Matrix Infrared Spectra and ab Initio Calculations of the Nitrous Acid Complexes with Nitrogen Monoxide[†]

Zofia Mielke,* Zdzisław Latajka, Adriana Olbert-Majkut, and Robert Wieczorek

Faculty of Chemistry, Wrocław University, Joliot-Curie 14, 50-383, Wrocław, Poland

Received: November 3, 1999; In Final Form: February 14, 2000

Complexes between trans and cis isomers of nitrous acid and nitrogen monoxide have been isolated in argon matrices and studied using FTIR spectroscopy and ab initio calculations at the ROMP2 level. The calculations indicate formation of four hydrogen-bonded complexes with *trans*- or *cis*-HONO isomer bound to nitrogen or oxygen atoms of NO molecule. Comparison of the calculated frequencies with the frequencies of the complexes trapped in solid argon proved that the more stable ON···HONO trans and ON···HONO cis complexes with an acid molecule attached to nitrogen atom are trapped in the matrix.

Introduction

The structure and dynamics of weakly bound molecular complexes have been extensively investigated in recent years using both a variety of experimental techniques and theoretical calculations. The aim of these studies has been a more complete understanding of intermolecular interactions which play an important role in many physical and chemical processes. Most of the performed studies were concentrated on the interaction of two closed-shell atoms or molecules. Precise structural information on weak molecular complexes have been obtained using radio frequency, microwave,[1−5] and high-resolution infrared laser−molecular beam spectroscopy.[7−9] A number of high-level ab initio calculations performed for these systems proved that reliable structural predictions can be made for the smaller closed-shell complexes.[10−15]

Less is known about weakly bound complexes involving open-shell molecules. Experimental or theoretical data are available[16,17] for only a few complexes formed by open-shell species. In the complex formed between an open-shell species and a closed-shell partner, the interaction is expected to resemble that observed in the weakly bound complexes of two closed-shell partners as the exchange energy, characteristic for two interacting open-shell species, is no longer expected to play a major role in stabilization of such complexes. The role which an odd electron plays in the bonding of these complexes is not known though one may expect that in the case of hydrogen-bonded complexes an odd electron density increases a basicity of a particular site of the molecule on which it is concentrated.

Weak complexes between nitrogen monoxide and hydrogen halides, being model complexes between stable open-shell and closed-shell species, have been recently extensively studied. Davis, Andrews, and Trindle[18] were the first who studied the NO and NO_2 complexes with HF by using matrix infrared spectroscopy and ab initio UHF SCF calculations. The complex between NO and HF was later investigated in the gas phase by Fawzy et al.[19] with high-resolution infrared laser spectroscopy. Saxce et al.[20] performed mid-infrared matrix isolation and ab initio studies for the NO complex with HCl; these studies were recently completed by Krim and Alikhani[21] who carried out far-infrared matrix isolation studies and DFT calculations for the NO···HCl complex. Saxce et al.[20] reported also infrared studies of the NO···HBr complex in solid argon. All the above experimental studies prove that nitrogen monoxide forms weakly hydrogen-bonded complexes with hydrogen halides but they do not provide information whether the hydrogen bond is to the O atom or N atom of nitrogen monoxide. On the other hand, the theoretical calculations performed for this complex demonstrate the difficulty in predicting general features such as stability, structure, and vibrational spectrum of the complex involving open-shell species. However, the recent calculations performed at the CASSCF levels of theory and using the density functional theory approach indicate that hydrogen halide is hydrogen bonded to the nitrogen atom of NO.[21] Very accurate calculations on the ab initio G2 theory level were carried out by Ball[22] for the complex formed between NO and H_2O. Several structures were received on the potential energy surface. In the most stable structure the water interacts through a hydrogen atom and the nitrogen monoxide through the N atom.

In the present work, we report the results of matrix isolation studies and ab initio calculations for the NO complexes with nitrous acid. These complexes are particularly interesting because both HONO acid and NO oxide play an important role in atmospheric chemistry; and the NO oxide is the product of decomposition of the $(HONO)_2$ dimer. In contrast with hydrogen halide complexes, the formation of nitrous acid−nitrogen monoxide complexes will be well reflected in the perturbation of all six vibrations of nitrous acid.

Experimental Section

Infrared Matrix Isolation Studies. NO/Ar and HONO/Ar mixtures were co-deposited simultaneously through two separate spray-on lines. Ammonium nitrite was used as a source of nitrous acid, and HONO/Ar gas mixtures were prepared in the same way as previously described.[23−25] The concentration of the HONO/Ar mixture varied in the range 1/300−1/800. The NO/Ar mixtures were prepared by standard manometric technique; the concentration of the NO/Ar mixture varied in the range 1/200−1/2400.

The gaseous mixtures were sprayed onto a gold-plated mirror held at 20 K during matrix deposition by means of a closed-

---

[†] Part of the special issue "Marilyn Jacox Festschrift".

* Corresponding author. E-mail: zm@wchuwr.chem.uni.wroc.pl. Fax: 48 71 328-23-48.

10.1021/jp993889i CCC: $19.00

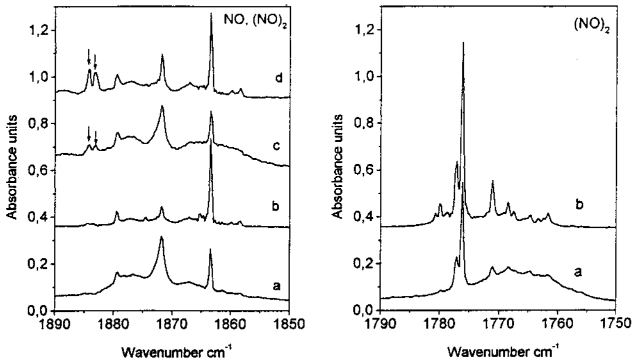

Figure 1. Region of the N=O stretching vibrations of NO monomer and $(NO)_2$ dimers in the spectra of matrices: NO/Ar = 1/2400 (a), NO/Ar = 1/300 (b), NO/HONO/Ar = 1/1/1200 (c), and NO/HONO/Ar = 3/2/1200 (d).

cycle helium refrigerator (Air Product Displex 202A). The matrix was maintained at 11 K for infrared measurements. The spectra were registered at 0.5 cm^{-1} resolution in a reflection mode with a Bruker 113v FTIR spectrometer.

Computational Details. All calculations were performed within the framework of the ab initio approach using the GAUSSIAN 94 package of computer codes.[26] Electron correlation was considered via the restricted open-shell Moeller−Plesset perturbation theory [27,28] to the second order (ROMP2), including explicitly all electrons. The structures of the isolated monomers, HONO and NO, and the structures of HONO complexes with NO were fully optimized by using the 6-311++G(2d,2p) basis set.[29,30] Vibrational frequencies were computed both for the monomers and for the complexes. Interaction energies were corrected by the Boys−Bernardi full counterpoise correction[31] at both the SCF and ROMP2 levels.

Results

Experimental Spectra. The spectra of HONO/Ar matrices are in good agreement with those previously reported.[23−25] Weak bands due to NH_3 and HONO decomposition products (NO, NO_2, H_2O) were also present in the matrix but their concentration was low which permitted the study of nitrous acid complexes.

The spectra of NO monomer and dimer in low-temperature matrices were extensively studied.[32−36] Our spectra are in general agreement with those previously reported.

Figure 1 presents the spectra of NO/Ar and NO/HONO/Ar matrices in the region of the N=O stretching vibrations. In the spectrum of the most diluted NO/Ar = 1/2400 matrix (see Figure 1a) strong band due to NO stretch was observed at 1871.8 cm^{-1} with a weak accompanying band at 1879.5 cm^{-1} apparently due to splitting by the matrix cage.[33,36] Bands due to the symmetric and antisymmetric stretching of *cis*-$(NO)_2$ dimer were observed, correspondingly, at 1863.5 cm^{-1} and at 1776.2 cm^{-1} (with a shoulder at 1772.2 cm^{-1}).[33] In more concentrated matrices the relative intensity of the 1879.5 cm^{-1} monomer band increased with respect to the 1871.8 cm^{-1} one and a weak band appeared at 1874.5 cm^{-1}(see Figure 1b). The relative intensities of the $(NO)_2$ dimer bands at 1863.5, 1777.2 (sh), and 1776.2 cm^{-1} strongly increased with respect to NO monomer bands. Additional bands also appeared at 1780.7 and 1779.9 cm^{-1} and at 1771.1, 1768.4, 1767.5 (sh), and 1761.6 cm^{-1}. The pattern of bands at 1776.2, 1777.2, 1779.9, and 1780.7 cm^{-1} observed for the ν_5(N=O) antisymmetric stretch of *cis*-$(NO)_2$ dimer at higher NO/$(NO)_2$ ratio is in good agreement with that reported recently by Saxce et al.[20] The band at 1771.1 cm^{-1} is probably due to aggregates of *cis*-$(NO)_2$ and the absorption at 1768.4 cm^{-1} to the *trans*-$(NO)_2$ dimer.[32,34]

TABLE 1: Frequencies (cm^{-1}) and Absorbances of the Product Absorptions Appearing after Co-deposition of NO/Ar and HONO/Ar Gaseous Mixtures

freq	*A*	assignment[a]	freq	*A*	assignment
3511.0	0.15	1:1, t	1627.3	0.10	2:1, c
3508.5	0.13	1:1, t	1299.5	0.14	1:1, t
3500.0	0.03	2:1, t	867.5	0.07	2:1, c
3365.0	0.05	1:1, c	864.7	0.23	1:1, c
1884.2	0.09	1:1	812 (sh)	0.04	2:1, t
1883.2	0.08	1:1	809.5	0.12	1:1, t
1683.1	0.47	1:1, t	622.0	0.10	1:1, t
1681.1	0.06	2:1, t	616.5	0.06	1:1, t
1628.3	0.29	1:1, c			

[a] (1:1, t); (1:1,c) bands assigned to 1:1 complexes of trans or cis HONO isomers with NO; (2:1,t); (2:1,c) bands assigned tentatively to complexes of $(NO)_2$ dimers with *trans*- or *cis*-HONO isomers.

When nitrous acid was added to NO/Ar matrices, an additional doublet of bands appeared in the NO stretch region at 1884.2, 1883.2 cm^{-1} which was not observed in the spectra of NO/Ar matrices. Figure 1 compares the spectra of NO/Ar matrices with the spectra of NO/HONO/Ar matrices of concentration 1/2/1200 and 3/2/1200. As one can see in the figure, the intensity of the 1884.2, 1883.2 cm^{-1} doublet increases with respect to NO monomer bands with an increase of NO concentration. In the most concentrated matrices in which the NO/$(NO)_2$ ratio strongly decreased, the intensity of the 1884.2, 1883.2 cm^{-1} doublet decreased with respect to NO, $(NO)_2$ absorption. No other product band was identified in the N=O stretch region.

The two bands in the N=O stretch region are accompanied by the product bands occurring in the vicinity of the absorption due to *trans*- and *cis*-HONO isomers. Figures 2b, 3b, and 4b present the spectra of NO/HONO/Ar matrix of approximate concentration 3/2/1200 in the region of three HONO modes: OH stretch, N=O stretch, and N−O stretch. The spectra of HONO/Ar = 1/800 matrix are presented for comparison. As one can see in the figures, the product bands were observed at 3511.0, 3508.5, and 3500 cm^{-1} in the region of the OH stretch and at 1683.1, 1681.1, 812(sh), and 809.5 cm^{-1} in the regions of the N=O and N−O stretches of the *trans*-HONO isomer. The relative intensities of the weak bands at 3500, 1681.1, and 812 cm^{-1} increased slightly with respect to their partners at 3511.0, 1683.1, and 809.5 cm^{-1} with a decrease of NO/$(NO)_2$ ratio in the studied matrices. In addition to the bands presented in the figures, one weak band was observed at 1299.5 cm^{-1} in the vicinity of the NOH bending absorption and two weak bands were observed at 622.0, 616.5 cm^{-1} in the region of the ONO bending and OH torsion vibrations of the *trans*-HONO isomer. The relative intensities of the 3511.0, 3508.5, 1683.1, 1299.5, 809.5, 622.0, and 616.5 cm^{-1} product bands were constant, within experimental error, in all matrices studied.

The corresponding product bands for *cis*-HONO isomer occurred at 3365.0, 1628.3, 1627.3(sh) and at 867.5, 864.7 cm^{-1}. The weak bands at 1627.3(sh), 867.5 cm^{-1} increased with respect to the 1628.3, 864.7 cm^{-1} ones with a decrease of (NO)/$(NO)_2$ ratio. The relative intensities of the 1628.3, 864.7 cm^{-1} absorption were not affected by matrix concentration and matrix annealing. The frequencies of all product absorptions observed in the spectra of NO/HONO/Ar matrices are collected in Table 1.

Ab Initio Calculations. In the case of complexes formed by the NO molecule, electron correlation effects play an important role not only in a proper description of a value of interaction

TABLE 2: Calculated Properties of Isolated and Protonated of NO Molecule[a]

	NO			
property	calc	expt[b]	HNO^+	NOH^+
r(NO)	1.162	1.151	1.137	1.182
r(NH)			1.065	
r(OH)				1.017
Θ(HNO)			130.0	
Θ(NOH)				115.9
m	0.374	0.159		
ΔE_{prot}			−134.5	−109.3
PA (298 K)			126.6	103.2
ω	1875.9	1876 [1904][c]		

[a] Bond lengths in Å, angles in degrees, dipole moments in D, energies in kcal mol^{-1} , frequencies in cm^{-1}, protonation energy, ΔE_{prot}, proton affinity, PA, in kcal mol^{1}. [b] References 41 and 42. [c] The experimental harmonic frequency is given in brackets.

energy but also in the correct description of the electron distribution of NO molecule. Similar to the CO molecule,[37−40] the NO dipole moment is very sensitive to the inclusion of electron correlation. [41,42] At the Hartree−Fock level the negative partial charge is located on the oxygen and the dipole moment is incorrectly described as N^+O^-. However, inclusion of electron correlation effects in calculations gives the correct sign of dipole moment which is described by the N^-O^+ structure. It can be explained in terms of back-bonding in the π orbital set. [42]

Unrestricted Hartree−Fock (UHF) calculations performed by Davis, Andrews, and Trindle[18] as well as our preliminary calculations at the second-order unrestricted Moeller−Plesset (UMP2) theory have shown very severe spin contamination. For this reason we decided to use in all calculations the restricted open-shell MP2 formalism.

In Table 2 are presented the results of ROMP2/6-311++G-(2d,2p) calculations for an isolated molecule in the lowest electronic state ($^2\Pi$) as well as for the protonated NO molecule. As is evident in Table 2, the calculated bond length for NO as well as the dipole moment is slightly too large in comparison with available experimental data. On the other hand, the calculated harmonic vibrational frequency of the N═O stretching mode is underestimated by about 30 cm^{-1} in comparison with the estimated harmonic frequency but is in accord with experimental anharmonic frequency.

The calculated geometrical parameters of the structure of *cis*- and *trans*-HONO isomers and their vibrational frequencies have been published previously.[43]

The attack of a naked proton on two sides of the NO molecule may be thought of as an extreme or limiting case of the approach of a HONO molecule to form a hydrogen bond with NO. The calculated proton affinity of NO should therefore serve as an appropriate test of the adequacy of our approach for the study of the complexes. Results obtained for protonated NO and presented in Table 2 clearly show that proton may be attached to both sides of molecule. Calculated protonated energies, ΔE_{prot}, and values of proton affinities (PA) at 298 K indicate that proton is more strongly bound by the nitrogen atom of NO molecule. The calculated value of the PA for the nitrogen-protonated NO molecule is equal to 126.6 kcal/mol and is in a good accord with an experimental estimation of 127 kcal/mol of the PA value.[46] Moreover, estimation of the PA of the nitrogen and oxygen sites of NO molecule given by Barnes and co-workers,[47] on the basis of thermochemical data for HNO^+ and NOH^+, gave values of 131 and 113 kcal/mol, respectively. The above data strongly suggest the nitrogen atom as the preference proton acceptor site for the hydrogen bonding.

TABLE 3: Calculated Properties of HONO−NO Complexes[a]

	trans-HONO		*cis*-HONO	
property	t-NO	t-ON	c-NO	c-ON
R(O···N)	3.168	3.233		
R(O···O)			3.187	3.336
R(OH)	0.970	0.967	0.980	0.977
Δr(OH)	0.003	0.003	0.004	0.001
r(N═O)	1.182	1.180	1.197	1.194
r(N−O)	1.424	1.433	1.390	1.396
Θ(ONO)	111.2	111.0	113.6	113.4
Θ(NOH)	101.3	101.4	105.4	104.9
r(NO)[b]	1.161	1.162	1.161	1.162
Θ(OH···O)	170.3	177.5		
Θ(OH···N)			173.4	172.4
ϕ(NO···N═O)	−65.2	−39.4		
ϕ(NO···O═N)			−40.8	71.6
ΔE^{CP}	−2.02	−0.51	−1.75	−0.46
E_{dis}	−1.41	−0.17	−1.20	−0.17

[a] Bond lengths in Å, angles in degrees, energies in kcal mol^{-1}. [b] Bond length of the NO molecule.

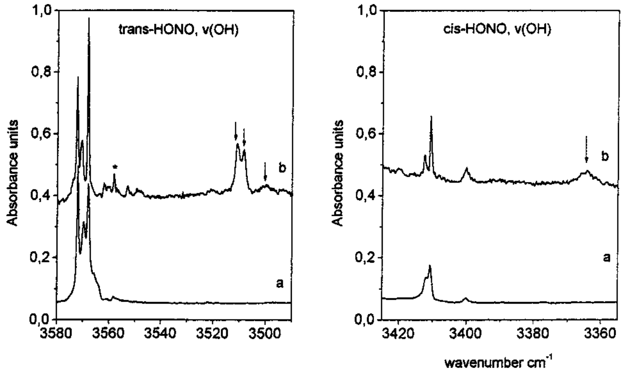

Figure 2. Region of OH stretch of *trans*- and *cis*-HONO isomers in the spectra of matrices: HONO/Ar = 1/1800 (a), NO/HONO/Ar = 3/2/1200 (b). The bands assigned to the complexes of nitrous acid−nitrogen monoxide are indicated by arrows; the bands indicated by asterisks are due to the presence of N_2 contaminant.

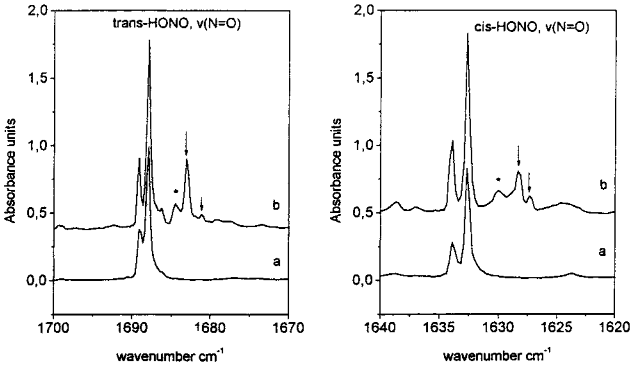

Figure 3. Region of N═O stretch of *trans*- and *cis*-HONO isomers in the spectra of the same matrices as presented in Figure 2.

The results of geometry optimizations of *trans*- and *cis*-HONO complexes with NO molecule are collected in Table 3. Two stationary points for the *trans*-HONO complexes (described as t-NO and t-ON) and another two stationary points for the *cis*-HONO complexes (designated as c-NO and c-ON) calculated by using the 6-311++G(2d,2p) basis set at the ROMP2 level, are presented in Figure 5. All obtained structures describe the hydrogen-bonded complexes with HONO molecule acting as a proton donor, but they have different orientation of NO molecule. Structures t-NO and c-NO describe the hydrogen-bonded complexes with the nitrogen atom of NO molecule as

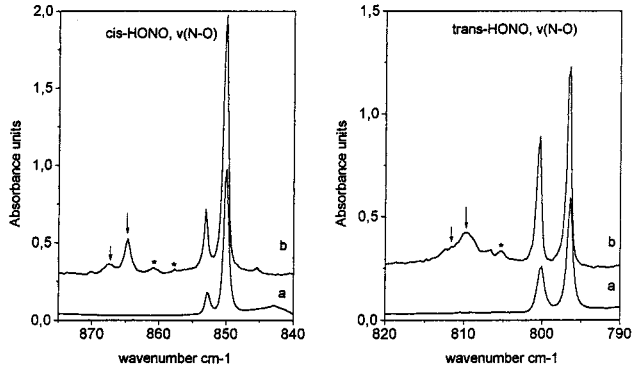

Figure 4. Region of N−O stretch of *trans*- and *cis*-HONO isomers in the spectra of the same matrices as presented in Figure 2.

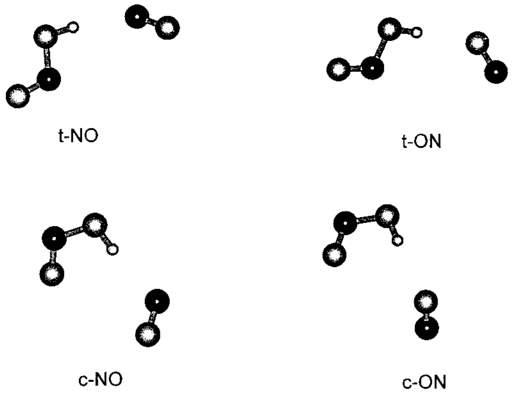

Figure 5. Optimized structures of the nitrous acid complexes with nitrogen monoxide.

TABLE 4: Calculated (ω) and Observed (ν) Frequencies (cm^{-1}) and Frequency Shifts ($\Delta\omega = \omega_{com} - \omega_{mon}$, $\Delta\nu = \nu_{mon} - \nu_{com}$)[a] for the Complexes of *trans*-HONO Isomer with NO

trans-HONO···NO		*trans*-HONO···NO		*trans*-HONO···ON		
ω	$\Delta\omega$	ν	$\Delta\nu$	ω	$\Delta\omega$	assignment
3728.1	−62.6	3511.0	−60.8	3782.1	−8.6	O−H stretch
		3508.5				
1630.3	−13.1	1683.1	−4.8	1639.9	−3.5	N═O stretch
1324.5	+35.0	1299.5	+34.7	1308.9	+19.4	NOH bend
817.2	+24.6	809.5	+11.3	802.3	+9.7	N−O stretch
615.7	+32.3	622.0	+13.3	595.8	+12.4	ONO bend
677.3	+96.8	616.5	+68.3	610.4	+29.9	OH torsion
1881.1	+5.2	1884.5	+12.5	1872.3	+2.8	NO

[a] In the case where site splitting occurs the shifts were measured with respect to the average frequency of the two-site components.

TABLE 5: Calculated (ω) and Observed (ν) Frequencies (cm^{-1}) and Frequency Shifts ($\Delta\omega = \omega_{com} - \omega_{mon}$, $\Delta\nu = \nu_{mon} - \nu_{com}$) for the Complexes of *cis*-HONO Isomer with NO

cis-HONO···NO		*cis*-HONO···NO		*cis*-HONO···ON		
ω	$\Delta\omega$	ν	$\Delta\nu$	ω	$\Delta\omega$	assignment
3567.0	−69.8	3365.0	−46.6	3632.4	−4.4	O−H stretch
1586.9	−8.4	1628.3	−5.0	1592.8	−2.5	N═O stretch
1351.6	+23.0			1334.8	+6.2	NOH bend
893.9	+23.6	864.7	+13.2	876.4	6.1	N−O stretch
638.2	+16.0			626.5	4.3	ONO bend
744.0	+62.4			702.4	+20.8	OH torsion
1878.7	+2.8	1883.1	+11.1	1871.4	−4.5	NO

the proton acceptor site whereas complexes denoted as t-ON and c-ON present the systems with the oxygen atom of NO involved directly in O−H···O hydrogen bridge.

The ROMP2-optimized intermolecular distances, *R*, measured between two heavy atoms involved in the hydrogen bridge are in the range 3.17−3.34 Å. Particularly noteworthy is slightly shorter intermolecular distance for *trans*- and *cis*- HONO complexes with nitrogen atom of NO molecule involved directly in a hydrogen bridge in comparison to complexes bound by the oxygen site. Unfortunately, there are no available experimental structures for these systems but their basic nature can be verified on the basis of the IR spectra in matrix environment which are presented in this paper. Because of the complex formation, very small elongation of the O−H bond of HONO is noted which is less than 0.005 Å. The other intramolecular parameters of HONO subunits are only slightly perturbed by the formation of the complexes. We also note some sensitivity of the bond length of NO molecule to complex formation. For complexes labeled t-NO and c-NO, with nitrogen atom as proton acceptor, a small shortening of 0.001 Å in the NO bond length is observed when the complex is formed whereas for complexes formed by the oxygen site of the NO subunit the NO length is not changed.

Counterpoise-corrected ROMP2 interaction energies, ΔE^{CP}, and dissociation energies, E_{dis}, are presented in the last two rows of Table 3. The results indicate that HONO molecule forms rather weak complexes with NO; the values of dissociation energy do not exceed 1.5 kcal/mol. The complexes formed by the *trans*-HONO isomer are more strongly bound than those formed by the *cis*-HONO isomer and the difference in dissociation energy is larger than 1 kcal/mol. In all cases the strongest complexes are formed by the nitrogen site of NO subunits which is in a good accord with the trends of PA values of the NO molecule. The calculated frequencies for the four complexes, t-NO, t-ON, c-NO, and c-ON, are displayed in Tables 4 and 5 and compared with experimental data.

Discussion

The matrix isolation studies were performed at low concentration of both dopants: NO and HONO. However, even in highly diluted matrices, both NO monomer and *cis*-$(NO)_2$ dimer are present and the formation of HONO complexes with NO and $(NO)_2$ in the studied matrices should be considered. Davis, Andrews, and Trindle[18] and Saxce et al.[20] in their studies of hydrogen halide complexes with NO and Barnes et al.[47] in the studies of the HNO_3−NO system observed formation of HX or HNO_3 complexes with both NO monomer and $(NO)_2$ dimer. In contrast with the studies of hydrogen halide and nitric acid complexes, we observe in the region of the N═O stretch of NO monomer and $(NO)_2$ dimers only one product absorption, a doublet at 1884.2, 1883.2 cm^{-1} which is assigned with confidence to the perturbed NO vibration of the NO molecule in the 1:1 complexes with nitrous acid. First, the 1884.2, 1883.2 cm^{-1} doublet appears in the spectra of very diluted NO/HONO/Ar matrices in which concentration of the *cis*-$(NO)_2$ dimer is low (see Figure 1). Second, the 1884.2, 1883.2 cm^{-1} frequencies have very close values to the frequencies of NO molecule in complexes with HF (1887 cm^{-1}),[18] HCl (1880 cm^{-1}),[20] and HNO_3 (1889 cm^{-1})[47] as expected for complexes of similar strength. As was reported earlier, nitrous acid with weak bases forms complexes of comparable strength to HCl complexes with the same bases.[25] Consequently, the set of bands observed at 3511.0, 3508.5, 1683.1, 1299.5, 622.0 and 616.5 cm^{-1} in the vicinity of *trans*-HONO absorption and a set of bands at 3365.0, 1628.3, and 864.7 cm^{-1} in the vicinity of *cis*-HONO bands are assigned respectively to 1:1 *trans*-HONO and *cis*-HONO complexes with NO. The relative intensities of all the above bands and the 1884.2, 1883.2 cm^{-1} doublet are constant in all spectra studied; they do not depend on matrix concentration and are not affected by matrix annealing. The three weak bands at 3500, 1681.1, and 812.0 cm^{-1} and the two weak bands at 1627.3 and 867.5 cm^{-1} which appear, respectively, in the vicinity of *trans*-HONO and *cis*-HONO absorption are assigned tentatively to 2:1 complexes of *cis*-$(NO)_2$ dimer with *trans*- and *cis*-HONO isomers. The intensities of these bands increase slightly with respect to bands assigned to 1:1 complexes when the NO/$(NO)_2$ ratio in matrix decreases.

In Tables 4 and 5 the frequencies observed for the 1:1 *trans*- and *cis*-HONO complexes with NO are compared with the calculated ones for t-NO, c-NO and t-ON, c-ON complexes. The comparison of the observed frequency shifts for the complexes trapped in the matrix with the predicted ones for the optimized t-NO, c-NO and t-ON, c-ON structures allows to determine the site of the NO molecule to which HONO is bonded in the 1:1 complexes isolated in solid argon.

The observed blue shift of the perturbed vibration of NO molecule in the complexes trapped in the matrix strongly suggests that they have the t-NO, c-NO type of structure with *trans*- or *cis*-HONO isomer bonded to nitrogen atom of NO. Ab initio calculations predict blue shift of the perturbed vibration of NO in t-NO, c-NO complexes and red shift of this vibration in t-ON, c-ON complexes. The performed experimental studies do not give definitive answer whether the 1884.2, 1883.2 cm^{-1} doublet is due to *trans*-HONO complex or to both *trans*- and *cis*-HONO complexes. In agreement with ab initio calculations, we tentatively assigned the higher frequency component (1884.2 cm^{-1}) to the *trans*-HONO complex and the lower frequency component (1883.2 cm^{-1}) to the *cis*-HONO one. The calculations predict larger blue frequency shift for the complex formed by the *trans*-HONO isomer (5.2 cm^{-1}) than by the *cis*-HONO one (2.8 cm^{-1}). However, the possibility that the two components of the observed doublet are due to site splitting cannot be excluded. The 1884.2, 1883.2 cm^{-1} bands are ca. 12.4, 11.4 cm^{-1} blue-shifted with respect to the NO monomer band at 1871.8 cm^{-1} or ca. 4.7, 3.7 cm^{-1} blue-shifted with respect to the second monomer band at 1879.5 cm^{-1}. The predicted shifts of the NO vibration in the t-NO and c-NO complexes are equal, respectively, 5.2 and 2.8 cm^{-1}.

The observed frequencies of the perturbed *trans*- and *cis*-HONO modes also support the t-NO, c-NO structures for the complexes isolated in argon.

The 3511.0, 3508.5 cm^{-1} doublet assigned to the perturbed OH stretch in NO complex with *trans*-HONO isomer is ca. 60 cm^{-1} red-shifted with respect to the corresponding *trans*-HONO band (as measured with respect to the average frequency of the two site components). The relative intensity of the 3511.0, 3508.5 cm^{-1} pair does not depend on matrix concentration and therefore the pair is assigned to site splitting. The 1299.5 cm^{-1} absorption assigned to perturbed NOH in plane bending vibration is 35 cm^{-1} blue-shifted with respect to the monomer band. The observed shifts match very well the predicted ones for the t-NO complex (-62.6 cm^{-1} for OH stretch, $+35.0$ cm^{-1} for NOH in plane bend, see Table 4). The calculations predict much smaller shifts for the corresponding modes in the t-ON complex (-8.6 cm^{-1} for OH stretch, $+19.4$ cm^{-1} for NOH bend).

The other perturbed vibrations of *trans*-HONO molecule were identified at 1683.1, 809.5, 622.0, and 616.5 cm^{-1}. The 1683.1 and 809.5 cm^{-1} bands are readily assigned to the perturbed N=O and N−O stretches; the N=O stretch is 4.8 cm^{-1} red-shifted and N−O stretch is 13.3 cm^{-1} blue-shifted from the corresponding vibrations of *trans*-HONO monomer. The 622.0 and 616.5 cm^{-1} bands are assigned respectively to the perturbed ONO bending and OH torsion vibrations. In weakly hydrogen-bonded complexes of *trans*-HONO with N_2 and CO, the perturbed ONO bending was observed at 618.8 and 629.6 cm^{-1}, respectively.[24] The perturbed frequencies of the *trans*-HONO molecule respond almost linearly to the perturbation of OH vibration.[25] The perturbation of OH stretch in *trans*-HONO complex with NO is larger than in the complex with N_2, so the ONO bending vibration in the NO complex is expected to be more perturbed than in the complex with N_2. The ONO bending vibration is observed at 608.7 cm^{-1} for isolated *trans*-HONO monomer and at 618.8 cm^{-1} for the *trans*-HONO complex with N_2. Consequently, we assigned the 622.0 cm^{-1} band to the perturbed ONO bending vibration and the 616.5 cm^{-1} one to the perturbed OH torsion in t-NO complex. The frequencies of the perturbed ONO bending and OH torsion vibrations are respectively 13.3 and 68.3 cm^{-1} shifted toward higher frequencies with respect to the corresponding absorptions of *trans*-HONO monomer. The relatively large red shift of OH torsion is expected for the t-NO structure. As one can see in Table 4 the calculations overestimate the frequency shifts for the N=O, N−O stretches, ONO bending, and OH torsion modes.

For the *cis*-HONO complex with NO molecule only three perturbed vibrations of nitrous acid were identified. This is probably due to smaller concentration of *cis*-HONO complexes than *trans*-HONO ones in the studied matrices.[23] The 3365.0 cm^{-1} band is assigned to the perturbed OH stretch in the NO complex. The band is 46.5 cm^{-1} red-shifted from the corresponding absorption of the *cis*-HONO monomer which supports the c-NO structure. Ab initio calculations predict a 69.8 cm^{-1} red shift for the c-NO structure and very small, 4.4 cm^{-1}, red shift for the c-ON one. The 1628.3 and 864.7 cm^{-1} absorptions are readily assigned to the perturbed N=O and N−O stretches of *cis*-HONO in the complex with NO. The 1628.3 cm^{-1} band is ca. 5.0 cm^{-1} shifted toward lower frequencies and the 864.7 cm^{-1} band is 13.2 cm^{-1} shifted toward higher frequencies with respect to corresponding *cis*-HONO absorptions.

The larger shift of the OH stretch in the *trans*-HONO complex (ca. 61 cm^{-1}) than in the *cis*-HONO one (ca. 47 cm^{-1}) indicates that *trans*-HONO isomer forms a slightly stronger complex than the *cis*-HONO one which is in accord with earlier studies of other nitrous acid complexes and in agreement with the performed calculations. The calculated interaction energies are equal to -2.02 and -1.75 kcal/mol, respectively, for the *trans*- and *cis*-HONO complexes with NO (see Table 3).

The complexes of the trans and cis isomers with NO show some similarity to the complexes of the two isomers with carbon monoxide.[24] In the case of HONO complexes with CO the more stable structures are formed when the acid molecule is attached to the carbon atom and not to the oxygen atom. Both systems are characterized by a nearly linear hydrogen bridge and similar intermolecular distance (ca. 3.2 Å). However, comparison of calculated interaction energies shows that more stable complexes are formed by HONO with CO than with NO. This is reflected in slightly larger perturbation of HONO vibrations in complexes with CO trapped in the matrix. In particular, the OH stretching vibration is observed at 3498.9 cm^{-1} and NOH bending at 1312.6 cm^{-1} in OC⋯HONO-trans complex whereas they occur, respectively, at 3511, 3508.5 and at 1299.5 cm^{-1} in ON⋯HONO-trans complex.

We did not identify in the studied matrices the oxygen-attached NO⋯HONO complexes. This is due to their much lower stability and, consequently, to their low concentration in the studied matrices. The oxygen-bound complexes are less stable by more than 1 kcal/mol from the nitrogen-attached ones and the calculated dissociation energy for both trans and cis complexes is very small (−0.17 kcal/mol).

The weak bands at 3500.0, 1681.1, and 812.5 cm^{-1} and at 1627.3 and 867.5 cm^{-1}which appeared at low NO/(NO)$_2$ ratio and increased with respect to the 1:1 complex bands at higher (NO)$_2$ concentration are tentatively assigned to the complexes of *trans*- and *cis*-HONO with *cis*-(NO)$_2$ dimers. The HONO modes are slightly more perturbed in the *cis*-(NO)$_2$···HONO complexes (see Table 1) than in the ON···HONO heterodimers but the particular modes are shifted in the same direction as for the 1:1 complexes. This indicates a slightly stronger interaction of the HONO isomers with *cis*-(NO)$_2$ dimer than with NO monomer and is in accord with earlier studies of hydrogen halide complexes with NO and *cis*-(NO)$_2$ bases. Davis, Andrews and Trindle[18] reported the 3846.5, 3845.0 cm^{-1} frequencies for the perturbed HF vibration in complexes with NO and *cis*-(NO)$_2$ and Saxce et al.[20] reported the 2827.0, 2815.1 cm^{-1} frequencies for the perturbed HCl vibration in complexes with NO and *cis*-(NO)$_2$.

Conclusions

Ab initio calculations carried out for the nitrous acid−nitrogen monoxide system indicate formation of four stable complexes in which the *trans*- or *cis*- HONO isomers are attached to nitrogen or oxygen atoms of nitrogen monoxide. The complexes with nitrogen-attached *trans*- and *cis*-HONO isomers are predicted to be much more stable than the oxygen attached complexes. The binding energy at the ROMP2 level with the 311++G(2d,2p) basis set is −2.02 and −1.75 kcal/mol for the nitrogen-attached *trans*- and *cis*-HONO isomers, respectively, and −0.51and −0.46 kcal/mol for the oxygen-attached trans and cis isomers. Infrared matrix isolation studies led to identification of ON···HONO-trans and ON···HONO-cis complexes in solid argon. Six perturbed *trans*-HONO vibrations and three perturbed *cis*-HONO vibrations were identified for the *trans*- and *cis*-HONO complexes. The blue shift of NO vibration as well as the relatively large perturbation of the OH stretches in both *trans*- and *cis*-HONO complexes prove the ON···HONO type of geometry for the complexes trapped in argon.

Acknowledgment. The authors gratefully acknowledge financial support from the Polish State Committee for Scientific Research (Grant KBN No 543 96 11). Z.L. and R.W. acknowledge the Wrocław Supercomputer Centre and Poznan Supercomputer Centre for providing computer time and facilities.

References and Notes

(1) Dyke, T. R. *Top. Curr. Chem*. **1984**, *120*, 85.
(2) Legon, A. C. *Annu. Rev. Phys. Chem*. **1983**, *34*, 275.
(3) Legon, A. C.; Millen, D. J. *Chem. Rev*. **1986**, *86*, 635.
(4) Peterson, K. I.; Fraser, G. T.; Nelson, D. D. Jr.; Klemperer, W. In *Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules*; Bartlett, R. J., Ed.; Reidel: Dordrecht, 1985; pp 217−244.
(5) Bevan, J. W. In *Structure and Dynamics of Weakly Bound Molecular Complexes*; Weber, A., Ed.; Reidel: Dordrecht, 1987; p 149.
(6) Howard, B. J. In *Structure and Dynamics of Weakly Bound Molecular Complexes*; Weber, A., Ed.; Reidel: Dordrecht, 1987; p 69.
(7) Celii, F. G.; Janda, K. C. *Chem. Rev*. **1986**, *86*, 507.
(8) Miller, R. E. *J. Phys. Chem*. **1986**, *90*, 3301.
(9) Zeng, Y. P.; Sharpe, S. W.; Reifschneider, D.; Wittig, C.; Beaudet, R. A. *J. Chem. Phys*. **1990**, *93*, 183.
(10) Woon, D. E.; Dunning Jr., Th. H.; Peterson, K. A. *J. Chem. Phys*. **1996**, *104*, 5883.
(11) Klopper, W.; Quack, M.; Suhm, M. A. *Mol. Phys*. **1998**, *94*, 105.
(12) Rablen, P. R.; Lockman, J. W.; Jorgensen, W. L. *J. Phys. Chem. A* **1998**, *102*, 3782.
(13) Chandra, A. K.; Nguyen, M. T.*J. Phys. Chem. A* **1998**, *102*, 6865.
(14) Alkorta, I.; Rozas, I.; Elguers, J. *Theor. Chem. Acc*. **1998**, *99*, 116.
(15) Jiang, J. C.; Tsai, M. H. *J. Phys. Chem. A* **1997**, *101*, 1982.
(16) Johnsson, K.; Engdahl, A.; Ouis, P.; Nelander, B. *J. Phys. Chem*. **1992**, *96*, 5778.
(17) Francisco, J. S.; Sander, S. P. *J. Am. Chem. Soc*. **1995**, *117*, 9917.
(18) Davis, S. R.; Andrews, L.; Trindle, C. O. *J. Chem. Phys*. **1987**, *86*, 6027.
(19) Fawzy, W. M.; Fraser, G. T.; Hougen, J. T.; Pine, A. S. *J. Chem. Phys*. **1990**, *93*, 2992.
(20) De Saxce, A.; Sanna, N.; Schriver, A.; Schriver-Mazzuoli, L. *Chem. Phys*. **1994**, *185*, 365.
(21) Krim, L.; Alikhani, M. E. *Chem. Phys*. **1998**, *237*, 265.
(22) Ball, D. W. *J. Phys. Chem. A* **1997**, *101*, 4835.
(23) Mielke, Z.; Tokhadze, K. G.; Latajka, Z.; Ratajczak, E. *J. Phys. Chem*. **1996**, *100*, 539.
(24) Mielke, Z.; Latajka, Z.; Kołodziej, J.; Tokhadze, K. G. *J. Phys. Chem*. **1996**, *100*, 11610.
(25) Mielke, Z.; Wierzejewska, M.; Olbert, A.; Krajewska, M.; Tokhadze, K. G. *J. Mol. Struct*. **1997**, *436−437*, 339.
(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian Inc.: Pittsburgh, PA, 1995.
(27) Moeller, C.; Plesset, M. S. *Phys. Rev*. **1934**, *46*, 619.
(28) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem*. **1974**, *9*, 229.
(29) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys*. **1980**, *72*, 650.
(30) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys*. **1984**, *80*, 3265.
(31) Boys, S. F.; Bernardi, F. *Mol. Phys*. **1970**, *19*, 553.
(32) Guillory, W. A.; Hunter, C. E. *J. Chem. Phys*. **1969**, *50*, 3616.
(33) Hawkins, M.; Downs, A. J. *J. Phys. Chem*. **1984**, *88*, 1527.
(34) Jacox, M. E.; Thompson, W. E. *J. Chem. Phys*. **1990**, *93*, 7609.
(35) Legay, F.; Legay-Sommaire, N. *Chem. Phys. Lett*. **1993**, *211*, 516.
(36) Kometer, R.; Legay, F.; Legay-Sommaire, N.; Schwentner, N. *J. Chem. Phys.* **1994**, *100*, 8737.
(37) Scuseria, G. E.; Miller, M. D.; Jensen, F.; Geertsen, J. *J. Chem. Phys*. **1991**, *94*, 6660.
(38) Barnes, L. A.; Liu, B.; Lindh, R. *J. Chem. Phys*. **1993**, *98*, 3972.
(39) Guan, J.; Duffy, O.; Carter, J. T.; Chong, D. P.; Casida, K. C.; Casida, M. E.; Wrinn, M. *J. Chem. Phys*. **1993**, *98*, 4753.
(40) Ernzerhof, M.; Marian, C. M.; Peyerimhoff, S. D. *Chem. Phys. Lett*. **1993**, *204*, 59.
(41) Walsh, S. P.; Goddard, W. A. *Chem. Phys. Lett*. **1974**, *33*, 18.
(42) Ferguson, W. I. *Mol. Phys*. **1981**, *42*, 371.
(43) Latajka, Z.; Mielke, Z.; Olbert-Majkut, A.; Wieczorek, R.; Tokhadze, K. G. *Phys. Chem. Chem. Phys*. **1999**, *1*, 2441.
(44) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, Vol. 4; Constants of Diatomic Molecules*; Van Nostrand: Princeton, NJ, 1979.
(45) Neumann, R. M. *Astrophys. J*. **1970**, *161*, 779.
(46) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.
(47) Barnes, A. J.; Lasson, E.; Nielsen, C. J. *J. Chem. Soc., Faraday Trans*. **1995**, *91*, 3111.