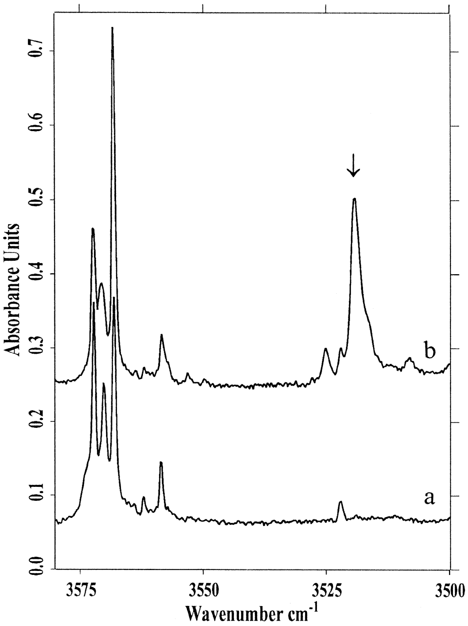

Fig. 4. The ν_1 OH stretching region in the spectra of matrices: HONO/Ar = 1:800 (*a*) and HONO/Ar = 1:800 codeposited with SO_2 /Ar = 1:100 (*b*).

occurred only in the ν_1 OH stretching mode region. A slight broadening from the high-frequency side of the 3343.3 cm^{-1} band was observed. The frequencies of all product absorptions observed in the spectra of $HNO_3/SO_2/Ar$ matrices are collected in Table 3.

3.1.2. Nitrous acid–sulphur dioxide complex

Due to the way of production of HONO and its instability in the gas phase some amounts of NH_3, H_2O, NO_2 and NO were always present in the matrices as impurities. However, the concentrations of HONO decomposition products and NH_3 were low enough for studying the HONO complex with sulphur dioxide. In turn, examination of the $SO_2/NH_3/Ar$ matrices allowed us to identify the absorptions due to perturbed SO_2 vibrations in the SO_2–NH_3 complex at 1335.4, 1019.0 and 525.6 cm^{-1}. Weak bands due to this complex are also present in the studied SO_2/HONO(NH_3)/Ar spectra but are not discussed in the paper. The detailed analysis of the spectra of HONO monomers was recently published. All six fundamentals of HONO-trans and four fundamentals of HONO-cis were identified [19].

When HONO/Ar mixture was codeposited with sulphur dioxide/Ar mixture several new bands were observed in the spectra which were neither due to the parent molecules nor due to the contaminations.

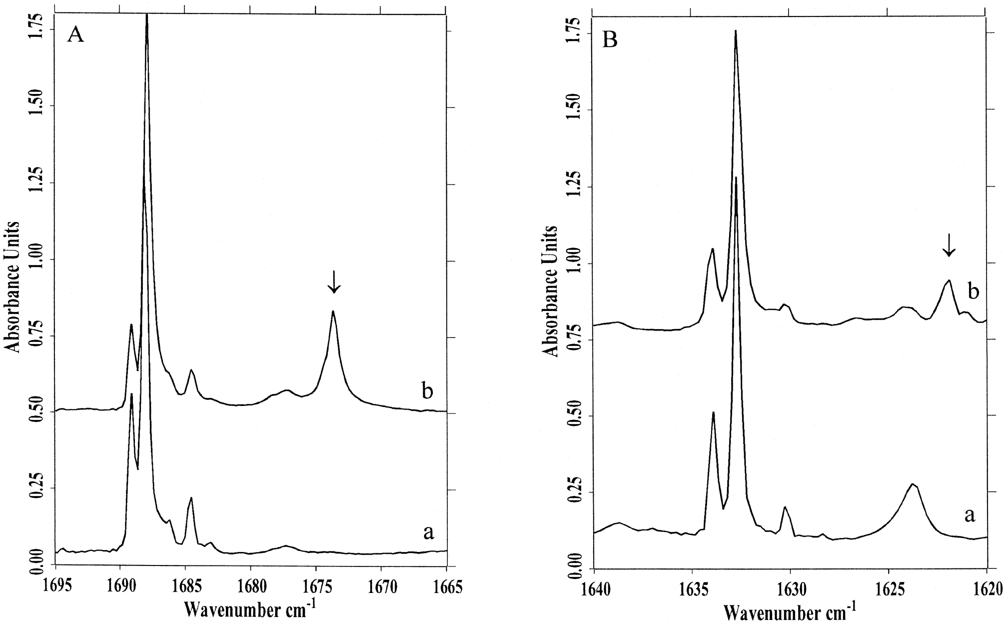

Fig. 5. The ν_2 N=O stretching region for trans (A) and cis (B) SO_2–HONO complexes in the spectra of the same matrices as in Fig. 4.

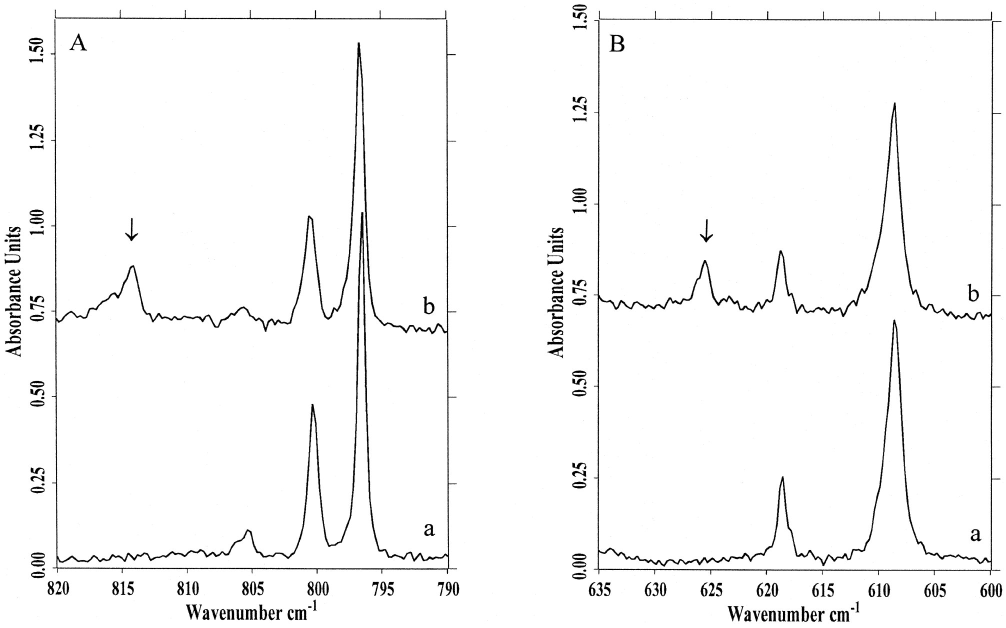

Fig. 6. The ν_4 N–O stretching and ν_5 ONO bending regions in the spectra of the same matrices as in Fig. 4.

Figs. 4–6 present selected regions of the infrared spectra obtained for HONO/SO_2/Ar matrices. The product absorptions appeared at 3525.3, 3519.5, 3516.9(sh), 1673.8, 815.8(sh), 814.1 and 625.6 cm^{-1} in the vicinity of HONO-trans absorptions, and at 1621.9 cm^{-1} in the vicinity of HONO-cis band. In addition, a very weak absorption in the ν_1 OH stretching region of cis-HONO was localized at 3372.3 cm^{-1}. The band appeared only in the spectra of the matrices containing relatively high concentra-

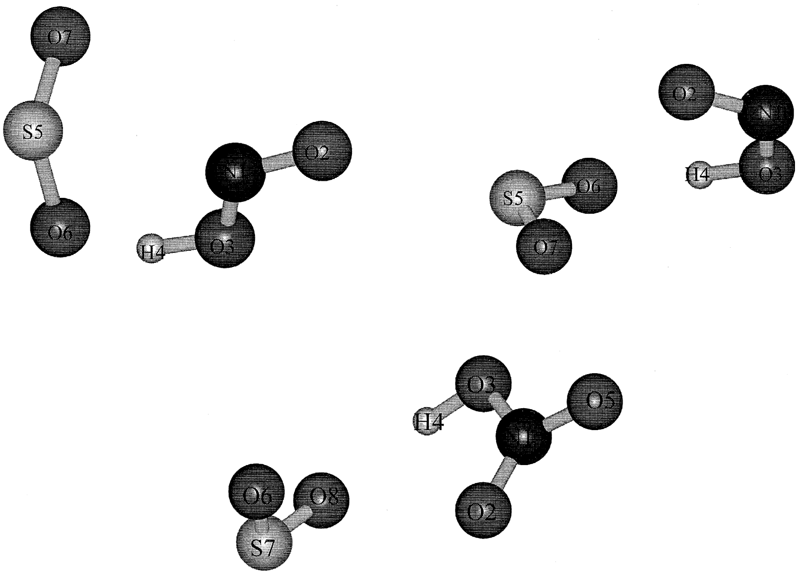

Fig. 7. Optimized structures of the SO_2–HNO_3, SO_2–HONO-trans and SO_2–HONO-cis complexes.

Table 4
Comparison of experimental and calculated frequencies ν (cm^{-1}) and intensities I (km mol^{-1}) for HONO monomers and SO_2–HONO complexes

trans-HONO monomer					trans-HONO–SO_2					Assignment
exp.		calc.			exp.	calc.				
ν	I/I_N	ν	I^a	I/I_N^b	ν	I/I_N	ν	I	I/I_N	
3572.6 3568.5	1.1	3700	79	0.4	3525.3 3519.5 3516.9 sh	1.6	3633	273	1.5	ν_1 OH stretch
1689.1 1688.0	1.5	1665	65	0.3	1673.8	1.2	1656	58	0.3	ν_2 N=O stretch
1265.8 1263.9	1.2	1320	199	1.1			1391	207	1.2	ν_3 NOH bend
800.4 796.6	1.0	867	185	1.0	814.1 815.8 sh	1.0	924	178	1.0	ν_4 N–O stretch
608.7	0.8	631	99	0.5	625.6	0.5	675	53	0.3	ν_5 ONO bend
549.4 548.2	0.7	607	120	0.6			729	105	0.6	ν_6 OH torsion
1355.0		1312	81				1307	102	0.6	ν_3 SO_2 asym. stretch
1152.0		1083	13		1150.1 1151.0 sh	0.6	1089	23	0.1	ν_1 SO_2 sym. stretch
519.9		488	32				490	32	0.2	ν_2 SO_2 bend

cis-HONO monomer					cis-HONO–SO_2				Assignment
exp.		calc.			exp.	calc.			
ν	I/I_N	ν	I^a	I/I_N^b	ν	ν	I	I/I_N	
3412.4 3410.7	0.1	3526	30	0.1	3372.3	3483	266	0.9	ν_1 OH stretch
1634.0 1632.8	0.7	1624	122	0.4	1621.9	1617	110	0.4	ν_2 N=O stretch
		1363	4	0.01		1402	3	0.01	ν_3 NOH bend
853.1 850.2	1.1	947	324	1.0		1004	283	1.0	ν_4 N–O stretch
		655	14	0.04		680	8	0.03	ν_5 ONO bend
638.4	0.2	751	122	0.4		844	113	0.4	ν_6 OH torsion

[a] In the experimental intensities both component bands were included in the case where splitting due to the site effect was observed.

[b] I_N is the intensity of the ν_4 N–O stretching vibration.

tions of the complexes, e.g. in the annealed matrices with considerable excess of sulphur dioxide ($SO_2/Ar = 1:200$ or 1:100). One absorption at 1150.1 cm^{-1} with a weaker band at 1151.0 cm^{-1} close to the sulphur dioxide absorption were detected as well.

The frequencies of all product absorptions observed in the spectra of $HONO/SO_2/Ar$ matrices are collected in Table 4.

3.2. Ab initio calculations

Three different structures for each of the 1:1 sulphur dioxide–nitric (nitrous) acid complexes have been taken into account in the calculations. In two of them HONO or HNO_3 was acting as a proton donor with the OH group directed toward one of the oxygen atoms of the sulphur dioxide molecule or along the bisecting line of the OSO angle. In the third structure an oxygen atom of the acid and a sulphur atom of the SO_2 molecule were considered as sites of interaction. For all studied systems the hydrogen-bonded complex with the OH group interacting with one oxygen atom of SO_2 appeared to be the only stable structure. Similar geometry has been reported for SO_2–HF and SO_2–HCl complexes [7].

The fully optimized geometrical parameters of the complexes and isolated subunits calculated at the MP2 level with the 6-31G(d) basis set are presented in Tables 1 and 2 whereas the corresponding structures are shown in Fig. 7.

The calculated structural parameters change very little from the monomer values upon complexation. Nevertheless, the largest perturbation clearly correlates with the sites of complexation. We observed a rather small elongation of the O–H bond due to complex formation, which indicates a molecular and not an ion-pair type of hydrogen bond in the complexes. The intermolecular distance, measured between oxygen atoms of both subunits, is relatively long and equal to 2.908 Å for HNO_3 and trans-HONO complexes and 2.999 Å for cis-HONO system. We also find that all studied complexes are nonplanar, and mainly the oxygen atom of the SO_2 subunit which is not involved in hydrogen-bond bridge is above the complex plane. The energetics of binding of the studied complexes is reported in the last rows of Tables 1 and 2. In order to obtain a better determination of the binding energy additional single-point calculations were performed with a much larger 6-311++G(2d,2p) basis set applying the MP2 level and the previously optimized geometry. The strongest interaction was received for the SO_2–HNO_3 complex ($\Delta E_{MP2} = -17.6$ kJ/mol). Slightly less stable are complexes formed by HONO. The structure of the complex with trans-HONO form was found to be more stable than the structure with cis-HONO form by ~1.8 kJ/mol.

The calculated frequencies and intensities of the SO_2–HNO_3 and SO_2–HONO complexes and monomers are displayed in Tables 3 and 4, respectively, and compared with the experimental data. The relative intensities of the bands of both systems were calculated in respect to their ν(N–O) absorptions.

4. Discussion

4.1. Nitric acid–sulphur dioxide complex

Deposition of the $HNO_3/SO_2/Ar$ mixtures give rise to new infrared absorption bands which could not be assigned to the parent molecules and therefore must be due to product species. Furthermore, the relative intensities of the new bands are independent on matrix concentration. So, they can be assigned with confidence to the 1:1 SO_2–HNO_3 complexes.

In the ν_1 OH stretching region two new features were found at 3369.1 and 3343.3 cm^{-1} (Fig. 1A). They are 153.3 and 179.1 cm^{-1} red shifted from the corresponding vibration of the free HNO_3 in solid argon. Two weak product bands found at 631.0 and 627.1 cm^{-1} (see Fig. 1B) may be attributed to the perturbed out-of-plane deformation, ν_9 NOH, of nitric acid bonded to sulphur dioxide. The corresponding torsion vibration in the HNO_3 monomer spectrum appears as a doublet situated at 451.0 and 450.3 cm^{-1}, which gives the approximate blue shift equal to 178.4 cm^{-1}. The position of the ν_9 NOH mode for the SO_2–HNO_3 system matches with the out-of-plane deformation absorptions observed for other B–HNO_3 complexes. In the slightly weaker OC–HNO_3 complex the corresponding band is situated at 589 cm^{-1} and is 138 cm^{-1} blue shifted from the monomer value [20].

The doublet structure of the ν_1 OH stretching and ν_9 NOH out-of-plane deformation modes observed for the SO_2–HNO_3 complex is attributed to different matrix sites. This explanation is the most likely one considering the obtained data. The relative intensities of the two component bands of both fundamentals constantly are within the experimental error in the studied concentration range and after annealing experiments.

The ab initio calculations performed for the SO_2–HNO_3 complex predict the 119 cm^{-1} red shift for the ν_1 OH stretch and 173 cm^{-1} blue shift for the ν_9 NOH out-of-plane deformation in the SO_2–HNO_3 complex as compared to the HNO_3 monomer. These shifts match relatively well with the experimental data.

The formation of the SO_2–HNO_3 complex leads also to perturbation of several other HNO_3 modes. The product absorptions at 1687.2 and 1302.8 cm^{-1} are shifted down by 12.1 and 18.8 cm^{-1} from the ν_2 asymmetric NO_2 stretching and ν_3 symmetric NO_2 stretching modes of the HNO_3 monomerm, respectively. Another product band at 906.0 cm^{-1} corresponds to the ν_5 O–NO_2 stretching mode and shows 9.0 cm^{-1} blue shift from the corresponding mode of the non-bonded nitric acid. The calculated frequency shifts for the perturbed HNO_3 vibrations are slightly overestimated or underestimated, but the directions of the changes are properly predicted. The calculated intensities predicted for the bands due to the perturbed nitric acid in the SO_2–HNO_3 complex agree very well with the experimental spectra. The bands which are calculated to be the most intense ones appear to be the most pronounced features in the experimental spectra while those for which small intensities are predicted are not observed in the spectra.

Upon the complex formation new features are observed in the regions of all three fundamental modes of sulphur dioxide. They are situated at 1338.4, 1143.4 (1142.1 sh) and 530.8 cm^{-1} in the vicinity of the asymmetric and symmetric stretching and deformation SO_2 modes, respectively. Both asymmetric and symmetric stretching modes are red shifted by 16.6 and 8.6 (9.9) cm^{-1}, respectively, while the SO_2 bending vibration is moved to higher wavenumbers by 10.9 cm^{-1} compared to the sulphur dioxide monomer. The results of previous studies on various SO_2 complexes suggest that the magnitude and direction of the perturbation of SO_2 modes are not very conclusive as to the structure of the SO_2 complexes (see Table 5). For instance, the observed perturbation of the asymmetric and symmetric stretching SO_2 modes in the SO_2–HNO_3 complex is very much the same as that observed for the SO_2–$(CH_3S)_2$ complex [34] in spite of the entirely different type of interaction expected for these two aggregates.

4.2. Nitrous acid–sulphur dioxide complex

The set of bands observed in the spectra of HONO/SO_2/Ar matrices in the vicinity of trans-HONO modes can be assigned with confidence to the 1:1 SO_2–HONO-trans complex. Similarly, product bands found at close frequencies to the cis-HONO absorptions are attributed to the 1:1 SO_2–HONO-cis complex. As can be noted in Table 4 one new band at 3519.5 cm^{-1} with two weaker components at 3525.3 and 3516.9 cm^{-1} are observed in the stretch-

Table 5
Comparison of the SO_2 modes in various SO_2–X complexes isolated in argon matrices

Complex	ν_1 SO_2 sym. stretch	ν_2 SO_2 bend	ν_3 SO_2 asym. stretch	Reference
SO_2	1152.0	519.9	1355.0	[4]
SO_2–SO_2	1146.6	519.5	1341.3	[4]
SO_2–H_2O	1150.0	519.5	1343.3	[14]
SO_2–HF	1158.5			[15]
SO_2–$(CH_2SH)_2$	1144	522	1339	[34]
SO_2–$(CH_3S)_2$	1144	523	1338	[34]
SO_2–HNO_3	1143.4	530.8	1338.4	this work
SO_2–HONO	1150.1			this work

ing region of trans-HONO. The multiple structure of the ν_1 OH absorption is attributed to different trapping sites. A relatively large red shift of this mode in the SO_2–HONO-trans complex (~ 51 cm^{-1}) is remarkable for this hydrogen-bonded structure. The corresponding calculated ν_1 OH frequency (3633 cm^{-1}) is overestimated but its perturbation (67 cm^{-1}) is well predicted by ab initio calculations.

Three other perturbed modes of the complexed trans-HONO molecule were identified. The product band at 1673.8 cm^{-1} corresponds to the ν_2 N=O stretch and is 14.2 cm^{-1} red shifted with respect to the trans-HONO monomer. Both the frequency of the ν_2 N=O mode (1656 cm^{-1}) and its shift (9 cm^{-1}) are well predicted by the calculations. The ν_4 N–O stretching vibration of the SO_2–HONO-trans complex is identified at 814.1 cm^{-1} (see Fig. 6A). This band is shifted towards higher frequencies by 17.5 cm^{-1} from the corresponding absorption of the trans-HONO monomer. Analysis of the spectra of the B–HONO-trans complexes studied so far in argon matrices [36] shows that the perturbed ν_4 N–O mode is present as an intense band in most systems. The frequency of the N–O stretch increases in line when the frequency of the O–H stretch decreases due to the hydrogen-bond formation. The position of the ν_4 N–O band at 814.1 cm^{-1} in the SO_2–HONO-trans complex fits well to the series. The blue shift of the ν_4 N–O band in this complex agrees with the calculated shortening of the N–O bond (see Table 2) but the predicted ν_4 N–O frequency (924 cm^{-1}) is overestimated.

The band at 625.6 cm^{-1} (see Fig. 6B) is assigned to the ν_5 ONO bending mode. This band is blue shifted by 16.9 cm^{-1} with respect to the ν_5 ONO absorption of trans-HONO monomer. The calculations gave overestimated values of both the ν_5 ONO frequency (675 cm^{-1}) and its shift after complex formation ($\Delta\nu_{\text{calc}} = 44$ cm^{-1}).

Weaker shoulders observed from few wavenumbers apart from the main ν_1 OH and ν_4 N–O band in the spectra of the SO_2–HONO-trans complex are attributed to the site effect. Their relative intensities do not depend on SO_2 concentration in the matrix.

The existence of the SO_2–HONO-cis complex in the studied matrices is also proved by the measured spectra. However, in contrast with the SO_2–HONO-trans complex only two bands were identified for the cis complex. A very weak band at 3372.3 cm^{-1} is assigned to the ν_1 OH stretching vibration and the 1621.9 cm^{-1} band (see Fig. 5B) is assigned to the ν_2 N=O stretching mode. They are red shifted by ca. 40 cm^{-1} and 10.9 cm^{-1}, respectively in comparison with the corresponding cis-HONO monomer frequencies. The ab initio calculations performed for the SO_2–HONO-cis complex predicted very well the absolute value of the ν_2 N=O stretching mode (1617 cm^{-1}) and the frequency shifts of the ν_1 OH and ν_2 N=O stretching modes in the complex with respect to the HONO-cis monomer ($\Delta\nu_1^{\text{calc}} = 43$ cm^{-1}, $\Delta\nu_2^{\text{calc}} = 7$ cm^{-1}) but the calculated ν_1 OH frequency is overestimated.

The attempts to locate other modes of the SO_2–HONO-cis complex were fruitless. The concentration of the cis complex in the studied matrices may be expected to be smaller than the SO_2–HONO-trans complex [19] and is probably too low for weaker absorptions to be detected.

4.3. Nitric and nitrous acids complexes with various bases

The displacement of the OH stretching mode in a hydrogen-bonded complex from the corresponding monomer value is a good indication of the strength of the interaction. In the B–HNO_3 complexes the observed shift of the OH stretching vibration increases in line with the increasing strength of the base (the latter can be related to the gas-phase proton affinity, PA). Sulphur dioxide (PA = 657 kJ/mol) forms a complex of intermediate strength between OC–HNO_3 (PA = 590 kJ/mol) and C_2H_4–HNO_3 (PA = 669 kJ/mol). The corresponding $\Delta\nu$ (OH) shifts are equal to 179.1, 123.4 and 215.0 cm^{-1} for SO_2–HNO_3, OC–HNO_3 and C_2H_4–HNO_3 complexes, respectively. The red shift of the OH stretch in a given complex is accompanied by the blue shift of the OH out-of-plane deformation mode. The perturbation of the OH out-of-plane deformation is equal to 138.4 cm^{-1} for OC–HNO_3 and 158.7 cm^{-1} for the C_2H_4–HNO_3 complex. The shift observed here for the SO_2–HNO_3 system (178.5 cm^{-1}) is slightly higher than might be expected in the series. This indicates increase in rigidity [35] of the SO_2–HNO_3 complex as compared to the neighbouring system: C_2H_4–HNO_3.

Trends observed in the series of complexes formed by HONO-trans with various bases have been recently presented [36]. The shift of the OH stretching vibration in the SO_2–HONO-trans complex is relatively small (51 cm^{-1}). This value places this system between CH_4–HONO and OC–HONO complexes in spite of the higher proton affinity value of SO_2 (PA = 657 kJ/mol) than those of CH_4 and CO (540 and 590 kJ/mol, respectively). The perturbation of the OH stretching mode in the CH_4–HONO and OC–HONO systems is equal to 23 and 72 cm^{-1}, respectively.

Comparison of the OH stretching vibration shifts in the complexes of nitrous and nitric acids with the same base shows that much stronger hydrogen bonds are formed in B–HNO_3 than in corresponding B–HONO-trans complexes. The same is true for the here studied SO_2–HNO_3 and SO_2–HONO systems.

5. Conclusions

Infrared matrix isolation studies and ab initio calculations indicate that HNO_3 and trans- and cis-HONO form with sulphur dioxide hydrogen-bonded complexes with the OH group directed toward one oxygen atom of the SO_2 molecule. The binding energy at the MP2 level with 6-311 + + G(2d,2p) basis set is equal to 17.6, 13.6 and 11.8 kJ/mol for SO_2–HNO_3, SO_2–HONO-trans and SO_2–HONO-cis complexes, respectively. Five perturbed HNO_3 vibrations and all three perturbed SO_2 fundamentals were identified for the 1:1 SO_2–HNO_3 complex isolated in argon matrix. The SO_2–HONO-trans system is characterized by four frequencies of the HONO-trans molecule and one frequency of the SO_2 subunit in the complex. Only two perturbed HONO modes were found for the SO_2–HONO-cis complex due to the much smaller concentration of the latter in comparison with the trans complex. The shifts of the OH stretching vibration in respect to the corresponding monomer values are equal to 179, 51 and 40 cm^{-1} for SO_2–HNO_3, SO_2–HONO-trans and SO_2–HONO-cis complexes, respectively. This confirms the predicted (by ab initio calculations) weakening of the hydrogen-bond interaction in the same order. The observed perturbation of other internal modes in complexes is consistent with this conclusion. The calculated spectra reproduce well the frequencies and the intensities of the measured spectra of the studied complexes.

Acknowledgements

ZM gratefully acknowledges financial support from the Polish State Committee for Scientific Research (Grant KBN No. 2 0848 91 01). RW and ZL gratefully acknowledges financial support from the University of Wroclaw. Wroclaw Supercomputer Centre, Poznań Supercomputer Centre and Interdisciplinary Centre for Mathematical and Computational Modeling in Warszawa are gratefully thanked for providing computing facilities and generous computing resources.

References

[1] D. Maillard, M. Allavena, J.P. Perchard, Spectrochim. Acta A 31 (1975) 1523.

[2] L. Nord, J. Mol. Struct. 96 (1982) 19.

[3] M. Wierzejewska-Hnat, A. Schriver, L. Schriver-Mazzuoli, Chem. Phys. 183 (1994) 117.

[4] L. Schriver-Mazzuoli, A. Schriver, M. Wierzejewska-Hnat, Chem. Phys. 199 (1995) 227.

[5] L.M. Nxumalo, T.A. Ford, J. Mol. Struct. 347 (1995) 495.

[6] J.R. Sodeau, E.K.C. Lee, J. Phys. Chem. 84 (1980) 3358.

[7] A.J. Fillery-Travis, A.C. Legon, Chem. Phys. Lett. 123 (1986) .

[8] D.J. Pauley, R.E. Bumgarner, S.G. Kukolich, Chem. Phys. Lett. 132 (1986) 4.

[9] K. Matsumura, F.J. Lovas, R.D. Suenram, J. Chem. Phys. 91 (1989) 5887.

[10] A.M. Andrews, K.W. Hillig II, R.L. Kuczkowski, J. Chem. Phys. 96 (1992) 1784.

[11] Y.D. Juang, M.A. Walsh, A.K. Lewin, T.R. Dyke, J. Chem. Phys. 97 (1992) 832.

[12] L. Nord, J. Mol. Struct. 96 (1982) 27.

[13] C.S. Sass, B.S. Ault, J. Phys. Chem. 88 (1984) 432.

[14] A. Schriver, L. Schriver, J.P. Perchard, J. Mol. Spectrosc. 127 (1988) 125.

[15] L. Andrews, R. Withnall, R.D. Hunt, J. Phys. Chem. 92 (1988) 78.

[16] W.A. Guillory, M.L. Bernstein, J. Chem. Phys. 62 (1975) 1058.

[17] B.-M. Cheng, J.-W. Lee, Y.-P. Lee, J. Phys. Chem. 95 (1991) 2814.

[18] W.-J. Chen, W.-J. Lo, B.-M. Cheng, Y.-P. Lee, J. Chem. Phys. 97 (1992) 7167.

[19] Z. Mielke, K.G. Tokhadze, Z. Latajka, E. Ratajczak, J. Phys. Chem. 100 (1996) 539, and references therein.
[20] A.J. Barnes, E. Lasson, C.J. Nielsen, J. Mol. Struct. 322 (1994) 165.
[21] A.J. Barnes, E. Lasson, C.J. Nielsen, J. Chem. Soc., Faraday Trans. 91 (1995) 3111.
[22] Z. Mielke, K.G. Tokhadze, M. Hulkiewicz, L. Schriver-Mazzuoli, A. Schriver, F. Roux, J. Phys. Chem. 99 (1995) 10498.
[23] Z. Mielke, A. Schriver, L. Schriver-Mazzuoli, J. Phys. Chem. 101 (1997) in press.
[24] Z. Mielke, Z. Latajka, J. Kolodziej, K.G. Tokhadze, J. Phys. Chem. 100 (1996) 11610.
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 94, Gaussian, Inc., Pittsburgh, PA, 1995.
[26] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.
[27] P.C. Hariharn, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
[28] M. Speis, V. Buss, J. Comput. Chem. 13 (1992) 142.
[29] M. Flock, M. Ramek, Int. J. Quantum Chem., Quantum Chem. Symp. 27 (1993) 331.
[30] J.Y. Lee, O. Hahn, S.J. Lee, H.S. Choi, H. Shim, B.J. Mhin, K.S. Kim, J. Phys. Chem. 99 (1995) 1913.
[31] M.J. Frisch, J.A. Pople, J.S. Binkley, J. Chem. Phys. 80 (1984) 3265.
[32] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, Chem. Phys. 72 (1980) 650.
[33] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.
[34] S. Li, Y.-S. Li, J. Mol. Struct. 301 (1993) 21.
[35] L. Andrews, R. Withnall, R.D. Hunt, J. Phys. Chem. 92 (1988) 78.
[36] Z. Mielke, M. Wierzejewska, A. Olbert, M. Krajewska, K.G. Tokhadze, J. Mol. Struct. (in press).