Hydrogen-bonded complexes of nitrous and nitric acids with ethene Ab initio and DFT studies

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Abstract

The complexes formed by ethene with nitric and nitrous (*trans* and *cis*) acids have been investigated by ab initio (SCF and MP2) and B3LYP calculations with 6-311++G(d,p) basis set. Full geometry optimisation has been performed for the complexes studied. The most stable structures of the complexes are established. Bearing in mind the corrected values of the dissociation energy the studied hydrogen-bonded complexes can be ordered as follows: $C_2H_4\cdots HONO_2 > C_2H_4\cdots HONO\text{-}trans > C_2H_4\cdots HONO\text{-}cis$. In the complexes the acids act as proton donors forming the π-type of hydrogen bond with ethene. The predicted changes in the vibrational characteristics (vibrational frequencies and infrared intensities) arising from the hydrogen bonding are in good agreement with the experimentally measured. The predicted frequency shift of the stretching OH vibration in the nitric acid is largest ($-210\,\text{cm}^{-1}$), followed by the shifts in the *trans*-HONO ($-141\,\text{cm}^{-1}$) and *cis*-HONO ($-109\,\text{cm}^{-1}$). The calculations predict an increase of the IR intensity of the stretching O–H vibration in the complexes from 6 to 10 times.
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1. Introduction

The structure and dynamics of weakly bound molecular complexes has become of greater and greater interest to chemists in a variety of fields. Hydrocarbons, nitrogen oxides (NO_2, NO_3), nitric and nitrous acids are major constituents of polluted urban environments. Nitric and nitrous acids play an important role in atmospheric chemistry, forming hydrogen-bonded complexes with number of atmospheric bases. The direct measurements of the rates and mechanisms of heterogeneous reactions on surfaces or in liquid droplets are hard to carry out under the conditions of the Antarctic stratosphere. For this reason the computer simulations of such reactions are very useful for the clarification of the structure and stability of the hydrogen-bonded complexes important for atmospheric chemistry [1,2]. The knowledge about such complexes has opened up an area of surface science that has previously had little attention.

Numerous workers have demonstrated that matrix isolation studying of the hydrogen-bonded complexes [3–6] 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 [7,8].

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 [9–15] by ab initio calculations at SCF and MP2 levels with various basis sets and density functional calculations.

The object of the present study is the hydrogen-bonded complexes of nitric and nitrous acids with ethene. The hydrogen bond interactions of nitric and nitrous acids with ethene have been investigated by infrared spectroscopy in low-temperature argon matrices [8].

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 [16] (DFT) with the non-local three-parameter gradient-corrected exchange-correlation functional of Becke and Lee, Yang and Parr including partially exact HF-exchange (B3LYP) [17].

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Table 1
Optimised geometries for free and complexed $HONO_2$, *trans*-HONO, *cis*-HONO and C_2H_4, obtained from B3LYP/6-311++G(d,p) calculations

Parameter[a]	*trans*-HONO		*cis*-HONO		$HONO_2$	
	Monomers	Complex (**1A**)	Monomers	Complex (**1B**)	Monomers	Complex (**2**)
Bond length[b]						
$r(C_1C_2)$	1.3289	1.3318	1.3289	1.3315	1.3289	1.3324
$r(C_1H_4)$	1.0851	1.0852	1.0851	1.0852	1.0851	1.0852
$r(C_1H_5)$	1.0851	1.0851	1.0851	1.0850	1.0851	1.0852
$r(C_2H_3)$	1.0851	1.0852	1.0851	1.0852	1.0851	1.0852
$r(C_2H_6)$	1.0851	1.0851	1.0851	1.0850	1.0851	1.0852
$r(C_1H_7)$	–	2.4375	–	2.5028	–	2.3799
$r(C_2H_7)$	–	2.4561	–	2.5017	–	2.3738
$r(H_7O_8)$	0.9694	0.9764	0.9801	0.9860	0.9722	0.9825
$r(O_8N_9)$	1.4333	1.4144	1.3915	1.3840	1.4167	1.4029
$r(N_9O_{10})$	1.1654	1.1709	1.1795	1.1831	1.2099	1.2125
$r(N_9O_{11})$	–	–	–	–	1.1939	1.1972
Angle[c]						
$C_2C_1H_4$	121.7	121.6	121.7	121.6	121.7	121.6
$C_2C_1H_5$	121.7	121.7	121.7	121.7	121.7	121.7
$H_4C_1H_5$	116.6	116.6	116.6	116.7	116.6	116.7
$C_1C_2H_3$	121.7	121.7	121.7	121.6	121.7	121.6
$C_1C_2H_6$	121.7	121.7	121.7	121.7	121.7	121.7
$H_3C_2H_6$	116.6	116.6	116.6	116.7	116.6	116.7
$H_7O_8N_9$	102.9	103.8	106.8	107.9	103.6	105.0
$O_8N_9O_{10}$	111.1	111.6	113.8	114.1	115.8	116.3
$O_8N_9O_{11}$	–	–	–	–	113.9	114.1
$E^{tot.}$ (a.u.)	−205.771764[d]	−284.392094	−205.770051[e]	−284.389365	−280.978606[f]	−359.600275
	−78.615538[g]		−78.615538[g]		−78.615538[g]	

[a] See Fig. 1 for numbering of atoms.
[b] In angstrom.
[c] In degrees.
[d] $E^{tot.}$ for *trans*-HONO.
[e] $E^{tot.}$ for *cis*-HONO.
[f] $E^{tot.}$ for $HONO_2$.
[g] $E^{tot.}$ for C_2H_4.

2. Results and discussion

2.1. Complex structures and stability

In order to establish the most stable structures for the binary complexes of nitric and nitrous (*trans* and *cis*) acids with ethene full geometry optimisation has been performed by ab initio and B3LYP calculations with 6-311++G(d,p) basis set using the GAUSSIAN 98 [18] series of programs. The optimised structural parameters for the monomers (HONO (*trans* and *cis*), $HONO_2$ and C_2H_4) and for the complexes $C_2H_4\cdots$HONO-*trans* (**1A**), $C_2H_4\cdots$HONO-*cis* (**1B**) and $C_2H_4\cdots$HONO$_2$ (**2**) are presented in Table 1. In Fig. 1 are shown the optimised structures of the complexes studied with B3LYP/6-311++G(d,p) calculations.

As can be seen from the results in Table 1, the optimised values of the bond lengths and angles for the complexes **1A**, **1B** and **2** are slightly perturbed from their values in the monomers. The calculations 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_7O_8, N_9O_{10}, N_9O_{11} and C_1C_2 are lengthened in the complexes, while the bond O_8N_9 is shorted upon formation of the hydrogen bond. The angles $O_8N_9O_{10}$, $O_8N_9O_{11}$ and $H_7O_8N_9$ are also sensitive

to the complexation. Their values in the complexes **1A**, **1B** and **2** are larger in comparison with the corresponding values in the monomers. The largest changes in the structural parameters are calculated for the complex $C_2H_4\cdots$HONO$_2$ (**2**), followed from the changes for the complex $C_2H_4\cdots$HONO-*trans* (**1A**) and for the complex $C_2H_4\cdots$HONO-*cis* (**1B**).

The next step in the study was to investigate the stability of the complexes of C_2H_4 with nitrous (**1A** and **1B**) and nitric (**2**) acids. 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 the studied hydrogen-bonded complexes can be ordered as follows: **2** > **1A** > **1B**.

2.2. Changes in the vibrational characteristics upon hydrogen bonding

It is known [19–23] that the hydrogen bond formation between two or more monomers leads to the changes in the vibrational characteristics of the monomers. The displacement of the OH stretching mode in a hydrogen-bonded complex from the corresponding monomer value is a good indication of the strength of the interaction.