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Ab initio study of energies, structures and vibrational spectra of the complexes of water with carbon oxysulfide and nitrous oxide

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Abstract

The interaction energies, structures and vibrational band wavenumbers of the binary complexes formed between water and carbon oxysulfide, and water and nitrous oxide, have been predicted by means of ab initio molecular orbital theory. The results are discussed in the light of high resolution gas phase infrared and microwave, and matrix isolation infrared spectroscopic studies, and of previous theoretical calculations on similar and containing carbon dioxide complexes. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The numerous studies of the structures, energetics and vibrational spectra of weakly bounded complexes formed between water and other small molecules, atoms and ions have been recently published [1–10]. Especially the carbon dioxide–water system, due to its importance in biology and technological processes, has become the subject of many experimental [11–14] and theoretical [14–25] studies. All these studies predicted a T-shaped planar structure for the $CO_2 \cdots H_2O$ complex, of C_{2v} symmetry, with the carbon atom attached to the oxygen atom of the water. In oxygen matrices there is some support for the presence of another linearly hydrogen-bonded $O–H \cdots O$ isomer [12] for this complex. Another important system is the

nitrous oxide–water complex, studied experimentally by the gas-phase molecular beam electric resonance (MBER) [26] and theoretically by ab initio treatments [3,4,27,28]. These studies support the planar T-shaped structure of the complex, with the water molecule tilted in the direction of the nitrous oxide by about 20° [26].

In this Letter we present the results of our ab initio calculations of the interaction energies, structures and vibrational spectra for the $COS \cdots H_2O$ complex. We compare them with the data obtained for the complex of water with carbon dioxide and discuss the effects of S/O replacement. The Letter presents also our results obtained for the $N_2O \cdots H_2O$ complex.

2. Ab initio method and basis set

The structures of the $COS \cdots H_2O$ and $N_2O \cdots H_2O$ complexes was optimized and the

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vibrational frequencies were computed using the GAUSSIAN 92 programs [29] at the MP2 level [30] with the 6-31++G** basis set. For optimization of the carbon oxysulfide complex we used very tight option [29]. The calculations have been performed without taking into account the basis set superposition error in the optimization procedure. In previous calculations made in our group in South Africa [1–5] the level of theory was the same (MP2) however the basis set did not include diffuse functions (6-31G**). Present computations were carried out at the Computer Centre of the University of Natal in Durban, South Africa.

3. Results and discussion

3.1. COS···H$_2$O complex

The optimized geometry of the carbon oxysulfide–water complex is depicted in Fig. 1 and the optimized parameters are summarized in Table 1. In the equilibrium the COS···H$_2$O complex assumes a planar structure in accordance with the T-shaped structure of the carbon dioxide–water complex [3,13,25]. The water is slightly bent towards oxygen of the COS molecule which is more electronegative than sulphur (see Table 2) thus forming a very weak hydrogen bond O_1–H_1···O_2. The calculated binding energy of the complex is -4.3835×10^{-3} a.u. $= -11.513$ kJ mol^{-1}. The MP2 binding energies for the T-shaped form of the
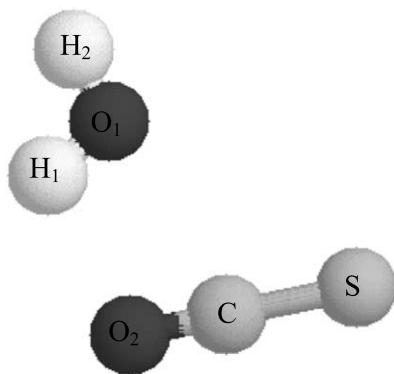

Fig. 1. Geometry of the COS···H$_2$O complex optimized at MP2/6-31++G** level.

Table 1
Optimized geometries of the COS···H$_2$O complex

Bond lengths (Å)	
O_1–H_1	0.9647
O_1–H_2	0.9637
C–O_2	1.1845
C–S	1.5603
C···O_1	3.0119
O_1···O_2	2.9278
H_1···O_2	2.4776
Bond angles (deg)	
C$O_2$$O_1$	82.51
O_1CS	106.04
O_2CS	179.43
$O_1$$O_2$S	82.84
C$H_1$$O_1$	84.99
C$O_2$$H_1$	100.74
$O_1$$H_1$$O_2$	108.32
SCH_1	124.65
S$O_2$$H_1$	101.07
C$O_1$$H_2$	177.97
$O_2$$O_1$$H_2$	159.08
C$H_1$$H_2$	122.16
$H_2$$O_1$$H_1$	105.63
$O_2$$H_1$$H_2$	145.49

Table 2
Total atomic charges in the COS···H$_2$O complex

Atom	Charge, e
H_2	0.37
H_1	0.37
O_1	−0.73
O_2	−0.41
S	−0.04
C	0.43

CO_2···H_2O complex reported in the literature are dependent on the basis set used: Sadlej et al. [25] reported -4.0338×10^{-3} a.u. and Cox et al. [4] -14.87 kJ mol^{-1} [4], which is of the same order as our result for the COS···H$_2$O complex. The level of calculations of Sadlej et al. was the supermolecular Moller–Plesset perturbation theory (MPPT) with the dimer-centered basis set (DCBS), and those of Cox et al. were done at the MP2/6-31G** level. The structure of the complex primarily results from coulombic attractions between the water oxygen and the COS carbon and the water hydrogen and the COS oxygen engaged in hydrogen bonding (Table 2).

Table 3
Computed normal mode frequencies and intensities of the $COS \cdots H_2O$ complex

Wavenumber (cm^{-1})	IR intensities $(km\ mol^{-1})$	Description
3997.6	66.5	O–H stretch. asym.
3851.5	4.9	O–H stretch. sym.
2081.6	658.5	$C–O_2$ stretch.
1616.6	170.6	$H_1–O_1–H_2$ bending i.p.
905.9	3.7	C–S stretch.
486.7	3.8	S–C–O bending out of plane
485.4	1.5	S–C–O bending in plane
210.1	95.1	$O_1–H_1$ out of plane
180.1	109.3	$H_1–O_1–H_2$ twisting
124.2	212.3	$O_1–H_2$ out of plane
118.5	0.3	$C–O_1$ stretch. (intermolecular)
46.6	15.4	$H_1–O_1–H_2$ bending (intermolecular)

The bond lengths and angles are reported in Table 1. The geometry of water and the $C–O_2$ bond length in the carbon oxysulfide–water complex are similar to the parameters in the carbon dioxide–water complex, reported by Cox et al. [3]. The $C \cdots O_1$ distance is substantially longer (3.0119 Å compared with 2.73 Å). The hydrogen bond $O_1–H_1 \cdots O_2$ is strongly bent, the angle is equal 108.3°, and the $O_1 \cdots O_2$ length 2.9278 Å.

The calculated normal mode frequencies, IR intesities and mode descriptions are summarized in Table 3. The reported frequencies are non-scaled. The O–H stretching frequencies are slightly lower than the frequencies reported for the $CO_2 \cdots H_2O$ complex [3], which we attribute to better basis set used in our calculations (6-31++G** versus 6-31G**). The intermolecular $C \cdots O_1$ stretching mode in the $COS \cdots H_2O$ complex has a frequency 118.5 cm^{-1} compared with 125 cm^{-1} in the $CO_2 \cdots H_2O$ complex [3].

Table 4
Optimized geometries of the $N_2O \cdots H_2O$ complex

Bond lengths (Å)	
$O_1–H_1$	0.9640
$O_1–H_2$	0.9638
$N_1–O_2$	1.1958
$N_1–N_2$	1.1696
$H_1 \cdots O_2$	3.1507
$N_1 \cdots O_1$	2.7988
$N_2 \cdots O_1$	3.1236
$O_1 \cdots O_2$	2.9596
Bond angles (deg)	
$H_2O_1H_1$	105.61
$H_1O_1N_1$	116.15
$H_2O_1N_1$	138.24
$O_1N_1N_2$	94.87
$O_1N_1O_2$	85.68
$N_2N_1O_2$	179.45
$O_1H_1O_2$	69.81

Fig. 2. Geometry of the $N_2O \cdots H_2O$ complex optimized at MP2/6-31++G** level.

Table 5
Total atomic charges in the $N_2O \cdots H_2O$ complex

Atom	Charge, e
O_1	−0.76
H_1	0.37
H_2	0.37
N_1	0.48
N_2	−0.19
O_2	−0.28

Table 6

Computed normal mode frequencies and intensities of the $N_2O \cdots H_2O$ complex

Wavenumber (cm^{-1})	IR intensities (km mol^{-1})	Description
4003.2	73.8	O–H stretch. asym.
3857.6	9.6	O–H stretch. sym.
2228.1	334.8	N_2O stretch. asym.
1631.9	107.8	H_1–O_1–H_2 bending i.p.
1287.4	14.1	N_2O stretch. sym.
553.0	3.9	N–N–O bending out of plane
548.1	3.9	N–N–O bending in plane
159.3	30.2	H_2O twisting
138.2	75.9	O_1–H_1 out of plane
116.0	0.0	$N_1 \cdots O_1$ stretch. (intermolecular)
94.3	243.4	O–H_2 out of plane
27.9	36.2	H_1–O_1–H_2 bending (intermolecular)

3.2. $N_2O \cdots H_2O$ complex

The optimized geometry of the nitrous oxide–water complex is depicted in Fig. 2 and the optimized parameters are summarized in Table 4. In the equilibrium the $N_2O \cdots H_2O$ complex assumes a planar structure [3,4,26–28]. The water is slightly bent towards oxygen O_2 which is more electronegative than nitrogen N_2 (see Table 5) thus forming a weak hydrogen bond O_1–$H_1 \cdots O_2$. The calculated binding energy of the complex is -5.0978×10^{-3} a.u. $= -13.389$ kJ mol^{-1}. The MP2 energy for the planar form of the $N_2O \cdots H_2O$ complex reported by Cox et al. [4] equals -12.77 kJ mol^{-1}. Their calculations did not include diffused functions. The structure of the complex is primarily the result of the coulombic attraction between the water oxygen and the positively charged nitrogen N_1, and to some extend between the positively charged water hydrogens and the negatively charged atoms O_2 and N_2 (Table 5).

The bond lengths and angles are reported in Table 4. The geometry of water and nitrous oxide in the nitrous oxide–water complex is in qualitative agreement with the parameters reported by Cox et al. [3]. The $N_1 \cdots O_1$ distance is equal 2.7988 Å compared with 2.7763 Å of Cox et al. [3]. The $H_1 \cdots O_2$ length equals 3.1507 Å.

The calculated normal mode frequencies, IR intesities and mode descriptions are summarized in Table 6. The O–H stretching frequencies are slightly lower than the frequencies reported for the $NO_2 \cdots H_2O$ complex [3], which we attribute to larger basis set used in our calculations. The intermolecular $N_1 \cdots O_1$ stretching mode has a frequency 116 cm^{-1} compared with 127 cm^{-1} of Cox et al. [3].

4. Conclusions

Theoretical ab initio calculations at the MP2/6-31++G** level of the binary complexes formed between water and carbon oxysulfide, and water and nitrous oxide, presented in this Letter, give new information concerning the binding energies, structures and vibrational band wavenumbers of the complexes. They are in qualitative agreement with previous experimental and theoretical studies on the nitrous oxide and carbon dioxide–water complexes. The results for the carbon oxysulfide–water complex are new and the level of calculations improves the previous results for the nitrous oxide–water complex.

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