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### Thermal reactivity of HNCO with water ice: an infrared and theoretical study

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### Abstract

The structure and energy of the 1:1 complexes between isocyanic acid (HNCO) and H<sub>2</sub>O are investigated using FTIR matrix isolation spectroscopy and quantum calculations at the MP2/6-31G(d,p) level. Calculations yield two stable complexes. The first and most stable one ( $\Delta E = 23.3 \text{ kJ/mol}$ ) corresponds a form which involves a hydrogen bond between the acid hydrogen of HNCO and the oxygen of water. The second form involves a hydrogen bond between the terminal oxygen of HNCO and hydrogen of water. In an argon matrix at 10 K, only the first form is observed. Adsorption on amorphous ice water at 10 K shows the formation of only one adsorption site between HNCO and ice. It is comparable to the complex observed in matrix and involves an interaction with the dangling oxygen site of ice. Modeling using computer code indicates the formation of polymeric structure on ice surface. Warming of HNCO, adsorbed on H<sub>2</sub>O ice film or co-deposited with H<sub>2</sub>O samples above 110 K, induces the formation of isocyanate ion (OCN<sup>-</sup>) characterized by its  $v_{as}$ NCO infrared absorption band near 2170 cm<sup>-1</sup>. OCN<sup>-</sup> can be produced by purely solvation-induced HNCO dissociative ionization. The transition state of this process is calculated 42 kJ/mol above the initial state, using the ONIOM model in B3LYP/6-31g(d,p).

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### 1. Introduction

More than 100 interstellar molecules have been identified in the interstellar medium [1]. Many of these molecules result from an efficient accretion

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and reaction of atoms and molecules from the gas on dust grains in the dense molecular clouds [2]. Present on the satellites of the outer planets and on the comets, amorphous water ice is also believed to be the major constituent of interstellar dust [3–6]. To understand the formation and evolution of interstellar molecules, numerous theoretical models with detailed physical and chemical reaction pathways, have been developed [7–10]. The tiny (micron and submicron) icy dust grains present in cold molecular clouds prove to

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be important catalysts. Heterogeneous reactions are developed on the ice surface or in the icy mantle of the grains [11] which are assumed to play an important role in interstellar chemistry [12]. For these reasons, we have been interested in small molecules interactions with amorphous ice surface [13–20].

Since its discovery in 1979 by Soifer et al. [21] in the protostar W33A, the 4.62 µm feature (2167 cm<sup>-1</sup>) has been extensively hunt up [22] and numerous carriers, such as nitriles [23] and isonitriles [24], have been proposed for this feature called "XCN" band. The position and width of this band led to assigning it to a solid molecular species. In 1987, Grim and Greenberg [25] discussed the spectroscopic validity of the assignment of this XCN band to nitriles and isonitriles and proposed the XCN feature to the intense asymmetric stretch of the isocyanate anion, OCN<sup>-</sup>. Ten years later, Schutte and Greenberg [26] detected three other weak bands of OCN<sup>-</sup> at 1296, 1206 and 630 cm<sup>-1</sup> and concluded that OCN<sup>-</sup> is a good candidate for the "XCN" band. The behavior of the XCN feature when the ice matrix was doped by electron donor or electron acceptor molecules gave direct evidence that the carrier is a negative ion [27,28]. Next, Hudson et al. [29] confirm, from irradiated and photolyzed ices, that the band produced in the laboratory is due to OCN<sup>-</sup>. Novozamsky et al. [30] proposed that the formation of OCN- is preceded by photochemical formation of isocyanic acid, HNCO, followed by proton transfer to some base such as NH<sub>3</sub>.

In this paper, we will be looking at the reactivity of isocyanic acid, which has been detected in the interstellar medium in gas phase but never in the cold (10–100 K) interstellar grains [31,32], on water ice surface or in bulk. The purpose of this work is threefold: (1) to obtain direct and accurate experiment results of the HNCO...H<sub>2</sub>O complexes trapped in rare gas cryogenic matrix, (2) to assess the chemical stability of HNCO adsorbed on water ice surfaces, and (3) to determine the favorable conditions for the OCN<sup>-</sup> formation.

Experiments were monitored by FT-IR spectroscopy. Quantum calculations were undertaken to compare the experimental IR spectra with the calculated ones. They are also instrumental in assigning observed absorptions, determining the complex and the structure of absorption sites and furthermore to modeling the reactivity of HNCO on ice surfaces.

### 2. Experimental section

Pure HNCO was synthesized using the method described by Herzberg and Reid [33] and modified by Sheludyakov et al. [34]. The isocyanic acid is degassed before each deposition. Moreover, the first fraction of isocyanic acid is evacuated.  $H_2O$  was degassed by successive freeze-thaw cycles under vacuum before each use.

The apparatus and experimental techniques used to obtain argon matrices have been described elsewhere in the literature [35]. The relative concentrations Ar/H<sub>2</sub>O (50/1), Ar/HNCO (700/1), Ar/H<sub>2</sub>O/HNCO (500/6/0.5) at room temperature, were adjusted by standard manometric techniques and sprayed onto a golden copper plate cooled at 20 K held at a constant pressure of 10<sup>-7</sup> mbar and a constant deposition rate (2 mmol/h). To study the reactivity of HNCO with H<sub>2</sub>O ice, two types of experiments were carried out. Gaseous HNCO ( $\sim 10^{-6}$  mol) was deposited at 10 K on a H<sub>2</sub>O amorphous ice film with a 0.1 µm thickness previously prepared. The techniques used to obtain amorphous ice films from water/argon (1/50) gaseous mixture have been described previously [15,19]. The deposited ice film thickness is deduced from the calibration of infrared absorbance versus film using optical interferences [36,37].

The behavior of HNCO was also studied when it was co-deposited with  $H_2O$  at 10 K, in a ratio 1/ 10. The thermal activation of the samples was realized by a progressive warming of the mirror (from 10 K to near of 180 K), with a heating rate of 0.9 K/min.

A Fourier Transform Infrared Spectrometer (Nicolet series II Magna system 750) was used to record the spectra samples in the range  $4000-400 \text{ cm}^{-1}$  with a resolution of 0.12 cm<sup>-1</sup> for matrix experiments and 0.5 cm<sup>-1</sup> for solid.

### 3. Experimental results

### 3.1. Study of the HNCO... $H_2O$ complexes: cryogenic matrix experiments

Argon matrixes containing only HNCO or H<sub>2</sub>O were prepared, yielding infrared absorptions that were similar to those previously reported. Table 1 summarizes the observed absorptions with spectral assignments based on the works of Ayers [38,39], Couturier-Tamburelli et al. [40] for H<sub>2</sub>O, and Teles et al. [41] for HNCO. Prior to the absorption study, matrix isolation experiments were conducted with different compound concentrations. The characteristic absorption bands of free or multimers H<sub>2</sub>O and HNCO multimers were well identified (Fig. 1) from these experiments. The spectra recorded after different co-depositions of Ar/HNCO/H2O at 20 K show new absorption bands with respect to the spectra of pure H<sub>2</sub>O and pure HNCO trapped in argon matrix (cf. Fig. 1(a) and Table 1). The two more intense vibrational bands located at 3296 and  $2272 \text{ cm}^{-1}$ , shifted, respectively, by  $215 \text{ cm}^{-1}$  to the lower frequencies and 13 cm<sup>-1</sup> to the higher frequencies with respect to the  $v_1$  and  $v_2$  mode of HNCO monomer. It can be attributed to the presence of a molecular complex. In addition, in the  $v_{OH}$ region, between 3800 and 3550  $\text{cm}^{-1}$  (cf. Fig. 1), a new weak absorption band observed at  $3722 \text{ cm}^{-1}$ . 17 cm<sup>-1</sup> lower than the value observed for free  $v_3$ mode of  $H_2O$  (3739 cm<sup>-1</sup>), is also attributed to the complex. In the  $\delta_{OH}$  region, a weak band at 1590 cm<sup>-1</sup> is also relative to this species. The strong shift, observed for the  $v_1$  mode of HNCO, suggests the formation of a 1:1 complex where HNCO interacts with H<sub>2</sub>O via its NH bond. Further, geometry and frequency calculations will be performed to investigate the type of formed complexes.

# 3.2. Adsorption of HNCO on ice surface: thermal evolution

Considering results obtained in argon matrix, we have studied the thermal behavior of HNCO adsorbed on amorphous water ice surface.

Amorphous ice spectra have been extensively described in the literature [3,42]. In addition to the bulk OH stretching and bending modes at 3250 and 1600 cm<sup>-1</sup>, respectively, they display a weak feature at  $3695 \text{ cm}^{-1}$  which is relative to the dangling OH mode. This latter is generally used to follow the adsorption of molecules on ice surfaces. Here, the dangling OH is not perturbed and this observation indicates that there is no interaction between HNCO and OH group. When HNCO is deposited at 10 K, no change in the position of the infrared ice absorption bands is observed. The line shape and the position of the  $v_2$  mode of HNCO at 2252 cm<sup>-1</sup>, the only band of the HNCO IR spectrum that can be observed, is the same that observed in the spectrum of solid isocyanic acid and similar to the

Table 1

Experimental and calculated frequency shifts (in cm<sup>-1</sup>) for HNCO...H<sub>2</sub>O complexes ( $\Delta \nu = \nu_{complex} - \nu_{monomer}$ )

Species		Experiment			Calculation (MP2/6-31G(d,p))					Assignments
		Monomer	Complex		Monomer	HO <sub>w</sub> compl	ex	OH <sub>w</sub> compl	ex	
		v	v	$\Delta v_{exp}$	v	v	$\Delta v_{\rm calc}$	v	$\Delta v_{\rm calc}$	
$H_2O$	<i>v</i> <sub>3</sub>	3739	3722 (1)	-17	4028	4013 (6.6)	-15	4024 (20)	-4	v <sub>OH</sub> asym
	v <sub>1</sub>	3639			3889	3881 (1.6)	-8	3894 (8.7)	5	v <sub>OH</sub> sym.
	<i>v</i> <sub>2</sub>	1589	1590 (6)	1	1682	1674 (7.1)	-8	1697 (12.6)	15	$\delta_{\rm HOH}$ sym.
HNCO	$v_1$	3511	3296 (52)	-215	3791	3536 (100)	-255	3799 (34.6)	8	v <sub>NH</sub>
	<i>v</i> <sub>2</sub>	2259	2272 (100)	13	2366	2375 (45.3)	9	2377 (100)	11	v <sub>NCO</sub> asym.
	<i>v</i> <sub>3</sub>	1316			1310	1315 (1)	5	1320 (0.4)	10	v <sub>NCO</sub> sym.
	<i>v</i> <sub>4</sub>	770			794	898 (33)	104	763 (45.4)	-31	$\delta_{ m HNC}$
	$v_6$	697			610	624 (0.3)	14	606 (0.1)	-4	$\delta_{ m NCO}$
	v5	573	575 (10)	2	559	559 (7.3)	0	563 (14.5)	4	$\delta_{ m NCO}$

 $\Delta v = v(\text{complex}) - v(\text{monomer});$  normalized intensities are in parenthesis.



Fig. 1. (a) Infrared spectrum of HNCO and  $H_2O$  trapped in argon matrix (0.5/6/600). (b) Infrared spectrum of HNCO trapped in argon matrix (1/700). (c) Infrared spectrum of  $H_2O$  trapped in argon matrix (1/50).

one published by Lowenthal et al. [43]. No change is observed in the spectrum when the sample is heated (0.9 K/min) until a temperature of 110 K is reached. Then, a weak new absorption band appears at 2170  $\text{cm}^{-1}$  (cf. Fig. 2) which match very well the frequency of the asymmetric stretch of OCN- reported in the literature data [11,43]. This observation is indicative of an ionization of HNCO molecule on ice surface as recently reported by Lowenthal et al. [43]. However we do not observe the formation of the other weak bands mentioned in the introduction at 1296, 1206, and 630  $cm^{-1}$  due to the weak abundance of OCN<sup>-</sup> formed at the interface of H<sub>2</sub>O film and solid HNCO. For the same reasons, the very weak and broadening absorption bands of  $H_3O^+$  [16], that can be assigned to the formed counterion, are not detected with IR spectroscopy owing to overlap of its features with those of H<sub>2</sub>O.

Above 110 K, the dangling OH signal begins to decrease in intensity, then disappears at 130 K. The latter phenomenon is due to the collapse of amorphous ice pores during its evolution in crystalline ice. This signal is similar to that observed during desorption experiments of ozone [18] or cyanoacetylene [20] adsorbed on amorphous ice surfaces. These results are comparable to those obtained in the matrix experiments reported in the former section. They indicate that HNCO principally interacts with the dangling ice oxygen sites (in a similar way than in  $H_2O...HNCO$  complex) than with the dangling ice H sites (like HNCO... $H_2O$  complex). This arrangement can be favorable to a proton transfer from the hydrogen of HNCO to the oxygen of  $H_2O$ .

In the following, we compare this result to the one obtained from the co-deposition of HNCO/ $H_2O$  mixture (1/10) where  $H_2O$  is in excess.



Fig. 2. IR spectra of HNCO deposited on amorphous water ice at 10 K (b) then warmed up with heating rate of 0.9 K/min. (a) Pure ice at 10 K, (c) 80 K, (d) 90 K, (e) 100 K, (f) 110 K, (g) 125 K, (h) 135 K, and (i) 145 K. The inserts refer to the difference spectra between the spectrum of HNCO deposited on ice at the temperature T and that of pure ice at the same temperature.

# 3.3. Co-deposition of HNCO with $H_2O$ at low temperature: thermal evolution

When HNCO and H<sub>2</sub>O are co-deposited at 10 K on the cold window, we observe the presence of two shoulders at 3591 and 2970 cm<sup>-1</sup> which are not observed on the IR spectra of the solid HNCO and solid H<sub>2</sub>O (Fig. 3). These new spectral features are likely associated with the HNCO:(H<sub>2</sub>O)<sub>n</sub> complexes formation in the solid and are different of the 1:1 HNCO:H<sub>2</sub>O molecular complex previously observed in matrix. These two bands can be assigned to a combination mode and to the  $v_{\rm NH}$  stretching mode of HNCO. The more intense bands of H<sub>2</sub>O and HNCO, i.e. the vOH mode and the  $v_{\rm as}$ NCO mode are also downshifted by nearly 40 and 10 cm<sup>-1</sup> with respect to the mode of solid HNCO and solid H<sub>2</sub>O.

When the sample is heated, about 130 K all the vibration bands of the HNCO: $(H_2O)_n$  complexes strongly decrease. In the  $v_{as}NCO$  region, only the solid component at 2252 cm<sup>-1</sup> expected for the solid HNCO can be again observed. A new absorption band is observed near of 2172 cm<sup>-1</sup>. This frequency is very closed to that expected for the OCN<sup>-</sup> species and suggests as previously described a full ionisation of the HNCO molecule. However in the bulk, OCN<sup>-</sup> is formed in a greatest amount as shown by the intensities of band at  $2172 \text{ cm}^{-1}$ . This band that appears here is slightly shifted but more intense than in the experiment adsorption. Although these conditions favour the OCN<sup>-</sup> formation, we do not detect the other weak bands of  $OCN^{-}$  and the  $H_3O^{+}$  ion absorptions.

Holding the temperature at 130 K during several minutes, whereas the vibrational bands of the



Fig. 3. Co-deposition of HNCO and H<sub>2</sub>O, (a) pure HNCO 10 K, (b) pure H<sub>2</sub>O 10 K, (c) HNCO/H<sub>2</sub>O 10 K, (d) 50 K, (e) 110 K, (f) 130 K, t = 0', (g) 130 K, t = 30', (h) 150 K. \* associated to CO<sub>2</sub>.

HNCO: $(H_2O)_n$  complexes goes on to decrease then disappear, we observe both a slight increasing of the  $v_2$  band of OCN<sup>-</sup> and the appearance of a feature at 2295 cm<sup>-1</sup> which is in good agreement with the vCN stretching mode of cyanic acid, HOCN, reported in the literature [41]. This observation suggests the possibility of a new proton transfer between protonated ice,  $H_3O^+(H_2O)_n$  and OCN<sup>-</sup> to lead at HOCN, isomer of the isocyanic acid. Above 135 K, the HOCN, HNCO and OCN<sup>-</sup> species are sublimated and only the water ice vibrational bands are observed.

### 4. Quantum calculations

Our experimental results point out to the formation of a 1:1 complex in the matrix, adsorption of HNCO on the dangling oxygen sites of the ice surface and thermal formation of OCN<sup>-</sup>. Quantum calculations were carried out to interpret our experimental results. The experimental IR spectra were compared with the calculated ones to assign observed vibrational absorptions and determine the structure of the complex in matrix. The structures of adsorption sites and the thermal ionization of HNCO on ice surface were also modeled.

### 4.1. Structure of the 1...1 complex

To establish the molecular structure of this complex, ab initio calculations were carried out with Gaussian 98 [44] at the MP2/6-31G(d,p) level of theory [45]. Several arrangements are possible in the H<sub>2</sub>O and HNCO subunits in the complexes. Water and isocyanic acid, are both simultaneous proton donor and acceptor compounds and are expected to form hydrogen bonds to nitrogen and oxygen, respectively. Four kinds of complexes are thus considered (Fig. 4). The NH<sub>w</sub> form which involves a hydrogen bonding between hydrogen of water (H<sub>w</sub>) with the nitrogen of isocyanic acid; the



Fig. 4. Starting for theoretical calculations of the complexes.

 $HO_w$  form, which involves an hydrogen bonding between the hydrogen of isocyanic acid and the oxygen of water ( $O_w$ ); the  $OH_w$  form, which involves an hydrogen bonding between hydrogen of water ( $H_w$ ) and the oxygen of isocyanic acid, and the T form, which involves an interaction between the electrophilic carbon of isocyanic acid and the nucleophilic oxygen of water.

Geometry of the complexes (cf. Table 2): From the starting geometries in Fig. 4, all the geometrical parameters were fully optimized using the Berny optimization procedure [46]. The harmonic vibrational frequencies were determined at the stationary points. Calculations give only two local minima with a C<sub>s</sub> symmetry structure. The first one, with a  $r_{0...H}$  value of 2.177 Å, corresponds to the OH<sub>w</sub> structure. The second corresponds to the HO<sub>w</sub> form and is stabilized by a strong hydrogen bond ( $r_{H...O} = 1.87$  Å). The NH<sub>w</sub> form and the T shaped structure do not correspond to a local minimum. The optimized structures of the complexes with bond lengths are reported in Fig. 5 and in Table 2.

Identification of the complex: The previous calculation provides valuable insight into the stability and the spectroscopic features of the complexes. First, the complexing effects can be observed on the geometry of the partner molecules (cf. Table 2) and on their most significant stretching mode frequencies (cf. Table 1). The HO<sub>w</sub> complex is predicted to be the most stable with respect to the monomers ( $\Delta E(E_{Tot}^{BSSE} - E_{HNCO}^{BSSE}) = -28.3$ kJ/mol). The energy difference, -23.3 kJ/mol, with

able 2 reometrical parar	neters calc	ulated for ]	HNCO.	$H_2O \text{ comp}$	lexes at the	MP2/6-310	G(d,p) level	l of theory					
Species	$\Delta E$	Bond let	ngth (Å)					Angles (d	leg)				
	(kJ/ mol)	N-H	N=C	C=0	Н0	0-H	H–O	HNC	NCO	СОН	0НО	0HN	НОН
HNCO		1.005	1.226	1.185				124.4	171.8				
$H_2O$						0.961	0.961						103.9
OH <sub>w</sub> complex	0	1.004	1.221	1.187	2.177	0.963	0.961	126.6	171.6	143.7	179.6		103.5
HO <sub>w</sub> complex	-23.3	1.018	1.220	1.189	1.867	0.963	0.963	128.2	172.2			173. 1	104.7

1

1



HO<sub>w</sub> Complex

OH<sub>w</sub> Complex

Fig. 5. Optimized structures of HNCO... H<sub>2</sub>O complexes (Cs symmetry).

respect to the OH<sub>w</sub> form, is significant at this level of theory and can explain the lack of the second structure. By comparing the  $v_1$  (NH stretch) and  $v_2$ (NCO antisymmetric stretch) vibrational frequency shifts of the complex compared to those calculated for the free HNCO, we are able to identify the form present in argon matrix (cf. Table 1). The predicted vibrational frequencies for the OH<sub>w</sub> complex are slightly perturbed in comparison to the values of the respective monomers. This is not the case of the HO<sub>w</sub> complex where the  $v_1$ mode of HNCO is very sensitive to the interaction with H<sub>2</sub>O. Experimentally, this mode is downshifted by 215 cm<sup>-1</sup> and this value is in good agreement with the calculated one's (255  $cm^{-1}$ ). The comparison of the experimental and theoretical shifts for the  $v_2$  mode of HNCO and for the  $v_1$ and  $v_3$  modes of H<sub>2</sub>O complex confirms the presence of a HO<sub>w</sub> complex and the lack of the OH<sub>w</sub> one. These results confirm the acidic character for isocyanic acid.

### 4.2. Structure of the adsorbed layer

The Periodic Hartree–Fock (PHF) method was successfully used in our earlier papers [16,47–50] to model the reactivity of small molecules adsorbed on amorphous ice; therefore it is also applied in the present case. The methodology is implemented in the CRYSTAL98 computer code [51]. As previously stated, the ice substrate is represented by a slab of two molecular bilayers, periodic in two dimensions, parallel to the [0001] face and well known as P-ice [52–54]. The orbital basis set is the standard 6-31g(d,p).

In the present section, we considered only the unrelaxed ice surface. Hence, the optimization process concerns only the adsorbed HNCO molecules. Each  $(1 \times 1)$  water surface unit cell contains one isocyanic acid molecule. The automatic gradient not being implemented in CRYSTAL98, the equilibrium adsorption structures are calculated by quadratic interpolation techniques [48]. The PHF energies were corrected by the electron correlation contribution evaluated by the GGA–DFT functional [55].

Various positions were explored in order to determine the nature of the adsorption sites. After optimization only two stable structures were found. Their total energies (in Hartree) are reported in Table 3.

- For the first structure (Fig. 6(a)), HNCO is upright above the dangling O site. The N-H...O distance (1.783 Å) is characteristic of a strong hydrogen bond. This structure coming from the HO<sub>w</sub> complex observed in matrix is illustrated in Fig. 6(a), and it is noted HO<sub>iv</sub> (i for ice and v for vertically HNCO).
- The structure displayed in Fig. 6(b) shows the geometry obtained for the second minimum (the most stable, cf. Table 3). In this structure, coming from a HO<sub>w</sub> complex (noted here HO<sub>if</sub>, i for oxygen of ice and f for flattened HNCO), the HNCO is flattened on the ice surface and HNCO is stabilized by two strong hydrogen bonds. One between the isocyanic acid

	Adsorption sites	5	Dimers		
	Total energy <sup>a</sup> (r	elative energy) <sup>b</sup>	Total energy <sup>a</sup> (		
	HO <sub>iv</sub>	HO <sub>if</sub>	D <sub>A</sub>	D <sub>B</sub>	D <sub>C</sub>
HF	-776.0922	-776.0967	-943.7561	-943.7591	-943.7633
	(11.8)	(0.0)	(18.9)	(11.0)	(0.0)
GGA	-779.7812	-779.7902	-948.2672	-948.2720	-948.2780
	(23.6)	(0.0)	(28.3)	(15.7)	(0.0)
$d^{c}$ (O H–O)	1.783	1.934	2.108 <sup>d</sup>	(2.004 <sup>d</sup>	2.616 <sup>d</sup>
$d^{c}$ (OH–N)		1.734	1.783 <sup>e</sup>	1.734 <sup>e</sup>	

Table 3 Total energies of HNCO adsorption sites and total energies of dimers per water unit of ice

<sup>a</sup> Hartree.

 $^{b}$  kJ/mol<sup>-1</sup>.

<sup>c</sup>Å from HF calculations.

 $^{d}(O_{4}\ldots H_{25}\text{--}O).$ 

 $e(O_{10}...H_1-N_2).$ 



Fig. 6. Optimized site structures of isocyanic acid adsorbed on ice surface (CRYSTAL98): (a)  $HO_{iv}$  (i for ice and v for vertically HNCO); (b)  $HO_{if}$  (i for ice and f for flattened HNCO).

and the dangling lone pair of electrons of a surface oxygen atom and one between the dangling OH and the carbonyl oxygen of HNCO. The associated N–H...O<sub>i</sub> and O...H–O<sub>i</sub> distances are 1.734 and 1.934 Å, respectively.

We also tried to adsorb the molecule above a point of low electronic density, i.e. above a dan-

gling hydrogen, but this site, corresponding to a  $OH_w$  complex, is less stable in total energy as calculated for isolated complex (cf. Table 2). These theoretical results show that on a proton ordered ice surface, HNCO exhibits two stable structures (HO<sub>iv</sub> and HO<sub>if</sub>). The appreciable difference in stability (23 kJ/mol) between the two structures

might justify in the experience the absence of the less stable one, HO<sub>iv</sub>. The HO<sub>if</sub> structure, the most stable, displays a shorter distance (1.935 A) compared with the value calculated for the OH<sub>w</sub> complex (2.177 Å). Thus, due to a stronger interaction between HNCO and H<sub>2</sub>O, a change of the vibrational frequency of the dangling OH's should be observed following adsorption. However, when HNCO is deposited at low temperature on the H<sub>2</sub>O surface, the dangling OH is not perturbed. Obviously, at this temperature, some solid aggregates have been deposited. Due to their hydrogen donor and acceptor properties, HNCO molecules could form more compact complexes on the ice surface. So, we think the interaction existing between HNCO molecules, can play a role on the spatial orientation of individual molecule and on the lack of perturbation of the OH group. We consider here only distributions containing two non-equivalent HNCO molecules per surface unit cell. These molecules tend to form dimers. From the precedent stable structure HO<sub>if</sub> three likely HNCO associations were investigated:

- In the first one, D<sub>A</sub>, the arrangement of the two molecules of HNCO corresponds to the dimer found in gaseous phase (Fig. 7).
- The other two associations D<sub>B</sub> and D<sub>C</sub> are assumed to be found for the solid state: D<sub>B</sub> corresponds to a "head to tail" form before

optimization and  $D_C$  corresponds to the  $(H-NC=O)_1 \dots (H-NC=O)_2$  dimer. Where  $(H-NC=O)_1$  denotes the initial HNCO molecule shown in Fig. 2.

These respective optimized topologies are displayed in Fig. 7 with atomic numbering. The total energies are reported in Table 3. The analysis relative to the  $D_C$  system suggests that the formation of adsorbate islands can largely transform the initial HO<sub>i</sub> configuration.

For the two  $D_A$  and  $D_B$  dimer forms, the  $(HNCO)_1 \dots H-O$  length are similar (2.106 and 2.004 A, respectively, instead of 1.934 A in HO<sub>i</sub> model). The situation is different for the most stable dimer structure  $D_{C}$ . The consequence of displacements of the second molecule in the vicinity is to attenuate the  $(HNC=O_4) \dots (H_{25}-O)$ hydrogen bond. This hydrogen bond length, estimated at 2.616 A, is significantly longer than 1.934 A in the HO<sub>i</sub> model. The resulting form of this penetration must be related to the formation of a weak interaction between the  $N_6$  of (HNCO), and the ice dangling  $H_{25}$  hydrogen:  $d(N_6-H_{25}) =$ 3.07 Å. The  $O_4$ -H<sub>5</sub> bond length is 2.251 Å, corresponding to a weak hydrogen bond. These changes could lead to further stabilization for the  $D_C$  form. Hence, the data in Table 3 show that the dimerization has a great impact on the spatial orientation of individual molecules. As a result



Fig. 7. Optimized structures of isocyanic acid dimers adsorbed on ice surface.

two consequences must be drawn: (i) the second molecule of HNCO breaks the former hydrogen bond,  $O_4$ - $H_{25}$  and forms new hydrogen bonds ( $O_4$ - $H_5$  and  $N_6$ - $H_{25}$ ), and (ii) the HO<sub>w</sub> structure becomes favored.

This dimer formation on ice surface is consistent with the lack of perturbation on the dangling OH absorption in the IR spectra. In conclusion of this paragraph, the best overall qualitative agreement with experiment is obtained with the dimer model.

### 4.3. Ionization of the isocyanic acid on ice

The periodic methods have proved to be very efficient in determining the structure of the adsorbed phases but they become very prohibitive and unsuited in dealing with the system reactivity. In this case, it is much easier to revert to the cluster model such as the model we used in a former work [16]. We therefore carried out the calculation on the system constituted with HNCO and its four nearest water molecule neighbors. Nevertheless, the model used in reference [16] has been refined by introducing 18 extra water molecules embedding the small cluster. The whole system is calculated using Gaussian 98 [44] and the ONIOM model [56] with B3LYP/6-31g(d,p) for the highlevel cluster and PM3 for the low-level. Due to the

structure of the system, no covalent bond had to be cut, the two subsystems being linked together only by van der Waals and hydrogen bonds. The choice of a quantum level for the low-level system, even if semi-empirical, ensures a better polarizability of the larger cluster and a better representation of the embedding of the reactive part in the entire cluster. From the former paragraph, it can be deduced that the lack of perturbation of the dangling OH IR band observed is due to the formation of HNCO dimers or polymers and because of these dimers, the isocyanate oxygen interacts weakly with the dangling OH. Nevertheless, it can be reasonably expected that the ionization process concerns the ad-molecule that lies close to the surface and not the other one. Therefore, the present study involves one isocyanic acid molecule only.

The whole system was optimized without any restriction. In fine, we can observe in Fig. 8 that the structure is very similar to the P-ice that formed the starting point of the periodic calculation: the chair-shape units constituting the ice structure are only slightly distorted but they remain quite recognizable. In good agreement with the periodic calculation, the system stability is ensured by a strong hydrogen bond (1.663 Å) (noted  $H_AO_1$ ) with a dangling O of the  $H_2O$  ice surface. The ONIOM calculation also confirms



Fig. 8. Adsorbtion of isocyanic acid (a) and ionized isocyanic acid (b) on relaxed ice surface (ONIOM cluster approximation).

that the oxygen isocyanic acid interacts to a lesser extent with the ice dangling OHs since the corresponding distances are 2.123 and 2.181 Å (noted  $OH_B$ ).

The isocyanic acid ionization on the ice surface was modeled in scanning the NH (noted  $NH_A$ ) distance, the remaining of the large cluster being relaxed without further constraint. The resulting potential energy surface is displayed in Fig. 9. This figure shows a maximum in energy at NH  $\sim 1.55$  Å. Given the size and the complexity of the system, it is difficult to automatically calculate the corresponding stationary state or to make an IRC calculation. However, we can reasonably consider that the maximum of Fig. 9 is a good approximation of the transition state of the ionization reaction of isocyanic acid. The energy of this point is 42 kJ/mol above the initial state. Due to the very large number of variables, it has not been possible to calculate the ZPE correction to this barrier. The geometry corresponds to the capture of the proton by the closest dangling oxygen on the ice surface. In this transition state (no displayed in Fig. 8), the  $H_3O^+$  counterion is located near the OCN<sup>-</sup>. The two being bonded by a hydrogen bond  $OCN^{-} \dots H^{-}O^{+}H_{2}$  of 1.571 Å (noted  $OH_{B}$ ). The isocyanate oxygen is bound to the ice surface by two H-bonds of 1.704 Å (NH<sub>A</sub>) and 1.806 Å, respectively.

The minimum in energy, corresponding to the isocyanate ion adsorbed on ice, occurs for the distance values  $NH_A = 1.704 \text{ Å}$  and  $H_AO_1 =$ 1.004 Å. The gain in energy is provided mainly by the contribution of two strong hydrogen bonds, with the already mentioned dangling OH, and the bond lengths are 1.571 and 1.806 Å. In the final geometry, the hydronium ion  $H_3O^+$  is H-bonded to the oxygen of OCN<sup>-</sup>, whereas in the transition state it was bonded to N. The energy gain generated is 17 kJ/mol (cf. Fig. 8(b)). The net Mulliken atomic charges are -0.52 electron on O, +0.19 electron on C and -0.46 electron on N. So the electrostatic potential field is roughly the same on the two ends of the moiety. The weak distance between O of OCN<sup>-</sup> and H of the H<sub>3</sub>O<sup>+</sup> can be a favourable condition to a new proton transfer to OCN<sup>-</sup>. Leading to the cyanic acid, HOCN, as previously reported in the experiment and corresponding to the transfer of  $H_B$  from  $O_2$  to O of OCN<sup>-</sup>.



Fig. 9. Potential energy surface corresponding to the isocyanic acid ionization process on ice surface, transfer of  $H_A$  from N to  $O_1$ .

### 5. Discussion and conclusion

The analysis of our results shows that HNCO trapped in an argon matrix or adsorbed on an amorphous ice surface, acts as an electrophil by means of its acid hydrogen atom. For this reason, only one kind of HO<sub>w</sub> complex (HO<sub>if</sub> adsorption site, respectively) is obtained which is stabilized by an hydrogen bond between the acid hydrogen atom of HNCO and the oxygen atom of water (the dangling O on the ice surface, respectively). From theoretical calculations, a second minimum, less stable, is obtained for a OH<sub>w</sub> complex (corresponding to the dangling OH adsorption site, respectively). This kind of complex stabilized by an hydrogen bond between the water hydrogen and the oxygen atom of isocyanic acid is not observed experimentally. For the dangling O adsorption site, the isocyanic acid is flattened on the ice surface and complexed by an other HNCO molecule. This polymer (HNCO...HNCO...) formation process on ice surface is consistent with the lack of perturbation on the dangling OH absorption, and the line shape and position of the HNCO modes are the same as those observed in solid isocyanic acid [43] infrared spectrum.

Above 110 K, the dangling OH begins to decrease in intensity, then disappears at 130 K. The latter phenomenon is due to the collapse of the amorphous ice pores during its evolution in crystalline ice. This study shows that HNCO is stable on ice below 140 K. The thermal behavior of adsorbed HNCO or trapped HNCO in the H<sub>2</sub>O solid, shows the appearance of a new infrared absorption band observed near 2170 cm<sup>-1</sup> which is attributed to the OCN<sup>-</sup>. Modeling of the thermal isocyanic acid ionization process on the ice surface, shows a low energy barrier of 42 kJ/mol which can explain that the formation of OCN<sup>-</sup> occurs at temperature about 130 K. OCN- is produced by purely solvation-induced dissociative ionization. The isocyanate ion adsorbed on ice, is stabilized by two strong hydrogen bonds and in the final geometry, the hydronium ion is H-bonded to the oxygen of OCN<sup>-</sup> with an energy gain of 17 kJ/mol. In this last arrangement the hydronium ion can transfer a proton to the OCN<sup>-</sup> ion to form cyanic acid (HOCN) characterized by an intense band at 2295 cm<sup>-1</sup>, so we can say that H<sub>2</sub>O solid supports this isomerization process. Such as proton transfer on amorphous ice film have been already observed to explain the formation of chloroformylketene from HCl and carbon suboxide  $(C_3O_2)$  [16]. Because of temperatures measured in the interstellar cloud (T < 100 K) [57], this study shows that the mechanism (ionization by solvation) could not occur, since the observed transition to OCN<sup>-</sup> begins above 100 K. In these conditions, it appear more probable that the OCN- ion observed by the ISO spectra from its intense band at 4.62 µm results from an acid/ base mechanism operable at cloud temperatures involving HNCO and NH<sub>3</sub> as reported by Hudson et al. [29].

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