Quantum Chemical Study of the Bimolecular Complex of HONO

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Received: February 18, 1999; In Final Form: May 24, 1999

Structures, energetics, and vibrational properties for the bimolecular complex of HONO have been studied by ab initio methods. Ten stable complexes of $(HONO)_2$ were found. Four of the complexes are formed between two *trans* isomers, three between two *cis* isomers, and three complexes are found between one trans and one cis isomer. All complexes involve a hydrogen bond from the OH tail of one of the subunits. The calculated interactions energies at the MP2/6-311++G(2d,2p) level vary between −10 and −20 kJ mol^{-1} representing a relatively strong interaction. The structural properties of the subunits were found strongly perturbed upon complexation, and the vibrational spectra of the various $(HONO)_2$ complexes are predicted to show large vibrational shifts compared with the monomer spectra.

Introduction

Weak chemical interactions are common in molecular science being profuse in, for example, catalytic reactions, surface chemistry, material science, and biological processes. By far, the most interest has been devoted to the hydrogen bond, which has been established as a major noncovalent or nonionic source of interaction between numerous chemical compounds.

Recently, weak chemical interactions have been noted to play a role in atmospheric chemistry.[1] Water−O_2 and water−N_2 interactions have been attributed as important channels for absorbing both short-wavelength solar radiation arriving in the atmosphere and the outgoing infrared (IR) surface radiation, thereby resulting in an additional "greenhouse" trapping of far-IR radiation.[2,3] Also, the $H_2O-O(^3P)$ complex has been observed to produce hydrogen peroxide in rare gas matrixes upon UV photolysis.[4] H_2O_2 itself is of great significance in atmospheric oxidation reactions mainly due to the production of OH radicals. Another source for atmospheric OH radicals is nitrous acid (HONO), which plays an important role in the chemistry of the polluted troposphere.[5] HONO is unstable in the gas phase and occurs in a complex equilibrium with the products of its decomposition:

$$2HONO \leftrightarrow NO + NO_2 + H_2O \tag{1}$$

The backward reaction to two HONO molecules in the troposphere occurs likely by exothermic termolecular reaction possibly initiated by, for example, lightning. Recently the bimolecular decomposition of HONO was studied by ab initio molecular orbital (G2M) and transition state theory calculations.[6] The reaction was found to take place via cyclic transition state structures with decreasing reaction barriers as the size of the ring increased, the lowest energy barrier (13.7 kJ mol^{-1}) was formed by the reaction of *cis*- and *trans*-HONO molecules through a six-membered-ring transition state.[6] For the HONO precursors only the energetics of the optimized monomers were considered, even though several studies on complexes of HONO have appeared,[7−11] showing the ability of HONO to engage in interactions of substantial strength. Both *cis*- and *trans*-HONO were found to form strong hydrogen-bonded complexes from the OH-tails with the ammonia nitrogen, the estimated interaction energies being ca. −40 kJ mol^{-1}.[7] Weaker interactions of HONO with molecules such as CO (−17 kJ mol^{-1}),[8] N_2 (−11 kJ mol^{-1}),[8] and SO_2 (−14 kJ mol^{-1})[11] have been studied both experimentally and computationally. In all of these studies the cis-isomer complexes are always estimated to be a few kJ mol^{-1} weaker than the corresponding trans complexes, corresponding roughly to the experimental cis−trans relative energy difference (∼ 1.5 kJ mol^{-1}).[12] The vibrational properties of several HONO complexes with SO_2,[11] C_2H_2,[9] and various oxygen bases[10] have been also studied in low-temperature matrixes indicating strong perturbations of HONO upon complexation compared with unperturbed monomers.

In this paper we will report quantum chemical results on different structures, energetics, and vibrational properties of bimolecular complexes formed by *trans*- and *cis*-HONO. We will also discuss the implications of the dimerization in the light of the existing gas-phase matrix isolation experiments failing to observe the $(HONO)_2$ dimer.

Computational Details

The structures of the monomers and the complexes were fully optimized at the MP2(FC) level using the split-valence 6-311++G(2d,2p) basis set augmented with diffuse and polarization functions. The larger basis set 6-311++G(3df,3pd) and the correlation consistent basis sets without (cc-pVTZ) and with (aug-cc-pVTZ) augmented diffuse functions were used to evaluate the binding energies of the various complexes in single-point calculations explicitly correlating all electrons. All interaction energies were corrected for basis set superposition error (BSSE) by the Boys−Bernardi counterpoise correction scheme.[13]

All calculations were carried out using the Gaussian 94 [14] package of computer codes on computers at the Wroclaw

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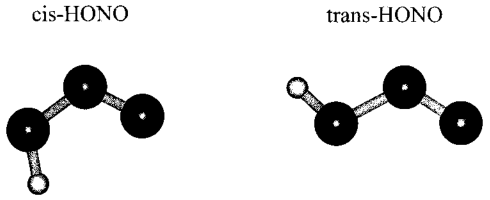


r N=O	1.193	r N=O	1.178
r N-O	1.397	r N-O	1.439
r O-H	0.976	r O-H	0.967
α O=N-O	113.4	α O=N-O	110.9
α N-O-H	104.7	α N-O-H	101.5
τ HONO	0.0	τ HONO	180.0

Figure 1. MP2/6-311++G(2d,2p) calculated equilibrium structures of *trans*- and *cis*-HONO. The structural parameters are presented under the molecules. Bond distances are given in angstroms and bond angles are in degrees.

Supercomputing Center (Wroclaw, Poland), the Poznan Supercomputing Center (Poznan, Poland), and the CSC—Center for Scientific Computing Ltd. (Espoo, Finland).

Results and Discussion

The monomer properties of nitrous acid (HONO) were estimated at the MP2/6-311++G(2d,2p) level of theory in accordance with the complex studies. The computational structures of *cis*- and *trans*-HONO are shown in Figure 1, and they are in reasonable agreement with the experimental equilibrium structures from microwave spectroscopy.[15−17] HONO is also one of the simplest molecules to undergo cis−trans isomerization. The cis−trans isomerization barrier is less than 50 kJ mol^{-1} enabling IR-induced isomerization processes,[18,19] and the experimental energy difference is ca. 1.5 kJ mol^{-1}.[20] In accordance with the experimental results, the MP2/6-311++G(2d,2p) calculations indicate the *trans*-HONO to be the lowest energy conformer, and the relative energy difference is estimated to be 2.5 kJ mol^{-1}.

Complex Structures. The search for the potential energy surface (PES) of the bimolecular $(HONO)_2$ complex was preliminarily conducted with various, economically feasible computations. The observed stationary points were thereafter studied by the larger MP2/6-311++G(2d,2p) level of theory. Computationally 10 different stable structures were found on the $(HONO)_2$ PES as shown in Figure 2. All the structures exhibit a single or double hydrogen bonding, and structural parameters describing the perturbation upon complexation are collected in Table 1.[21]

Computationally four different complexes are found between two *trans*-HONO monomers, three complexes are formed from a cis−cis pair, and three complexes are formed from one *trans*- and one *cis*-HONO molecule. For trans−trans complex one cyclic (**VIII**) structure is found representing the global minimum on the bimolecular complex PES as discussed below. This dimer involves two hydrogen bonds between the OH-tails and the nitrogen atoms, keeping the dimer in planar configuration. Complex **I** is also a planar trans−trans complex, but with only one hydrogen bond from the OH-tail of one of the subunits to the terminal oxygen electron lone pairs. Complex **II** is similar to complex **I** with the difference that it is nonplanar with a dihedral angle of ca. 74° between the two *trans*-HONO subunits. The fourth trans−trans complex (**IX**) shows a hydrogen bond from the OH-tail of one of the subunits to the OH-tail oxygen of the other trans isomer. This complex is nonplanar with a dihedral angle of ca. 19°. The intermolecular distance in this complex is also quite small (1.958 Å), being one of the shortest compared to all other bimolecular HONO complexes.

Three different complex structures are found between two *cis*-HONO subunits. Complex **III** is a cyclic complex with two hydrogen bonds from the OH-tails of the subunits to the doubly bonded terminal oxygens. This complex is predicted to be planar with equal intermolecular distances of 2.020 Å for both hydrogen bonds. Complex **X** involves also the terminal oxygen as the binding site for the hydrogen bonding. This complex differs from **III** by being nonplanar. The dihedral angle between the two subunits is ca. 35°. The intermolecular distance is estimated to be 2.067 Å, being longer than that found in the cyclic complex **III** (2.020 Å). The third complex (**IV**) between two cis isomers is formed between the OH-tail of one of the subunits and the OH-tail oxygen electron lone pairs of the other subunit. Structurally this complex resembles the trans−trans complexes **VIII** and **IX** where the interaction site is the OH-tail oxygen as well. The intermolecular distance in **IV** is

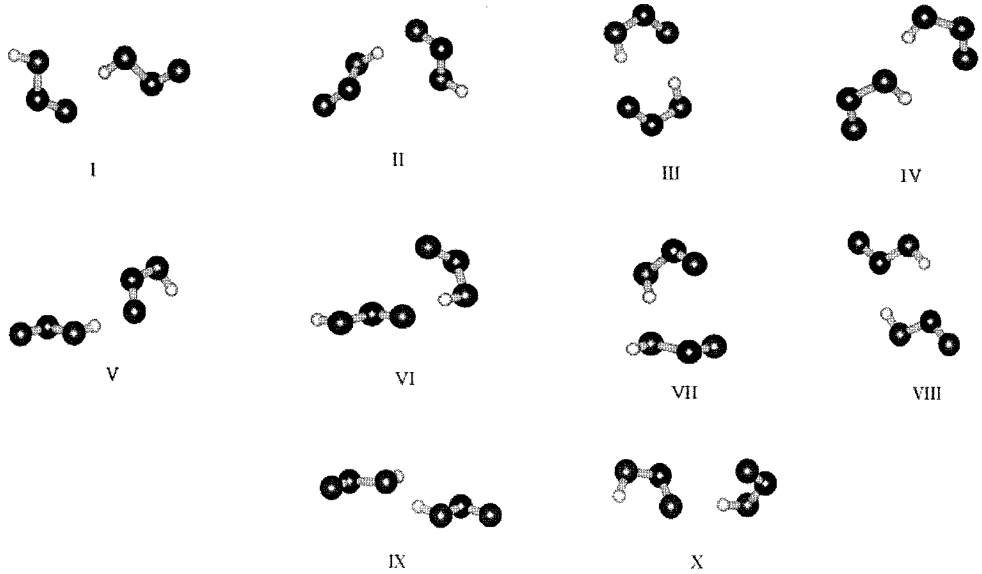


Figure 2. MP2/6-311++G(2d,2p) calculated structures of $(HONO)_2$ complexes.

TABLE 1: Geometrical Parameters[a] of the $(HONO)_2$ Complexes at the MP2/6-311++G(2d,2p) Level of Theory

	I (trans−trans)	**II** (trans−trans)	**III** (cis−cis)	**IV** (cis−cis)	**V** (cis−trans)	**VI** (cis−trans)	**VII** (cis−trans)	**VIII** (trans−trans)	**IX** (trans−trans)	**X** (cis−cis)
r(O−H)	0.970	0.970	0.982	0.981	0.971	0.980	0.984	0.975	0.973	0.980
r(H···X)	2.134	2.111	2.020	1.964	2.021	2.067	1.928	2.084	1.958	2.067
r_{PD}(N−O)	1.416	1.417	1.366	1.378	1.419	1.388	1.380	1.398	1.407	1.390
r_{PD}(N═O)	1.186	1.185	1.205	1.201	1.184	1.197	1.201	1.187	1.187	1.197
r_{PA}(N−O)	1.418	1.413	1.366	1.430	1.370	1.404	1.513	1.398	1.481	1.372
r_{PA}(N═O)	1.184	1.187	1.205	1.183	1.204	1.189	1.161	1.187	1.167	1.207
α_{PD}(O═N−O)	110.4	110.6	114.1	113.0	111.3	113.6	113.8	112.3	111.7	113.6
α_{PA}(O═N−O)	111.2	111.2	114.1	113.9	113.3	110.7	110.4	112.3	110.7	113.4
α(O−H···X)	171.1	166.5	175.1	170.3	175.2	170.7	173.5	150.7	154.1	173.0
φ(N−O−H···N−O−H)	0.0	74.3	0.0	0.0	64.7	55.8	60.3	0.0	19.2	34.5

[a] The bond distances are given in angstroms and the angles are in degrees. Abbreviations PD and PA denote the monomer acting as a proton donor and proton acceptor, respectively.

TABLE 2: MP2-Calculated Relative Energies (E_{rel}, kJ mol^{-1}) and BSSE-Corrected Interaction Energies (E_{cp-MP2}, kJ mol^{-1}) of the $(HONO)_2$ Complexes Using the 6-311++G(2d,2p) Basis Set Optimized Structures

	6-311++G(2d,2p)		6-311++G(3df,3pd)		cc-pVTZ		aug-cc-pVTZ	
	E_{rel}	E_{cp-MP2}	E_{rel}	E_{cp-MP2}	E_{rel}	E_{cp-MP2}	E_{rel}	E_{cp-MP2}
I(trans−trans)	6.801	−12.545	4.949	−13.622	5.703	−12.830	5.879	−13.879
II(trans−trans)	6.239	−12.727	4.500	−13.925	4.726	−13.230	5.384	−14.308
III(cis−cis)	8.353	−15.331	2.593	−17.929	0.000	−17.066	3.367	−18.891
IV(cis−cis)	7.774	−16.569	6.181	−17.776	3.073	−17.047	6.823	−18.607
V(cis−trans)	10.063	−11.674	7.643	−12.600	6.680	−12.045	9.013	−13.085
VI(cis−trans)	11.206	−10.609	8.568	−11.826	8.209	−11.022	9.801	−12.298
VII(cis−trans)	3.412	−18.941	3.762	−20.714	1.709	−19.483	3.547	−21.391
VIII(trans−trans)	0.000	−19.888	0.000	−20.814	0.280	−20.502	0.000	−21.561
IX(trans−trans)	0.045	−19.970	0.245	−20.974	0.325	−20.592	0.191	−21.668
X(cis−cis)	14.062	−9.941	11.130	−10.995	8.409	−10.215	12.789	−11.641

estimated to be 1.964 Å, being shorter than in the cyclic complex **III** but of similar length with the nonplanar trans−trans complex **IX**.

Along with the trans−trans and cis−cis complexes, possible structures of mixed complexes were considered. Scanning of the cis−trans complex PES revealed three stationary points resembling the structures found for the other complexes. Structures **V** and **VI** indicate hydrogen bonding of the OH-tail with the other subunit oxygen end. Both complexes are distorted from planarity, complex **V** by 56° and complex **VI** by 60°. The difference between these two complexes is that in complex **V** the *trans*-HONO subunit is acting as a proton donor. Instead, in complex **VI** *cis*-HONO acts as a proton donor and *trans*-HONO acts as a proton acceptor. The third mixed complex (**VII**) is also a nonplanar complex with *cis*-HONO as a proton donor while *trans*-HONO acts as a proton acceptor via the OH-tail oxygen electron lone pairs. Searches for a *trans*-HONO complexed from the OH-tail to the OH-tail oxygen of a *cis*-HONO were not successful, and relaxation to structure **V** was observed upon full optimization.

Generally the O−H bond of the proton donor is elongated by 0.002−0.008 Å, being the largest for **VII** and **VIII**. Most of the hydrogen bonds are almost linear, deviating from linearity by a few degrees. Complexes **VIII** and **IX** are exceptions in this respect. The calculated O−H···O angles are 151° and 154° for **VIII** and **IX**, respectively. For complex **VIII** this can be understood by the formation of the two hydrogen bonds in the cyclic conformation, and the nonlinearity is imminent from size considerations of the monomers. In the case of complex **IX** it is not clear why the hydrogen bond is bent. No steric hindrances should be restricting the formation of the hydrogen bond, and a similar type of interaction in complex **VII** deviates from linearity by only a few degrees. It is possible the complex follows the spatial orientation of the oxygen electron lone pairs in the plane of the proton acceptor *trans*-HONO, but is heavily perturbed by the delocalized double bond between the neighboring nitrogen and terminal oxygen.

The N−O and N═O bond distances are perturbed upon complexation for all complexes. For complex **I** the proton donor molecule shows an elongated N═O bond with shortened N−O distance, the proton acceptor undergoing similar changes. The N−O and N═O bonds appear to be similarly perturbed in complex **III**. In the cyclic cis−cis complex (**III**) the N═O bonds are longer (1.205 Å) and the two N−O bonds shorter (1.366 Å) than the corresponding monomer values. For the cyclic trans−trans complex (**VIII**) the N−O bonds are similar to the monomer value (1.397 Å) while the N═O bonds are shortened by 0.006 Å compared with the trans monomer. In complex **VII**, the cis subunit is the proton donor. The calculated N−O distance for this complex is 1.513 Å, being larger than in any other complex. Overall, the proton donor N−O bond in **VII** is elongated and the N═O bond shortened, whereas in the proton acceptor subunit these two bonds behave in an opposite manner.

Complex Energetics. The results of the BSSE-corrected calculations of the interaction energies for various complexes are presented in Table 2. It is interesting to note that the two complexes having strongly bent hydrogen bonds, i.e., complexes **VIII** and **IX**, are those found to be the most stable ones. At MP2/6-311++G(2d,2p) level the cyclic trans−trans (**VIII**) complex is a global minimum but complex **IX** is only a fraction higher in energy.

The lowest energy species formed from two *cis*-HONO molecules is **IV**, which is predicted to be 0.6 kJ mol^{-1} lower in energy than the cyclic cis−cis complex **III**. The third cis−cis complex (**X**) is the highest energy complex of all structures considered here, being ca. 14 kJ mol^{-1} higher in energy than the lowest energy species **VIII**.

Complex **VII**, where *trans*-HONO acts as a proton donor and *cis*-HONO acts as a proton acceptor, is only 3.4 kJ mol^{-1} higher in energy than the global minimum. The two other mixed cis−trans complexes are among the highest energy species found for these complexes.

The strongest interactions at the MP2/6-311++G(2d,2p) level are found for complexes **VIII** and **IX** which are also the two

TABLE 3: Comparison of the Vibrational Frequencies (in cm^{-1}) of the HONO Monomers and the $(HONO)_2$ Complexes Calculated at the MP2/6-311++G(2d,2p) Level

trans-HONO		cis-HONO		**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**
calcd	expt[a]	calcd	expt[a]	(trans−trans)	(trans−trans)	(cis−cis)	(cis−cis)	(cis−trans)	(cis−trans)	(cis−trans)	(trans−trans)	(trans−trans)	(cis−cis)
3791	3590.7	3637	3426	3783	3782	3552	3643	3713	3781	3780	3656	3773	3617
	(3573)		(3412)	3730	3727	3529	3547	3615	3572	3493	3618	3671	3578
1643	1699.8	1595	1640.5	1628	1628	1584	1616	1629	1615	1702	1632	1678	1591
	(1689)		(1634)	1620	1620	1575	1584	1575	1587	1582	1623	1623	1576
1290	1263.2	1329	1302.0	1332	1351	1386	1378	1357	1362	1383	1392	1383	1361
	(1266)			1302	1305	1376	1287	1347	1317	1226	1376	1245	1347
793	790.1	870	851.9	840	853	992	940	952	908	936	907	858	945
	(800)		(853)	826	834	948	812	829	873	857	856	748	902
581	595.6	682	609.0	709	675	822	794	730	781	713	790	736	782
	(609)			637	640	772	663	715	661	660	732	657	712
581	543.9	622	639.8	631	636	682	650	677	644	546	671	573	674
	(549)		(638)	591	596	681	538	633	613	419	663	490	642
				133	132	183	153	132	144	170	236	169	143
				100	118	146	134	121	116	157	152	137	117
				56	94	142	106	91	93	128	135	85	91
				43	62	112	96	48	56	80	124	63	39
				39	29	105	39	33	33	61	109	23	33
				18	16	48	27	21	29	33	71	10	25

[a] Gas phase (Q-branch) values according to ref 26. The numbers in parentheses are the corresponding experimental numbers in an Ar matrix according to ref 7.

TABLE 4: Comparison of Calculated Frequencies and Infrared Intensities for *trans*-HONO and the $(HONO)_2$ Complexes VIII and IX

trans-HONO			**VIII**			**IX**		
ω (cm^{-1})	I ($km mol^{-1}$)	assignt	ω (cm^{-1})	I ($km mol^{-1}$)	assignt	ω (cm^{-1})	I ($km mol^{-1}$)	assignt
3790.7	92	ν(OH)	3655.5	776	ν_{as}(OH)	3772.5	110	ν_{non-HB}(OH)
			3617.6	0	ν_s(OH)	3670.6	515	ν_{HB}(OH)
1643.4	108	ν(N═O)	1631.8	0	ν_s(N═O)	1677.8	145	ν(N═O)
			1623.3	181	ν_{as}(N═O)	1623.4	131	ν(N═O)
1289.5	178	δ(NOH)	1392.0	0	δ_s(NOH)	1382.9	162	δ(NOH)
			1375.5	309	δ_{as}(NOH)	1245.2	188	δ(NOH)
792.6	153	ν(N−O)	907.2	433	ν_{as}(N−O)	858.1	215	ν(N−O)
			856.4	0	ν_s(N−O)	490.2	402	ν(N−O)
581.4	222	δ(ONO)	671.3	158	δ(ONO)	735.8	121	δ(ONO)
			663.4	0	δ(ONO)	657.0	117	δ(ONO)
580.5	105	τ(OH)	789.9	156	τ(OH)	748.4	85	τ(OH)
			731.7	0	τ(OH)	572.7	94	τ(OH)

lowest energy structures. The computed interaction energies of ca. −20 kJ mol^{-1} for **VIII** and **IX** are about half the interaction energy of HONO−NH_3 complexes.[7] Smaller interaction energies of −15.3 and −16.6 kJ mol^{-1} are estimated for the cis−cis complexes **III** and **IV**, respectively. The weakest interaction is found between the two *cis*-HONO subunits in complex **X** (−9.9 kJ mol^{-1}). However, it must be noted that the calculated interaction energies of the weaker $(HONO)_2$ complexes are similar or even stronger compared with HONO−CO (−17 kJ mol^{-1}),[8] HONO−SO_2 (−14 kJ mol^{-1}),[9] and HONO−N_2 (−11 kJ mol^{-1}).[8]

The BSSE-corrected interaction energies of various $(HONO)_2$ complexes were additionally studied by varying the basis set but using the 6-311++G(2d,2p) optimized structure. It can be noted that when the basis set incompleteness error (BSIE) is reduced, i.e., the molecular orbital picture of the complex is refined, the estimated interaction potential deepens. For the two strongest complexes **VIII** and **IX** the interaction energy increases by 1 kJ mol^{-1} going from the 6-311++G(2d,2p) basis set to a larger and more flexible 6-311++G(3df,3pd) basis set. Similarly, the correlation consistent basis sets cc-pVTZ and diffuse-function augmented aug-cc-pVTZ basis sets predict a stronger interaction than the 6-311++G(2d,2p) calculation. The largest interaction energy at the MP2/aug-cc-pVTZ level is estimated for **IX** being −21.7 kJ mol^{-1}. It is interesting that even though **VIII** is the global minimum by a fraction of energy compared with **IX**, the latter is found to possess 0.1−0.2 kJ mol^{-1} stronger interaction of these two complexes. These two complexes could, in fact, be considered as isoenergetic, the differences in their energetics being within the computational accuracy. This leads also to the conclusion that if complex **VIII** is thought to be formed cooperatively by two hydrogen bonds, the energy involved in the formation of one of these hydrogen bonds is roughly −10 kJ mol^{-1}. It is known that nitrous acid has better acidic than basic properties, the formation of hydrogen bond from the OH-tail being prevalent. From the bimolecular energetics it can be further concluded that the oxygen in the OH-tail appears as a more basic site than the terminal oxygen or the nitrogen atom. Similar results have been obtained from preliminary computational studies of the protonated HONO as well.[22]

Vibrational Frequencies of $(HONO)_2$. The MP2/6-311++G(2d,2p) calculated vibrational frequencies of the various $(HONO)_2$ complexes are collected in Table 3. All the $(HONO)_2$ complexes involving the double-bonded oxygen or nitrogen as the interaction site exhibit typical behavior of a proton donor−acceptor pair. An example of this in presented in Table 4, where the vibrational assignment for the cyclic trans−trans complex **VIII** can be found. The vibrational bands at 3656 and 3618 cm^{-1} are assigned to the asymmetric and symmetric OH stretches, respectively. The OH bonds involved in hydrogen bonding are estimated to shift −135 and −173 cm^{-1} compared to the *trans*-HONO spectrum, and the observed shifts are typical for hydrogen-bonded X−H bonds of a proton donor molecule.[23]

Similarly to the OH bonds, the two ν(N═O) bonds are predicted to shift downward compared to unperturbed monomer values. In all the other vibrational modes, especially the bending and torsional modes, shifts upward are known to occur,[23] as witnessed also here by the calculated spectrum of the cyclic $(HONO)_2$ complex in Table 4. The torsion absorption of the *trans*-HONO is predicted to be split in **VIII** with an asymmetric and a symmetric mode showing shifts of +209 and 151 cm^{-1}, respectively.

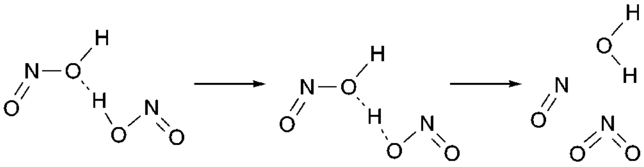
Even though most of the complexes show a "textbook" type behavior upon complexation, the OH-tail oxygen as the proton acceptor site makes an exception in complexes **IV**, **VII**, and **IX**. Complexation to the oxygen electron lone pairs induces drastic changes in the proton acceptor molecule, and large perturbations of the vibrational spectrum are expected. As an example of these ill-behaving complexes, i.e., **IV**, **VII** and **IX**, the last one has been included in Table 4 along with assignments of the computational vibrational frequencies.

For complex **IX**, two O−H bonds are found at 3773 and 3671 cm^{-1}. These bands correspond to free and hydrogen-bonded OHs, and they are shifted −18 and −120 cm^{-1}, respectively, compared with the monomer bands. Two N═O stretching bands are found shifted by +34 and −20 cm^{-1}, contrary to the general trend for the $(HONO)_2$ complexes having both N═O stretches shifting to lower wavenumbers. Similarly the NOH bending and OH torsion are predicted to split into two bands, the other shifted upward and the other downward compared with the monomer values.

The most drastic change is observed for the N−O stretches of **IX** where one band is found at 858.1 cm^{-1}, whereas the other band is at 490.2 cm^{-1}. These bands are predicted to shift + 64 and −302 cm^{-1}, respectively, from the calculated *trans*-HONO N−O stretching band. These vibrational shifts indicate that the HONO monomers involved in complexation through the OH-tail oxygen undergo substantial deformation in their electronic and geometrical structure. Generally for the three complexes of this type (**IV**, **VII**, and **IX**) the interaction weakens the N−O bond observed as a strong shift of the proton acceptor N−O stretching band. The predicted shifts of the proton acceptor N−O stretches for **IV**, **VII**, and **IX** complexes are −332, −374, and −302 cm^{-1}, respectively. The weakening of the N−O bond in certain $(HONO)_2$ complexes could have important consequences. Until now, the $(HONO)_2$ dimer has escaped detection.[7−11] All matrix isolation experiments reporting HONO complexes also report decomposition products from the reaction 2HONO → $NO + NO_2 + H_2O$ to appear in the matrixes as impurities. A possible explanation was given that the steel surface of the deposition lines could catalyze the decomposition process.[7] Also, a slowing of the dark decay of HONO in the gas phase was observed when steel surfaces were substituted for glass surfaces.[24,25]

The decomposition process of bimolecular HONO complex was computationally studied by Mebel and co-workers,[6] considering the relative energetics from the view of the sum of isolated molecules. The study concluded that the lowest energy barrier of ca. 60 kJ mol^{-1} leads from one *trans*-HONO and one *cis*-HONO to the decomposition products $NO + NO_2 + H_2O$.[6] However, this study reports a higher total energy for the decomposition products than for the precursor system, and the computational study presents a possible intermediate system of $H_2O + ONNO_2$ being more stable than either the precursor or the product systems. From matrix isolation experiments[7−11] it is evident that the $H_2O + ONNO_2$ system is not prevalent, leaving open the question of why the $(HONO)_2$ dimer is not observed. It must also be remembered that both *trans*- and *cis*-HONO have been identified in low-temperature matrixes.[7,12,18−20]

SCHEME 1



A possible explanation could be the following: The OH-tail oxygen appears to be the most basic interaction site of HONO upon complexation. When the bimolecular complex is formed, the proton acceptor N−O bond is strongly elongated. This would open a channel for intermolecular proton transfer according to Scheme 1. An additional proof for this scheme can be found in the computed geometries of $(HONO)_2$. For complex **IX** the N−O bond is almost 0.1 Å longer than in the corresponding monomer. Also, the N═O double bond is shortened (1.167 Å) beyond the NO monomer value of 1.178 Å, calculated at the MP2/6-311++G(2d,2p) level of theory.

The reaction channel in Scheme 1 would allow the formation of the observed decomposition products $NO + NO_2 + H_2O$. Unfortunately, the starting point for this proposed decomposition scheme is complex **IX**, being one of the lowest energy species found in this study. However, low-temperature matrix isolation studies should be able to trap the cyclic complex **VIII** since an energy barrier between **VIII** and **IX** should exist. It can be also argued that the observed decomposition products are not formed in the matrix but they have been present already before the deposition process; i.e., the decomposition of the HONO molecules happens in the gas phase, based on the previous experimental data.[7−11]

A reaction path study between the **VIII** and **IX** complexes is a difficult task due to several degrees of freedom to be considered to rotate and transfer one of the subunits with respect to the other *trans*-HONO. Complex **II** could be thought of as a possible geometrical intermediate between **VIII** and **IX**, and could give a rough estimate of the energy barrier. If the process goes as **VIII** → **II** → **IX**, then the relative energy barrier would be around 6 kJ mol^{-1}, which is enough to trap the complex in low-temperature matrix, and future experimental studies are encouraged. Also, computational studies of these mechanistic aspects are left for future studies.

Conclusions

The bimolecular complex of HONO involving cis and/or trans isomers can form 10 different complexes. The lowest energy forms are a cyclic trans−trans complex and a trans−trans complex forming a hydrogen bond to the OH-tail oxygen of the other complex subunit. Computationally these two complexes appear as isoenergetic species with a calculated interaction energy of ca. −20 kJ mol^{-1} at the MP2/6-311++G(2d,2p) level of theory. The weakest interaction is found for a cyclic cis−cis complex being ca. −10 kJ mol^{-1}.

Proton donors show generally a vibrational shift of several hundreds of wavenumbers downward for the hydrogen-bonded OH bond. The largest perturbation of the proton acceptors are noted for complexes interacting via the OH-tail oxygen. These complexes show a weakening of the adjacent N−O bond, which is believed to be a possible trigger for an intramolecular proton-transfer mechanism leading to the decomposition of the $(HONO)_2$ complex to $NO + NO_2 + H_2O$.

Acknowledgment. R.W. and Z.L. gratefully acknowledge financial support from the Polish State Committee for Scientific Research (Grant No. 3 T09A 00511). J.L. thanks the Academy of Finland for financial support. We thank Wroclaw Supercomputer Centre, Poznan Supercomputer Centre, and the CSC—Center for Scientific Computing Ltd. (Espoo, Finland) for computer mainframe time spent in the due course of this study.

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