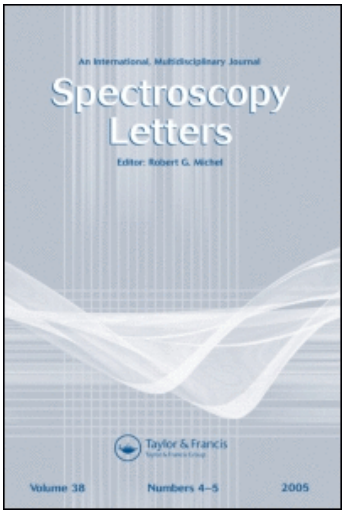

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Structures and Vibrational Spectra of the Hydrogen-Bonded Complexes Between Nitrous Acid and Acetone: *Ab Initio* and DFT Studies

Yordanka Dimitrova[a]
[a] Institute of Organic Chemistry, Center of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

Online publication date: 27 April 2010

To cite this Article Dimitrova, Yordanka(2010) 'Structures and Vibrational Spectra of the Hydrogen-Bonded Complexes Between Nitrous Acid and Acetone: *Ab Initio* and DFT Studies', Spectroscopy Letters, 43: 4, 282 — 289
To link to this Article: DOI: 10.1080/00387010903334557
URL: http://dx.doi.org/10.1080/00387010903334557

Spectroscopy Letters, 43:282–289, 2010

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903334557

Taylor & Francis
Taylor & Francis Group

Structures and Vibrational Spectra of the Hydrogen-Bonded Complexes Between Nitrous Acid and Acetone: *Ab Initio* and DFT Studies

Yordanka Dimitrova

Institute of Organic Chemistry, Center of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

ABSTRACT The structures, stability, and vibrational spectra of the binary complexes formed between acetone and nitrous (*trans* and *cis)* acid have been investigated using *ab initio* calculations at the SCF and MP2 levels and B3LYP calculations with 6-311++G(d,p) basis set. Full geometry optimization was made for the complexes studied. It was established that the complex $(CH_3)_2CO\cdots$HONO-*trans* is more stable than the complex $(CH_3)_2CO\cdots$HONO-*cis* by 0.5–0.8 kcal·mol^{-1}. The accuracy of the calculations has been estimated by comparison between the predicted values of the vibrational characteristics (vibrational frequencies and infrared intensities) and the available experimental data. It was established, that the methods, used in this study are well adapted to the problem under examination. The predicted values with the B3LYP/6-311++G(d,p) calculations are very near to the results, obtained with MP2/6-311++G(d,p). The calculated frequency shift $\Delta\nu$(O−H) for the complex $(CH_3)_2CO\cdots$HONO-*trans* (**1A**) is larger than for the complex $(CH_3)_2CO\cdots$HONO-*cis* (**1B**). In the same time the intensity of this vibration increases dramatically upon hydrogen bonding. The calculated increase for the complex **1A** is up to 15 times and for the complex **1B** is up to 30 times. The changes in the vibrational characteristics (vibrational frequencies and infrared intensities) of $(CH_3)_2CO$ upon the complexation are more insignificant than the changes in the vibrational characteristics of HONO-*trans* and HONO-*cis*.

KEYWORDS *ab initio* and DFT calculations, acetone-nitrous acid complexes, structures, vibrational spectra

Received 21 August 2009; accepted 14 September 2009.

Address correspondence to Yordanka Dimitrova, Institute of Organic Chemistry, Center of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 9, 1113, Sofia, Bulgaria. E-mail: yordankadimitrova@hotmail.com

1. INTRODUCTION

Weakly bound molecular complexes have been extensively investigated in the gas phase by radio frequency, microwave, and high-resolution infrared spectroscopy.[1] The matrix infrared spectra provide very common information about the hydrogen bonding and structure of such systems.[2]

The infrared matrix isolation studies on the complexes of nitrous acid with important atmospheric species: N_2, CO,[3] NH_3,[4] CH_4, C_2H_2[5] and oxygen bases (acetone and ethers)[6] have been reported. The interaction between nitrous acid and atmospheric species is of potential interest in connection with atmospheric modeling. Nitrous acid plays an important role in atmospheric chemistry, forming hydrogen-bonded complexes with number of atmospheric bases and it is one of the smallest molecules, which exhibits a *cis-trans* conformational equilibrium. Nitrous acid is unstable in the gas phase and occurs in complex equilibrium with the product of its decomposition.[7]

Numerous workers have demonstrated that matrix isolation studying of the hydrogen-bonded complexes[8–11] provides vibrational information to complement the gas-phase rotational data. The matrix infrared spectra provide very common information about the hydrogen bonding and structure of such systems.[2,5]

The structures, stability and vibrational spectra of the hydrogen-bonded complexes of nitric and nitrous acids with various atmospheric bases have been studied extensively in our previous studies[12–19] by *ab initio* calculations at SCF and MP2 levels and density functional calculations with various basis sets.

Acetone has been widely used as oxygen base in the studies of hydrogen bonding. Engdahl[20] studied the spectra of acetone-water complex in water. Mielke et al.[6] have been reported the infrared study of the $(CH_3)_2CO$–HONO complexes isolated in argon matrices. Nitrous acid is a strong proton donor and forms an O···H−O type of hydrogen bond with acetone. The O−H stretching vibration of perturbed *trans*-HONO monomer is 413 cm^{-1} red shifted, whereas the NOH bending mode is 138 cm^{-1} blue shifted, respectively, which formation of strong hydrogen bond in the complex.

The objects of the present study are the hydrogen-bonded complexes of nitrous acids (*trans*, *cis*) with acetone. The aim of the study is to establish the most stable structures of the hydrogen-bonded complexes and to predict the changes in the structural and vibrational characteristics of the monomers upon hydrogen bonding. For this aim the *ab initio* and DFT calculations with large basis sets have been used.

The DFT calculations are carried out in the framework of Kohn-Sham density-functional theory[21] (DFT) with the nonlocal three-parameter gradient-corrected exchange-correlation functional of Becke and Lee, Yang and Parr including partially exact HF-exchange (B3LYP).[22]

2. RESULTS AND DISCUSSION

2.1. Structures and Stability

The first step in this study was to establish the most stable structures for the complexes of acetone with HONO (*trans* and *cis*) by *ab initio* calculations at SCF and MP2 levels and B3LYP calculations. The calculations have been performed with the GAUSSIAN 03 series of programs.[23] Our aim was to select the most stable structures for the complexes studied: $(CH_3)_2CO\cdots$HONO-*trans* (**1A**), and $(CH_3)_2CO\cdots$HONO-*cis* (**1B**). Figure 1 and Table 1 show the structures, optimal values of the total energy and optimized structural parameters for the hydrogen-bonded complexes **1A** and **1B**. The calculated optimized structural parameters for the monomers are compared with the available experimental data. The comparison shows that the B3LYP/6-311++G(d,p)

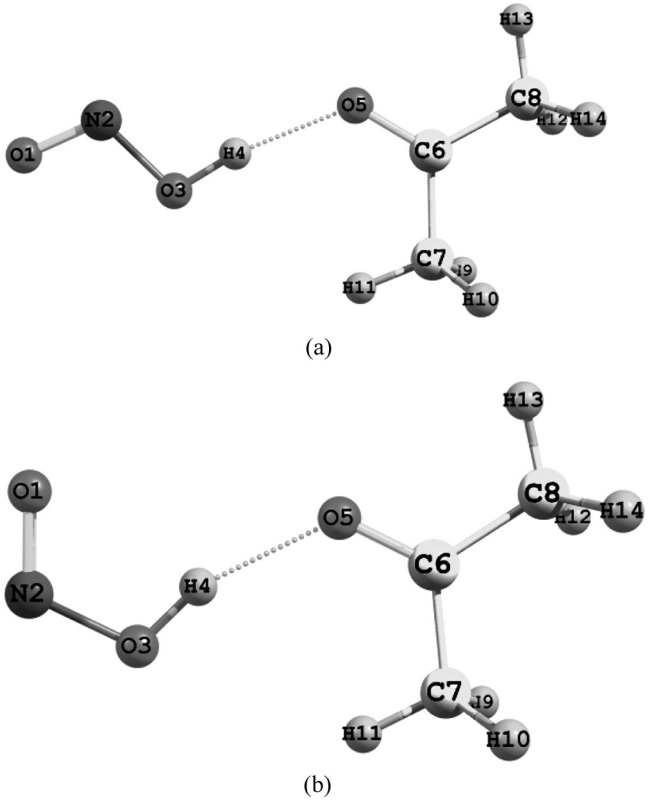

FIGURE 1 **Optimized geometries for hydrogen-bonded complexes between $(CH_3)_2CO$ and *trans*-HONO (1A) and *cis*-HONO (1B) obtained from B3LYP/6-311++G(d,p) calculations.**

TABLE 1 Optimized Geometries for Free and Complexed HONO and $(CH_3)_2CO$ Molecules, Obtained from B3LYP/6-311++G(d, p) Calculations

	trans-HONO				*cis*-HONO			
		Calc.				Calc.		
Parameter[a]	Exp.[b]	Mon.	Com. **1A**	Δ	Exp.[b]	Mon.	Com. **1B**	Δ
Bond length[c]								
$r(N_2O_1)$	1.170	1.165	1.176	0.011	1.185	1.179	1.185	0.006
$r(O_3N_2)$	1.432	1.433	1.398	−0.035	1.392	1.392	1.378	−0.014
$r(H_4O_3)$	0.958	0.969	0.987	0.018	0.982	0.980	0.996	0.016
$r(O_5 \cdots H_4)$	–	–	1.784	–	–	–	1.821	–
$r(C_6O_5)$	1.222	1.212	1.219	0.007	1.222	1.212	1.219	0.007
$r(C_7C_6)$	1.507	1.517	1.511	−0.006	1.507	1.517	1.511	−0.006
$r(C_8C_6)$	1.507	1.517	1.510	−0.007	1.507	1.517	1.511	−0.006
$r(H_9C_7)$		1.095	1.095	0.0		1.095	1.095	0.0
$r(H_{10}C_7)$		1.095	1.095	0.0		1.095	1.095	0.0
$r(H_{11}C_7)$		1.089	1.089	0.0		1.089	1.089	0.0
$r(H_{12}C_8)$		1.095	1.095	0.0		1.095	1.095	0.0
$r(H_{13}C_8)$		1.089	1.089	0.0		1.089	1.095	0.0
$r(H_{14}C_8)$		1.095	1.095	0.0		1.095	1.089	0.0
Angles[d]								
$O_1N_2O_3$	111.70	111.15	111.58	0.43	113.60	113.82	114.05	0.23
$H_4O_3N_2$	102.10	102.91	104.80	1.89	104.0	106.80	109.77	2.97
$O_5 \cdots H_4O_3$	–	–	170.30	–	–	–	162.15	–
$C_6O_5 \cdots H_4$	–	–	125.46	–	–	–	126.45	–
$C_7C_6O_5$		121.71	121.89	0.18		121.71	121.94	0.23
$C_8C_6O_5$		121.71	120.54	−1.17		121.71	120.59	−1.12
$H_9C_7C_6$		110.25	109.89	−0.36		110.25	109.90	−0.35
$H_{10}C_7C_6$		110.25	109.90	−0.35		110.25	109.90	−0.35
$H_{11}C_7C_6$		110.04	111.10	1.06		110.04	111.05	1.01
$H_{12}C_8C_6$		110.25	110.09	−0.14		110.25	110.10	−0.15
$H_{13}C_8C_6$		110.04	110.22	0.18		110.04	110.20	0.16
$H_{14}C_8C_6$		110.25	110.09	−0.14		110.25	110.10	−0.15
E^{tot} (a.u.)		−205.7150[e]	−398.9035			−205.7143[f]	−398.9010	
		−193.1745[g]				−193.1745[g]		

$\Delta = \Delta_i^{complex} - \Delta_i^{monomer}$.
[a]See Fig. 1 for numbering of atoms.
[b]Ref. [24].
[c]In angstrom.
[d]In degrees.
[e]E^{tot} for *trans*-HONO.
[f]E^{tot} for *cis*-HONO.
[g]E^{tot} for $(CH_3)_2CO$.

calculations give the values of the bond lengths and angles in very good agreement with the experimental data.[24] As can be seen from the results of the E(tot) in Table 1, the *trans*-complex **1A** is more stable than the *cis*-complex **1B**. The comparison between the bond lengths and angles for the binary complexes and those for the monomers show that as a result of the hydrogen bonding their values are slightly perturbed. In Fig. 1 are shown the optimized structures of the complexes studied with B3LYP/6-311++G (d,p) calculations.

The results in Table 1 show that the formation of the hydrogen-bonded complexes results in essential changes of the structural parameters, participating in the hydrogen bonding. The bonds H_4O_3, O_1N_2 and C_6O_5 are lengthened in the complexes, while the bond O_3N_2 is shorted upon formation of the hydrogen bonds. The angles $O_8C_6O_5$ and $H_4O_3N_2$ are also sensitive to the complexation. Their values in the complexes are changed in comparison with the corresponding values in the monomers. The larger changes in the structural parameters are calculated for the complex

TABLE 2 Dissociation Energies ΔE (Uncorrected and Corrected) in Kcal/mol and Hydrogen Bond Distances R in [A]

	ΔE^{uncorr}		$\Delta E_{(zp\ vib)}$		ΔE^{corr}		δE^{MP2}_{corr}		R[A]	
Basis set	1A(*trans*)	1B(*cis*)	1A(*trans*)	1B(*cis*)	1A(*trans*)	1B(*cis*)	1A(*trans*)	1B(*cis*)	1A(*trans*)	1B(*cis*)
SCF/6-311++G**	−7.0841	−6.3332	1.2749	0.9372	−5.8092	−5.3960			1.879	1.935
MP2/6-311++G**	−8.5573	−7.6919	1.4890	1.0996	−7.0683	−6.5923	−1.4732	−1.3587	1.802	1.846
B3LYP/6-311++G**	−8.4064	−7.4504	1.1144	0.9909	−7.2920	−6.4595			1.784	1.821

$(CH_3)_2CO\cdots$HONO-*trans* (**1A**) than for the complex $(CH_3)_2CO\cdots$HONO-*cis* (**1B**).

The next step in the study was to investigate the stability of the complexes of $(CH_3)_2CO$ with nitrous acid (**1A** and **1B**). In this connection the dissociation energy (uncorrected and corrected) was calculated by *ab initio* and B3LYP calculations with 6–311++G(d,p) basis set. The results from the calculations are summarized in Table 2. Bearing in mind the corrected values of the dissociation energy for the studied hydrogen-bonded complexes it can be concluded that the complex $(CH_3)_2CO\cdots$HONO-*trans* (**1A**) is more stable than the complex $(CH_3)_2CO\cdots$HONO-*cis* (**1B**). This conclusion is following also from the calculated hydrogen bond distances R(O···H). For the complex **1A** R(O···H) is shorter than for the complex **1B**.

2.2. Vibrational Spectra

The prediction of the vibrational characteristics (vibrational frequencies and infrared intensities) of the hydrogen-bonded systems by *ab initio* and DFT calculations at different levels[15,25–32] has become widely employed in order to elucidate the influence of the hydrogen bonding on the vibrational spectra of the monomers forming a complex.

The infrared (IR) spectroscopic signature of the hydrogen bond formation is the shift to the lower frequency and the increase in intensity of the stretching vibrations of the monomer bonds involving in hydrogen bonding.

The vibrational frequencies and infrared intensities for free monomers (HONO-*trans*, HONO-*cis* and $(CH_3)_2CO$) and for the binary complexes **1A** and **1B** (see Fig. 1) have been predicted by *ab initio* calculations at the MP2 level and B3LYP calculations with the 6-311++G(d,p) basis set (see Tables 3–5).

The first aim of this study is to predict the vibrational characteristics (vibrational frequencies and infrared intensities) for free monomers (HONO-*trans*, HONO-*cis* and $(CH_3)_2CO$). The predicted values of the vibrational frequencies and infrared intensities are compared with the available experimental data[4,33] (see Table 3). The aim is to established the accuracy of the calculations used in the study and to define the 'optimal' scale factors for each vibration from the ratio ν_i^{exp}/ν_i^{calc}. The concept of the 'optimal' scale factor has been proposed by Destexhe et al.[34] in order to obtained an estimation of the anharmonicity of the modes in H-bonded H_2O with pyridine. This procedure could only be applied for modes, which are experimentally accessible in the spectral region. In the present study the 'optimal' scale factors for the stretching and bending vibrations of the monomers are shown in Table 3.

The calculated vibrational frequencies and infrared intensities for the monomers (HONO-*trans*, HONO-*cis* and $(CH_3)_2CO$) are presented in Table 3 together with the available experimental data. In Table 3 is included a detailed description of the normal modes of the monomers based on the potential energy distribution (PED) obtained from MP2/6-311++G(d,p) calculations. The results from the calculations show that the predicted values of the vibrational frequencies are very near to the experimentally measured. The scale factors defined from the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) calculations for the normal modes are very near. This result show that the DFT calculations give results very near to the *ab initio* correlated methods, such as MP2, at a small fraction of the cost. The cost effectiveness of DFT over conventional methods is an additional attractive feature.

The accuracy of the *ab initio* MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) calculations for the prediction of the infrared intensities was also investigated. The comparison between the predicted values of the infrared intensities for the normal modes of the monomers with the available experimental data show that the calculations used in the study give a satisfactory

TABLE 3 Experimental and Calculated Characteristics (ν in cm^{-1}, A in $km \cdot mol^{-1}$) for *trans*-HONO, *cis*-HONO and $(CH_3)_2CO$

		Exp.		MP2/6-311++G(d, p)		B3LYP/6-311++G(d, p)	
Mode	Approximate description (PED)[a]	ν	A	ν/scale factor	A	ν/scale factor	A
***trans*-HONO**							
ν_1	100ν(O−H)	3572.6[b]		3811/0.9374	94.0	3769/0.9479	83.0
		3568.5[b]		0.9364		0.9468	
ν_2	89ν(N=O)	1689.1[b]	s	1772/0.9532	107.8	1785/0.9463	195.1
		1688.0[b]		0.9526		0.9457	
ν_3	85δ(NOH) + 11ν(N=O)	1265.8[b]	s	1294/0.9782	189.6	1291/0.9805	186.2
		1263.9[b]		0.9767		0.9790	
ν_4	49δ(NOH) + 42ν(N−O)	800.4[b]	s	826/0.9690	177.7	810/0.9881	133.9
		796.6[b]		0.9644		0.9835	
ν_5	60ν(N−O) + 40δ(ONO)	608.7[b]		616/0.9882	176.7	612/0.9946	154.6
ν_6	100τ(HONO)	549.4[b]	s	565/0.9724	116.4	581/0.9456	115.5
		548.2[b]		0.9703		0.9435	
***cis*-HONO**							
ν_1	100ν(O−H)	3412.4[b]		3552/0.9607	37.5	3584/0.9521	25.7
		3410.7[b]		0.9602		0.9516	
ν_2	77ν(N=O) + 17δ(NOH)	1634.0[b]	s	1643/0.9933	126.4	1714/0.9533	221.9
		1632.8[b]		0.9926		0.9526	
ν_3	71δ(NOH) + 23ν(N=O)	–		1306	7.1	1322	6.4
ν_4	41δ(ONO) + 47ν(N−O)	853.1[b]		898/0.95	376.3	872/0.9783	319.2
		850.2[b]		0.9468		0.9750	
ν_5	100τ(HONO)	–		706	121.9	684	119.9
ν_6	53ν(N−O) + 36δ(ONO)	638.4[b]		647/1.0231	46.8	626/1.0198	40.1
$(CH_3)CO$							
ν_1	94ν(C−H)	3020.2[c]	w	3205/0.9423	6.9	3160/0.9558	6.6
ν_2	73ν(C−H)	3020.2[c]	w	3191/0.9465	7.5	3159/0.9561	11.1
ν_3	98ν(C−H)	2973.8[c]	w	3161/0.9408	14.7	3103/0.9584	19.4
ν_4	99ν(C−H)			3155/0.9426	0.2	3096/0.9605	0.0
ν_5	80ν(C−H)	2933.2[c]	w	3076/0.9536	5.9	3043/0.9639	8.2
ν_6	81ν(C−H)			3070/0.9554	2.7	3036/0.9661	2.1
ν_7	85ν(C=O)	1721.7[c]	s	1764/0.9760	132.0	1792/0.9608	200.2
ν_8	52τ(HCCC)	1451.7[c]	w	1506/0.9640	23.3	1492/0.9730	24.9
ν_9	59τ(HCCC)	1444.3[c]	w	1490/0.9694	27.5	1474/0.9799	31.2
ν_{10}	58τ(HCCC)	1429.4[c]	m	1483/0.9639	0.1	1470/0.9724	0.0
ν_{11}	77τ(HCCC)	1406.9[c]	w	1481/0.9500	1.0	1464/0.9610	0.9
ν_{12}	66δ(HCC)	1361.6[c]	vs	1407/0.9677	63.9	1394/0.9768	60.6
ν_{13}	96δ(HCC)	1354.1[c]	s	1399/0.9679	17.3	1392/0.9728	20.6
ν_{14}	42ν(CC) + 32δ(HCC) + 18δ(CCO)	1216.6[c]	s	1257/0.9679	57.9	1237/0.9835	74.0
ν_{15}	43δ(HCC) + 26τ(CCCO)	–		1118	0.7	1118	2.5
ν_{16}	43δ(HCC)	1091.8[c]	m	1092/0.9998	0.0	1083/1.0081	0.0
ν_{17}	26δ(HCC) + 17ν(CC)	–		906	5.2	889	6.8
ν_{18}	84δ(HCC)	882.4[c]	w	884/1.0095	0.0	886/1.0072	0.0
ν_{19}	92ν(C−C)	780.9[c]	w	805/0.9701	1.5	787/0.9923	1.4
ν_{20}	79δ(CCO)	528.9[c]	m	537/0.9849	13.1	533/0.9923	13.9
ν_{21}	63τ(CCCO)	–		480	0.5	488	0.5
ν_{22}	86δ(CCC)	–		384	0.9	379	1.5
ν_{23}	54τ(HCCC)	–		98	1.2	124	0.0
ν_{24}	99τ(HCCC)	–		115	0.0	−36	0.0

[a]PEDs elements lower than 10% are not included. PEDs elements obtained with MP2/6-311++G(d,p) are given; [b]Ref.[4]; [c]Ref.[33]

TABLE 4 Experimental and Calculated Characteristics (ν in cm^{-1}, A in $km \cdot mol^{-1}$) for the Hydrogen Bonded Complex $(CH_3)_2CO \cdots HONO$-*trans*

Mode	Approximate description (PED)[a]	Exp. [6]	MP2/6-311++G(d,p)		B3LYP/ 6-311++G(d,p)	
		$\nu/\Delta\nu^{ex}$	$\nu/\Delta\nu^{scal}$	A/ΔA	$\nu/\Delta\nu^{scal}$	A/ΔA
ν_1	100ν(O−H)	3157.9/−413	3543/−251	1167.0/1073	3523/−224	1320.5/1237.5
ν_2	94ν(C−H)		3222/16	4.2/−2.7	3147/5	5.6/−1.8
ν_3	94ν(C−H)		3189/−2	2.6/−4.9	3142/5	4.8/−7
ν_4	97ν(C−H)		3162/−1	7.3/−7.4	3091/5	10.3/−9.2
ν_5	97ν(C−H)		3156/−1	0.2/0.0	3083/4	0.1/0.0
ν_6	94ν(C−H)		3081/5	3.5/−2.4	3036/5	5.4/−1.9
ν_7	94ν(C−H)		3070/0	1.4/−1.3	3028/4	0.0
ν_8	84ν(C=O)	1712.7/−9	1754/−10	180.1/48.1	1761/−21	222.8/21.2
ν_9	78ν(N=O) + 15δ(HON)		1749/−22	59.6/−48.2	1743/−40	240.2/−44.7
ν_{10}	65τ(HCCC)		1506/0	25.4/2.1	1486/−1	25.9/1.7
ν_{11}	51τ(HCCO) + 24τ(HCCC) + 15δ(HCC)		1492/0	49.7/22.2	1471/1	65.2/7.4
ν_{12}	80τ(HCCC)		1483/2	2.7/1.7	1463/−2	0.0
ν_{13}	32δ(HCC) + 28τ(HCCC)		1481/0	0.0	1460/−1	2.8/4.4
ν_{14}	64δ(HCC)	1372.1/10.5	1417/10	70.3/6.4	1409/7	342.7/6.6
ν_{15}	61δ(HCC)	1372.1/10.5	1408/9	16.6/−0.7	1395/6	74.2/8.7
ν_{16}	50δ(HON) + 16ν(N=O) + 11δ(O···HO)	1402.7/138	1396/100	412.4/222.8	1391/98	103.7/−82.5
ν_{17}	40ν(C−C) + 32δ(HCC)	1236.5/19.9	1274/16	67.8/9.9	1251/18	73.1/−6.3
ν_{18}	57δ(HCC) + 18τ(CCO···H)		1123/−5	1.2/0.5	1121/−3	4.5/1.8
ν_{19}	41δ(HCC)		1098/6	0.1/0.1	1089/7	0.0
ν_{20}	30ν(C−C) + 26δ(HCC)		917/11	3.1/−2.1	899/8	5.7/−1.8
ν_{21}	59ν(O−N) + 36δ(ONO)		903/284	336.9/160.2	893/289	315.2/181.3
ν_{22}	41δ(HCC)		892/8	1.6/1.6	876/14	268.6/268.6
ν_{23}	91ν(C−C)		816/10	0.6/0.6	857/96	83.7/83.7
ν_{24}	48τ(HONO) + 28τ(O···HON) + 17τ(CO···HO)		776/205	92.2/−24.2	797/204	82.6/−32.9
ν_{25}	55δ(ONO) + 39ν(O−N)		704/87	89.9/−86.8	694/110	96.3/−58.3
ν_{26}	77δ(CCO)		554/17	30.8/17.7	553/18	29.5/15.6
ν_{27}	66τ(CCO···H)		481	0.5	494	0.2
ν_{28}	85δ(CCO)		392	4.4	389	6.4
ν_{29}	56ν(O···H)		183	12.5	184	13.4
ν_{30}	37τ(HONO) + 16τ(CO···HO) + 13τ(CCO···H)		138	3.6	147	4.7
ν_{31}	47τ(HCCC) + 12τ(HONO)		113	1.6	116	1.4
ν_{32}	37ν(O···H) + 32δ(CO···H)		93	2.3	95	2.9
ν_{33}	37δ(O···HO) + 27δ(CO···H)		50	3.0	49	0.0
ν_{34}	11τ(HCCC) + 10τ(CCO···H)		25	2.1	29	2.7
ν_{35}	22τ(HCCC) + 19τ(CCO···H)		24	0.6	14	2.3
ν_{36}	89τ(HCCO)		103	0.1	47	0.0

[a]PEDs elements lower than 10% are not included. PEDs elements obtained with MP2/6-311++G(d,p) are given.

description for the infrared intensities of the stretching and deformation vibrations. The most intense vibrations for the *trans* and *cis* nitrous acids are the deformation δ(NOH) and τ(HONO) vibrations. The good agreement between the predicted values of the vibrational characteristics with the experimentally observed show that the methods used in the study are well adapted to the problem under examination.

The next aim in the study is to estimate the changes in the vibrational characteristics (vibrational frequencies and infrared intensities) arising from the hydrogen bonding. The shifts in the vibrational frequencies ($\Delta\nu^{scal}$) upon formation of the hydrogen-bonded complexes have been calculated by *ab initio* calculations at the MP2 level and B3LYP calculations with 6-311++G(d,p) basis set. The corresponding scale factor is used for each vibration. The predicted frequency shift is:

$$\Delta\nu_i^{scal} = k_i(\nu_i^{complex} - \nu_i^{monomer}),$$

where k_i is the corresponding 'optimal' scale factor.

TABLE 5 Calculated Characteristics (ν in cm^{-1}, A in $km \cdot mol^{-1}$) for the Hydrogen-bonded Complex $(CH_3)_2CO \cdots HONO$-*cis*

		MP2/6-311++G(d,p)		B3LYP/6-311++G(d,p)	
Mode	Approximate description (PED)[a]	$\nu/\Delta\nu^{scal}$	A/ΔA	$\nu/\Delta\nu^{scal}$	A/ΔA
ν_1	100ν(H−O)	3414/−132	750.9/713.4	3475/−104	934.0/907.7
ν_2	94ν(H−C)	3220/14	4.2/−2.7	3165/5	4.8/−1.8
ν_3	94ν(H−C)	3214/22	2.2/−5.3	3164/5	4.1/−7
ν_4	89ν(H−C)	3158/−3	8.3/−6.4	3108/5	10.2/−9.2
ν_5	100ν(H−C)	3152/−3	0.0/−0.2	3100/4	0.0/0
ν_6	85ν(H−C)	3079/3	5.8/−0.1	3048/5	6.3/−1.9
ν_7	86ν(H−C)	3074/4	0.2/−2.5	3040/4	0.2/−1.9
ν_8	84ν(C=O)	1752/−12	156.9/24.9	1770/−21	221.4/21.2
ν_9	83ν(N=O)	1602/60	243.6/117.2	1687/−26	347.1/131.1
ν_{10}	52τ(CCCH)	1507/1	25.5/2.2	1491/−1	26.6/1.7
ν_{11}	55τ(CCCH) + 15δ(HCC)	1494/4	30.5/3	1475/1	38.6/7.4
ν_{12}	38τ(CCCH) + 12δ(HCC)	1484/1	4.6/4.5	1468/−2	0.0/0
ν_{13}	59τ(CCCH)	1482/1	0.1/−0.9	1463/−1	5.3/4.4
ν_{14}	66δ(HCC)	1415/8	65.4/1.5	1401/7	67.2/6.6
ν_{15}	84δ(HCC)	1407/8	16.8/−0.5	1398/6	11.9/−8.7
ν_{16}	66δ(HON) + 17ν(N=O)	1379/73	81.0/73.9	1388/66	116.5/110.1
ν_{17}	41ν(C−C) + 32δ(HCC)	1275/17	56.6/−1.3	1255/18	67.7/−6.3
ν_{18}	56δ(HCC) + 17τ(CCO···H)	1125/7	1.3/0.6	1122/4	4.3/1.8
ν_{19}	41δ(HCC)	1099/7	0.0/0	1090/7	0.1/0.1
ν_{20}	61ν(O−N) + 31δ(ONO)	964/63	513.3/137	951/77	432.6/113.4
ν_{21}	31ν(C−C) + 28δ(HCC)	917/11	3.4/−1.8	926/40	89.3/82.5
ν_{22}	80δ(HCC)	898/14	3.8/3.8	900/14	4.7/4.7
ν_{23}	58τ(HONO) + 29τ(O···HON)	824/118	101.7/−20.2	884/186	9.6/−109.4
ν_{24}	91ν(C−C)	814/9	1.0/−0.5	798/11	0.4/−1
ν_{25}	56δ(ONO) + 40ν(N−O)	675/29	25.5/−21.3	672/33	20.6/−2.3
ν_{26}	77δ(HCC)	551	22.2	551	24.5
ν_{27}	55τ(HCO···H)	485	0.4	490	0.2
ν_{28}	87δ(CCO)	392/−143	3.8/−9.3	387/−145	5.5/−8.4
ν_{29}	61ν(O···H) + 14δ(O···HO) + 13δ(CO···H)	177	9.1	190	3.8
ν_{30}	34τ(O···HON) + 28τ(HONO) + 17τ(CCO···H)	167	3.3	188	13.3
ν_{31}	27τ(CO···HO) + 20τ(CCO···H) + 14τ(HONO) + 12τ(HCCC)	145	2.8	116	0.4
ν_{32}	46δ(CO···H) + 36ν(O···H)	84	0.6	87	1.2
ν_{33}	41τ(HCCC) + 17τ(CCO···H)	57	0.3	46	0.8
ν_{34}	44δ(O···HO) + 27δ(CO···H)	44	3.1	43	2.3
ν_{35}	39τ(CCO···H) + 20τ(HCCC) + 20τ(O···HON) + 15τ(CCO···H)	35	0.7	10	1.5
ν_{36}	31τ(C=O···HO) + 14τ(O···HON)	20	1.1	−51	0.0

[a]PEDs elements lower than 10% are not included. PEDs elements obtained with MP2/6-311++G(d,p) are given.

The changes in the infrared intensities (ΔA_i) upon hydrogen bond formation are also estimated using *ab initio* and DFT calculations.

$$\Delta A_i = A_i^{complex} - A_i^{monomer}$$

The predicted changes in the vibrational frequencies and infrared intensities are shown in Tables 4 and 5 together with the experimentally observed[6] shifts.

It known that the hydrogen bonding leads to the substantial changes in the vibrational characteristics for the vibrations of the monomer bonds participating in the hydrogen bonding. For the complexes $(CH_3)_2CO \cdots HONO$-*trans* (**1A**) and $(CH_3)_2CO \cdots HONO$-*cis* (**1B**) these vibrations are the stretching O−H vibration (ν_1) and the deformation τ(HONO) vibration. As can be seen from the results in Tables 4 and 5, the most sensitive to the complexation is the stretching O−H vibration (ν_1). In agreement with the experiment[6] its vibrational frequency in the complexes is shifted to lower wavenumbers. The calculated frequency shift $\Delta\nu$(O−H) for the complex

$(CH_3)_2CO\cdots HONO$-*trans* (**1A**) is larger than for the complex $(CH_3)_2CO\cdots HONO$-*cis* (**1B**). In the same time the intensity of this vibration increases dramatically upon hydrogen bonding. The calculated increase for the complex **1A** is to 15 times and for the complex **1B** is to 30 times.

The *ab initio* and B3LYP calculations show that the torsional HONO vibration in the complexes is shifted to higher frequencies. The predicted infrared intensity for the torsional HONO vibration in the complexes decreases.

The *ab initio* and B3LYP calculations show that the changes in the vibrational characteristics (vibrational frequencies and infrared intensities) of $(CH_3)_2CO$ upon the complexation are more insignificant than the changes in the vibrational characteristics of HONO-*trans* and HONO-*cis*.

As can be seen from the data in Tables 4 and 5, the remaining vibrations (stretching, bending and torsion) are less sensitive to the hydrogen bonding. The predicted changes in their vibrational characteristics are smaller.

3. CONCLUSIONS

The structure, stability, and vibrational spectra of the nitrous acid complexes with acetone have been studied by *ab initio* and DFT calculations. The main results of the study are:

1. The bond lengths and angles for the binary complexes $(CH_3)_2CO\cdots HONO$-*trans* (**1A**) and $(CH_3)_2CO\cdots HONO$-*cis* (**1B**) are slightly perturbed from their values in the monomers. The more sensitive to the complexation are the structural parameters of HONO-*trans* than the structural parameters of HONO-*cis*.
2. Bearing in mind the corrected values of the dissociation energy for the studied hydrogen-bonded complexes it can be concluded that the complex $(CH_3)_2CO\cdots HONO$-*trans* (**1A**) is more stable than the complex $(CH_3)_2CO\cdots HONO$-*cis* (**1B**).
3. The calculated frequency shift $\Delta\nu$(O—H) for the complex $(CH_3)_2CO\cdots HONO$-*trans* (**1A**) is larger than for the complex $(CH_3)_2CO\cdots HONO$-*cis* (**1B**). In the same time the intensity of this vibration increases dramatically upon hydrogen bonding. The calculated increase for the complex **1A** is to 15 times and for the complex **1B** is to 30 times.
4. The *ab initio* and B3LYP calculations show that the changes in the vibrational characteristics (vibrational frequencies and infrared intensities) of $(CH_3)_2CO$ upon the complexation are more insignificant than the changes in the vibrational characteristics of HONO-*trans* and HONO-*cis*.

REFERENCES

1. Bevan, J. V. In *Structure and Dynamics of Weakly Bound Molecular Complexes*; Weber, A., Ed.; Reidel: Dordrecht, 1987; 149.
2. Andrews, L. In *Chemical and Physics of Matrix Isolated Species*; Andrews, L.; Moskovits, M.; Eds.; North Holland: Amsterdam, Oxford, New York, Tokyo, 1989; 15.
3. Mielke, Z.; Latajka, Z.; Kolodziej, J.; Tokhadze, K. G. *J. Phys. Chem.* **1996**, *100*, 11610.
4. Mielke, Z.; Tokhadze, K. G.; Latajka, Z.; Ratajczak, E. *J. Phys. Chem.* **1996**, *100*, 539.
5. Krajewska, M.; Mielke, Z.; Tokhadze, K. G. *J. Mol. Struct.* **1997**, *404*, 47.
6. Mielke, Z.; Wierzejewska, M.; Olbert, A.; Krajewska, M.; Toknadze, K. G. *J. Mol. Struct.* **1997**, *339*, 436–437.
7. Finlayson-Pitts, B. J.; Pitts, Jr., J. N. *Atmospheric Chemistry; Fundamentals and Experimental Technics*; John Wiley & Sons: New York, 1986.
8. Andrrews, L. *J. Mol. Struct.* **1983**, *100*, 281.
9. Barnes, A. J. *J. Mol. Struct.* **1983**, *100*, 259.
10. Ault, B. S.; Pimentel, G. C. *J. Phys. Chem.* **1973**, *77*, 1649.
11. Ault, B. S. *Acc. Chem. Res.* **1982**, *15*, 103.
12. Dimitrova, Y.; Peyerimhoff, S. *Chem. Phys.* **2000**, *254*, 125.
13. Dimitrova, Y. *J. Mol. Struct. (Theochem)* **2000**, *532*, 41.
14. Dimitrova, Y. *Bulg. Chem. Comm.* **2001**, *33*, 206.
15. Dimitrova, Y. *Recent Res. Devel. Phys. Chem.* **2002**, *6*, 127.
16. Dimitrova, Y. *J. Mol. Struct. (Theochem)* **2003**, *623*, 179.
17. Dimitrova, Y.; Stamboliyska, B. A. *Int. J. Quant. Chem.* **2003**, *92*, 506.
18. Dimitrova, Y. *Spectrochim. Acta, Part A* **2004**, *60*, 2163.
19. Dimitrova, Y.; Slavova, I. *Spectrochim. Acta, Part A* **2005**, *61*, 2095.
20. Engdahl, A. *Chem. Phys.* **1993**, *178*, 305.
21. Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.
22. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
23. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. et al. Gaussian 03, Revision B.04, Gaussian, Inc.: Pittsburgh, PA, 2003.
24. Cox, P. A.; Brittain, A. H.; Finningan, D. J. *Trans. Faraday Soc.* **1971**, *67*, 2179.
25. Bürgi, T.; Schütz, M.; Leutwyler, S. *J. Chem. Phys.* **1995**, *103*, 6350.
26. Gerhards, M.; Kleinermanns, K. *J. Chem. Phys.* **1995**, *103*, 7392.
27. Jacoby, C.; Roth, W.; Schmitt, M.; Janzen, C.; Spangenberg, D.; Kleinermanns, K. *J. Phys. Chem. A* **1998**, *102*, 4471.
28. Hadzi, D. *Theoretical Treatment of Hydrogen Bonding*; John Wiley and Sons: New York, 1997.
29. Del Bene, J. E.; Jordan, M. J. T. *Intern. Rev. Phys. Chem.* **1999**, *18*, 119.
30. Smets, J.; McCarthy, W.; Maes, G.; Adamowicz, L. *J. Mol. Struct.* **1999**, *476*, 27.
31. Dimitrova, Y. *Recent Res. Devel. Phys. Chem.* **1999**, *3*, 133.
32. Dimitrova, Y. *Trends App. Spectros.* **2007**, *6*, 43.
33. Consani, K. *J. Phys. Chem.* **1987**, *91*, 5586.
34. Destexhe, A.; Smets, J.; Adamowicz, L.; Maes, G. *J. Phys. Chem.* **1994**, *98*, 1506.