

Experimental and theoretical study on the spontaneous formation of OCN^- ion: reactivity between HNCO and $\text{NH}_3/\text{H}_2\text{O}$ environment at low temperature

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Abstract

The reactivity of HNCO embedded in $\text{NH}_3/\text{H}_2\text{O}$ mixtures in astrophysical ratio (1/10) is investigated using FT-IR spectroscopy between 10 and 180 K and quantum calculations. A spontaneous reaction is observed at 10 K between HNCO and NH_3 , which leads to $\text{NH}_4^+\text{OCN}^-$ formation. Theoretically, we show that this can occur if HNCO is both in interaction with lone pair of one NH_3 molecule and surrounded by three H_2O molecules. The OCN^- produced is characterized by a band centered at 2167 cm^{-1} , which is well in agreement with the observations provided by infrared space observatory (ISO) spectrometer towards protostellar sources. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

The observations carried out by the infrared space observatory (ISO) have put in evidence the presence of many species in the cold interstellar dust grains (10–50 K) as H_2O , CO, CO_2 , CH_3OH and NH_3 [1,2]: however, some features observed in ISO spectra are assigned to other species than those latter. The presence of OCN^- ion in interstellar ices is characterized by a band observed at $4.62\text{ }\mu\text{m}$ (2167 cm^{-1}) in different protostellar objects such as W33A [3] or NGC7938 IRS9 [4]. This assumption has been evidenced in recent laboratory studies relative to UV irradiation of CO/ NH_3 and CO/ $\text{NH}_3/\text{H}_2\text{O}$ mixtures [4,5] at 10 K, and has shown that OCN^- could be formed in the grains [6–9]. OCN^- can also be formed from radiation chemistry, namely cosmic rays [5] and also by annealing of ices usually to 100 K or higher [10]. The mechanisms of OCN^- formation in the dust grains can be explained by reactions between isocyanic acid (HNCO), an intermediate compound

formed during the UV irradiation of previous mixtures, and ammonia [11] or water [12] (see reactions below). However, little reaction occurs when HNCO and H_2O are codeposited ($T < 100\text{ K}$) [10]. Up to this date, HNCO has been detected in the interstellar medium, in the gas phase [13–15] but never in the condensed phase of different protostellar objects



Alternatively, photodissociation of NH_3 generates NH radicals which will combine with CO to form HNCO in a reaction (3) [5]



After, HNCO can be react with NH_3 (4) or H_2O (5) present as follow



In a previous work, we characterized both experimentally and theoretically the existence of different HNCO: H_2O [16] and HNCO: NH_3 [17] complexes in

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argon matrix. In the condensed phase, we studied the reactivity of HNCO on the surface and in the bulk of pure water and ammonia ices [16–18]. We have found no spontaneous reaction at 10 K when HNCO is adsorbed or embedded with H₂O ice [16]. When HNCO is embedded in ammonia bulk at 10 K, a spontaneous reaction leads to NH₄⁺OCN[−] [17,18]. These results show that the cooperative effect of the hydrogen bonds between the NH₃ or H₂O molecules plays an important role in HNCO reactivity. OCN[−] is characterized by an intense infrared band, respectively, located at 2172 and 2151 cm^{−1} in H₂O and NH₃ environment. These frequency values show a relevant difference from the OCN[−] band position at 2167 cm^{−1} in ISO spectra. We may also assume that this difference is due to an environment effect of OCN[−], which is not only constituted in the grains of NH₃ or H₂O molecules. In fact, NH₃ abundance in astrophysical ices towards protostellar sources is generally less than 10% relative to H₂O [3] and could induce some changes in the OCN[−] IR frequency.

In this paper, we propose to confirm whether HNCO could react with NH₃/H₂O mixtures and gives a better OCN[−] frequency in accordance with ISO data. The purpose of this work is: (1) to establish the formation of OCN[−] at low temperature when HNCO is codeposited with a mixture of NH₃/H₂O, (2) to explain the reactivity of HNCO with the help of quantum calculations and (3) to compare the position of OCN[−] in different environments. The experiments were monitored by FT-IR spectroscopy and quantum calculations were undertaken to compare the experimental observations.

2. Experimental and theoretical details

The experimental device used in our experiments consisted of an vacuum sample chamber (10^{−7} mbar) containing a rotating gold-plated mirror kept at 10 K by CTI-CRYOGENICS compressor, coupled to a Fourier Transform Infrared spectrometer (Nicolet series II Magna system 750) equipped with a liquid N₂ cooled detector, a germanium-coated KBr beamsplitter and a global source.

Pure HNCO is synthesized from the thermal decomposition of cyanuric acid (Aldrich Chemical Co., 98%) at 650 °C, under primary vacuum [19,20]. HNCO is condensed and conserved in a tube cooled by liquid

nitrogen. HNCO is degassed before each experiment. Ammonia is supplied by Air Liquide (N36, H₂O ≤ 200 ppmv).

H₂O was degassed by successive freeze-thaw cycles under vacuum before each use. To study the reactivity of HNCO into the NH₃/H₂O solid, we co-deposited HNCO and NH₃/H₂O (1/10) from two separate inlets at a rate of 2 × 10^{−2} mol min^{−1} onto a gold mirror kept at 10 K. A sample of HNCO/(NH₃/H₂O) in a ratio of 0.1/ (1/10) was obtained from an estimation based on standard manometric techniques.

The thermal activation of the samples was achieved by an annealing of the mirror from 10 to 180 K using a heating rate of 0.7 K min^{−1}.

Infrared spectra were recorded, in the 4000–500 cm^{−1} range, with a resolution of 0.5 cm^{−1} and 100 scans were collected.

In order to explain our experimental results, we were carried out quantum calculations with GAUSSIAN 98 package programs [21] using DFT method at the B3LYP/6-31G(d,p) level of theory [22]. We used a similar approach, already described in our previous works to modelize the spontaneous dissociation of HNCO with NH₃ which leads to OCN[−] formation [17,18]. We added one by one water molecules to replace the approximate solvent field on HNCO:NH₃ structure. Each system will be hereafter referred to as HNCO:NH₃:(H₂O)_n in which *n* = 0–3.

The interaction energy of these systems, Δ*E*(BSSE), was calculated using the following equation:

$$\Delta E_{\text{BSSE}}(n) = E_{\text{BSSE}}^{\text{Tot}}[\text{HNCO:NH}_3:(\text{H}_2\text{O})_n] - E_{\text{BSSE}}[\text{HNCO}] - E_{\text{BSSE}}[\text{NH}_3:(\text{H}_2\text{O})_n]$$

Each term of this equation is evaluated using the entire orbital set as usual in the Boys counterpoise method (BSSE correction) [23].

3. Results and discussion

3.1. Experimental results

The infrared spectrum of solid HNCO has already been reported in the literature [7,19]. It displays six vibrational modes noted *v*₁ to *v*₆ (see Table 1), with the most intense being the *v*₂ mode. This mode, located at 2251 cm^{−1}, corresponds to the antisymmetric stretching

Table 1
Experimental frequencies (cm^{−1}) of *v*HNCO and *v*OCN[−] at 10 and 120 K in H₂O, NH₃/H₂O and NH₃ environment

	H ₂ O [16]		NH ₃ /H ₂ O		NH ₃ [17]	
	10 (K)	120 (K)	10 (K)	120 (K)	10 (K)	120 (K)
<i>v</i> HNCO	2242	2254	2261–2246	–	2259	–
<i>v</i> OCN [−]	–	2172	2167	2164	2151	2148

mode of NCO group (ν_{asNCO}) (Fig. 1(a)). No reaction occurs between HNCO molecules neither in the solid phase at 10 K nor when the sample is heated until it reaches the total sublimation temperature around 140 K.

When HNCO and H_2O are co-deposited at 10 K, we have found no spontaneous reaction [16], but little reaction is indicated in the work of others [10]. Some similarities are observed with the reaction between H_2O and hydrazoic acid (HN_3) where deprotonation seems occur at temperature above 150 K [24]. HNCO, which has not yet reacted, displays a similar spectrum (Fig. 1b) to that observed for the HNCO solid at 10 K. Only the ν_{NCO} mode is shifted from 2251 (solid) to 2242 cm^{-1} (water ice bulk) showing an influence of the environment on the position of this band. When the sample is heated above 110 K, however, we have reported the existence of the OCN^- ion, in very small amounts, which is marked by a band located at 2172 cm^{-1} relative to the OCN^- asymmetric stretching mode (Table 1).

When HNCO and NH_3 are codeposited at 10 K, we have shown the existence of a spontaneous acid-base reaction leading to isocyanate ammonium $\text{NH}_4^+\text{OCN}^-$ (Fig. 1(c)). In the NH_3 environment, OCN^- is vibrationally characterized by an intense infrared band at 2151 cm^{-1} and two other weaker bands at 1212 and 630 cm^{-1} , which are respectively relative to the symmetric stretching and bending modes of OCN^- ion [25]. However, the system is here more reactive than the HNCO/ H_2O system, which accounts for the strong intensity of the OCN^- and NH_4^+ bands found in the spectrum. NH_4^+ is marked by a broad and intense band near the 3000 cm^{-1} region which is the superposition of bonded NH stretch and combination modes and by a

low band at 1495 cm^{-1} assigned to the NH bending mode [26]. In the NH_3 environment, the HNCO which has not yet reacted, is characterized by a band with a peak located at 2259 cm^{-1} .

The spectrum of the deposited HNCO/($\text{NH}_3/\text{H}_2\text{O}$) mixture, in a ratio of 0.1/(1/10) at 10 K, is displayed in Fig. 2. $\text{NH}_3/\text{H}_2\text{O}$ mixtures are characterized by bands centered at 1670 and 2850 cm^{-1} relative to the NH bending and stretching modes [8]. The spectrum recorded at 10 K shows that HNCO reacts spontaneously, as it has been observed for the codeposited mixture of HNCO/ NH_3 , and that $\text{NH}_4^+\text{OCN}^-$ is formed. In this experiment, OCN^- is characterized by a band located at 2167 cm^{-1} and the position of this band is different from that observed for OCN^- in H_2O or NH_3 ices (Fig. 1(d) and Table 1). This frequency is in excellent agreement with the ISO data of protostellar sources. The HNCO, which has not yet reacted in the solid (Fig. 2(b)), is characterized by a broad band with two maxima components at 2261 and 2246 cm^{-1} (ν_{asNCO}). The positions of these bands are very close to those observed for HNCO in NH_3 or H_2O environment where they are located at 2259 and 2242 cm^{-1} , respectively. The presence of two frequencies for HNCO in $\text{NH}_3/\text{H}_2\text{O}$ mixtures could be explained by the difference of environment in the bulk: HNCO being both in interaction with NH_3 or H_2O molecules. When the sample is warmed up, the bands at 2246 and 2261 cm^{-1} continually decreases and the reaction goes on until the temperature of 130 K is reached. The remaining HNCO displays a very weak band which has the same position as the one observed for the solid at 2252 cm^{-1} . Above 130 K, HNCO is totally sublimated. At about 170 K, the $\text{NH}_3/\text{H}_2\text{O}$ mixtures sublime and we observe the IR spectrum of pure $\text{NH}_4^+\text{OCN}^-$, probably in crystalline form [27]. At this temperature, the OCN^- frequency is

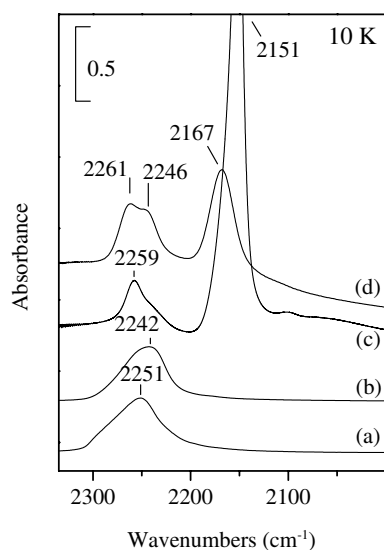


Fig. 1. Positions of ν_2 bands of HNCO and OCN^- at 10 K in pure HNCO (a), in HNCO/ H_2O (1/10) (b) [16], in HNCO/ NH_3 (1/10) (c) [17], and in HNCO/($\text{NH}_3/\text{H}_2\text{O}$) 0.1/(1/10) (d).

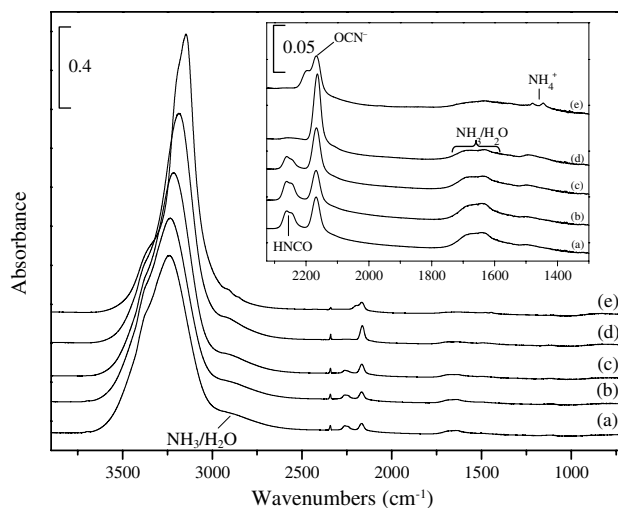


Fig. 2. Co-deposition of HNCO and $\text{NH}_3/\text{H}_2\text{O}$ mixtures in a ratio of 0.1/(1/10) at 10 K (a); 50 K (b); 110 K (c); 130 K (d); 170 K (e).

2164 cm^{-1} and presents a frequency redshift ($\Delta\nu = -3 \text{ cm}^{-1}$) with respect to the value observed for OCN^- in the $\text{NH}_3/\text{H}_2\text{O}$ mixtures. In the NH_3 bulk we have also observed that the νOCN^- band position was sensitive to a temperature effect. The frequency of OCN^- was 2151 cm^{-1} at 10 K and 2148 cm^{-1} in the NH_3 environment.

Therefore, we observe that OCN^- in astrophysical ices can result from a spontaneous reaction at 10 K between HNCO and $\text{NH}_3/\text{H}_2\text{O}$ mixtures present in ices. The non-detection of isocyanic acid in the interstellar grains could be explained by its high reactivity. HNCO, which is produced from UV irradiation of the CO/NH_3 system, can react as and when it comes in contact with NH_3 molecules to form $\text{NH}_4^+\text{OCN}^-$.

3.2. Theoretical results

In order to explain the spontaneous character of the reaction which occurs between HNCO and $\text{NH}_3/\text{H}_2\text{O}$ mixtures at 10 K, we suggested a theoretical model in which HNCO interacts with a NH_3 partner, the latter molecule being progressively solvated by one, two and three H_2O molecules. We started from the HNCO: NH_3 complex structure [17] and added H_2O molecules one by one. Each system will be referred to as HNCO: NH_3 :(H_2O) $_n$ in which $n = 0$ –3 and the $\Delta E(\text{BSSE})$ was calculated as mentioned above (Section 2).

The different systems are obtained by successive addition of H_2O molecule on the free H of the NH_3 molecule itself in interaction with the H of HNCO, this latter being proton donor. The optimized structures are reported in Fig. 3 and in Table 2.

$n = 0$: With NH_3 only, HNCO, being the proton donor, forms a strong hydrogen bond (H-bond) ($r_2 = 1.825 \text{ \AA}$) and an angle ($\text{N-H}\cdots\text{N}$) of 177.2° , as

shown in Fig. 3(a), between the hydrogen of HNCO and the nitrogen of NH_3 . The stabilizing energy of (a) system is -46 kJ mol^{-1} . In this configuration, the covalent bond length NH (r_1) of HNCO (H–NCO bond) is 1.040 \AA (1.008 \AA for isolated HNCO). In our previous study, we obtained the same system [17] to characterize the HNCO: NH_3 complex.

$n = 1$: For one H_2O molecule added interacting with the HNCO: NH_3 system, we obtained two optimized structures noted in Fig. 3(b) and (c) which display three H-bonds forming a quasi-planar cycle:

- The first, noted (b), is the least stable of the two and exhibits a first H-bond between the H of HNCO and the nitrogen of the NH_3 ($r_2 = 1.746 \text{ \AA}$, $\Delta r_2 = -0.079$) ($\Delta E(\text{BSSE}) = -63.2 \text{ kJ mol}^{-1}$). A second H-bond is obtained between one hydrogen of NH_3 and the oxygen of H_2O ($r_3 = 2.108 \text{ \AA}$) and a last weaker H-bond is found between the oxygen of HNCO and the hydrogen of the H_2O ($r_4 = 2.228 \text{ \AA}$).
- The second configuration (c) is more stable than (b) ($\Delta E(\text{BSSE}) = -68.2 \text{ kJ mol}^{-1}$). HNCO serves both as the proton donor to the NH_3 and as proton acceptor by its electron lone pair with H_2O . The (r_2) distance 1.727 \AA ($\Delta r_2 = -0.098$), is shorter and indicates a strong reinforcement of the hydrogen bond. Simultaneously, (r_1) very slightly increases to 1.060 \AA ($\Delta r_1 = +0.02$) and the length, between the N of HNCO and H of H_2O (r_4) is 2.087 \AA . This value denotes a rather weak H-bond. The bond length (r_3), between NH_3 and H_2O is 2.081 \AA .

The energy gain between (a) and (b) and between (a) and (c) is about -17.1 and $-22.1 \text{ kJ mol}^{-1}$, respectively. Adding the H_2O molecule reinforces the (r_2) hydrogen bonding (1.825 – 1.746 \AA and to 1.727 \AA for (b) and (c), respectively). A consequence is the weakening of the

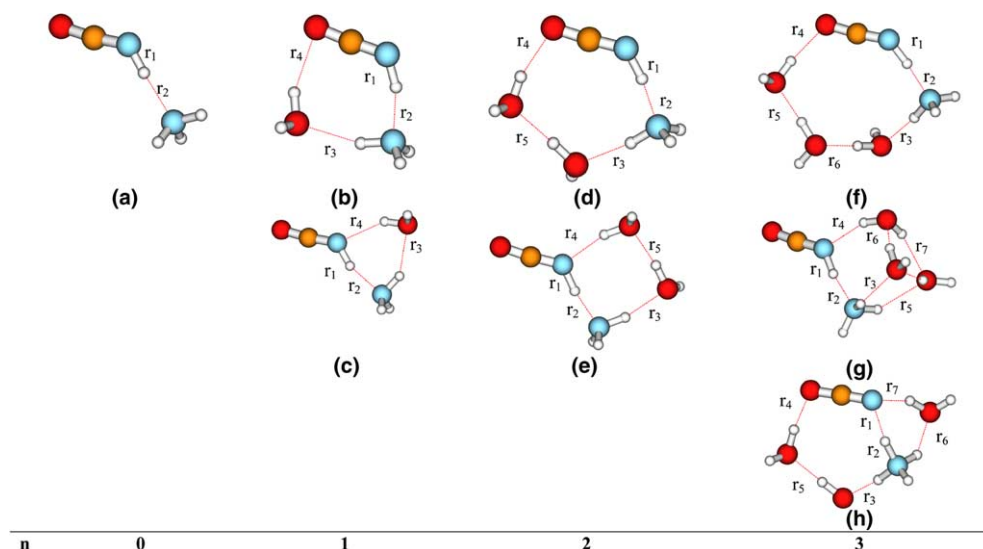


Fig. 3. Geometries of HNCO: NH_3 :(H_2O) $_n$ clusters with $n = 0$ –3, performed with B3LYP/6-31G(d,p) method.

Table 2

Geometrical and energetical parameters of $\text{HNCO}:\text{NH}_3:(\text{H}_2\text{O})_n$ clusters ($n = 0-3$), r_1-r_7 are given in Å and interaction energies, $\Delta E(\text{BSSE})$, are given in kJ mol^{-1}

	NH_3	1 H_2O		2 H_2O		3 H_2O		
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
r_1	1.040	1.059	1.060	1.083	1.086	1.095	1.075	1.638
r_2	1.825	1.746	1.727	1.621	1.629	1.576	1.664	1.082
r_3		2.108	2.081	1.905	1.893	1.873	2.195	1.684
r_4		2.228	2.087	1.917	1.899	1.852	1.969	1.767
r_5				1.794	1.770	1.749	2.210	1.689
r_6						1.743	1.715	1.861
r_7							2.032	1.888
$\Delta E(\text{BSSE})$	-46.1	-63.2	-68.2	-97.0	-95.4	-115.4	-83.4	-430.3

involved covalent bond (r_1) (1.040–1.059 Å for (b) and 1.060 for (c)) as already reported [28,29].

For these two systems, we have observed similar distances and energetic values with the $\text{HNCO}:\text{NH}_3$ complex solvated by one additional NH_3 molecule [17]. The electronic attractive effect is different between NH_3 and H_2O but the solvation effect is similar and can induce a spontaneous dissociation of HNCO as observed with NH_3 .

$n = 2$: We add an other H_2O molecule to (b) and (c) structures and we obtain two stable optimized structures noted (d) and (e) in Fig. 3. In these two systems, the additional H_2O is inserted into the cycle and interacts with both previous H_2O and NH_3 .

- The less stable ($\Delta E(\text{BSSE}) = -95.4 \text{ kJ mol}^{-1}$) (e) structure, is obtained by addition of H_2O onto the free H of the (c) systems NH_3 . This structure features a hetero-cycle with HNCO in exocyclic position. This new H_2O has an H-bond ($r_3 = 1.893 \text{ Å}$) with the (c) systems NH_3 and contributes to the lengthening of (r_1) to 1.086 Å and the shortening of (r_2) to 1.629 Å, through hyperconjugation. The H-bond length (r_5) is 1.770 Å between the two H_2O molecules and (r_4) is 1.899 Å between N of HNCO and H of this new H_2O .
- The second structure, noted (d), is more stable ($\Delta E(\text{BSSE}) = -97.0 \text{ kJ mol}^{-1}$) and is obtained by addition onto free H of the (b) systems NH_3 . This structure features four H-bonds forming a quasi-planar cycle with the NH_3 and the other two H_2O molecules. As observed in (e), (r_1) and (r_2) increase and decrease, respectively to 1.083 and 1.621 Å. The H-bond (r_5), between the two H_2O molecules, is 1.794 Å and (r_4), between N of HNCO and H of this new H_2O is 1.917 Å.

$n = 3$: The H_2O was added to the two systems (d) and (e). We obtained three optimized structures noted (f), (g) and (h).

- The (f) system was obtained when we inserted the H_2O molecule in the cycle of the (d) system. It features a non-planar cycle. This cycle is formed of five

molecules: HNCO , NH_3 , and three H_2O , which interact via five hydrogen bonds noted (r_2), (r_3), (r_4), (r_5) and (r_6) with respective lengths 1.576, 1.873, 1.852, 1.749, and 1.743 Å. The NH length (r_1) of HNCO increases to 1.095 Å. The interaction energy of this system is: $\Delta E(\text{BSSE}) = -115.4 \text{ kJ mol}^{-1}$.

- (g) is the least stable structure ($\Delta E(\text{BSSE}) = -83.4 \text{ kJ mol}^{-1}$). A new H_2O molecule is added into the cycle of the (e) system. Besides, two exo-cycles are formed with four H-bonds: r_2 (1.664 Å), r_4 (1.969) with r_3 and r_6 (2.195 and 1.715 Å, respectively), and with r_5 and r_7 (2.210 and 2.032 Å, respectively). In this structure, r_1 is found at 1.075 Å.
- When the new H_2O is added to the free H of NH_3 in the (d) system, the geometry optimization spontaneously converges to the (h) structure: $[\text{NH}_4^+\text{OCN}^-](\text{H}_2\text{O})_3$. The formation of NH_4^+ and OCN^- ions is obtained by spontaneous proton transfer from HNCO to NH_3 ($r_1 = 1.638 \text{ Å}$). A new hydrogen bond (r_7), with a length of 1.888 Å, which contributes to stabilize OCN^- . The new NH covalent bond formed is (r_2) (1.082 Å) and the previous (r_3), (r_4), (r_5) and (r_6) H-bonds are modified to 1.684, 1.767, 1.689, and 1.861 Å, respectively. In this structure, the isocyanate ion is stabilized by three H-bonds as observed with the dissociation of HNCO on water ice [16] or in the spontaneous formation of $[\text{NH}_4^+\text{OCN}^-](\text{NH}_3)_3$ [17]. The ammonium ion exhibits three hydrogen bonds (r_1), (r_4) and (r_7), and only one hydrogen remains free of interaction. The interaction energy of this system is $-430.3 \text{ kJ mol}^{-1}$.

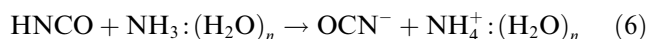
Our results show that the stabilization effect of the system increases with the number of H_2O . The gain obtained by each addition of H_2O is about 20 kJ mol^{-1} from $n = 1$ to 3. When $n = 2$, the total gain in energy is roughly equal to a covalent bond energy. As a consequence, for $n = 3$, the H–NCO bond breaking, is completely offset by the bulk effect and the solvation contribution.

This HNCO dissociation occurs without energetic barrier. Quantum calculations confirm the experimental

results, that is to say the spontaneous character of the reaction between HNCO and $\text{NH}_3/\text{H}_2\text{O}$ mixture at 10 K. Due to the proton donor character of the HNCO molecule, we confirm that the ionization process occurs if one NH_3 molecule is in interaction with HNCO via its electron lone pair, and if this NH_3 is solvated enough by H_2O molecules. At least, the threshold to be reached in order to involve a spontaneous proton transfer without supplying energy is of three water molecules.

4. Conclusion

We have shown in this study that the OCN^- ion is spontaneously formed when it is embedded with a $\text{NH}_3/\text{H}_2\text{O}$ environment in a ratio of 10/100 and we give a new path (6) to OCN^- formation which is supported both on experimental and theoretical results



where n is a number of water molecules present in the $\text{NH}_3/\text{H}_2\text{O}$ mixtures ($n \geq 3$).

Radiation chemistry and photochemistry are not necessary to form OCN^- if enough H_2O molecules are present in NH_3 and HNCO environment.

The resulting $\text{NH}_4^+\text{OCN}^-$ can be characterized by the vibrational bands at 2167 cm^{-1} ($\nu_2\text{OCN}^-$) and 1495 cm^{-1} ($\nu_4\text{NH}_4^+$). We have compared the νOCN^- mode with those obtained in different environments, NH_3 and H_2O , and we have observed that the position of this band was in excellent agreement with the value recorded by ISO towards different protostellar sources.

The quantum calculations confirmed that $\text{NH}_4^+\text{OCN}^-$ is produced by a solvation-induced dissociation ionization process. HNCO must be in an environment of four molecules: one of NH_3 and three of H_2O . The Hydrogen of HNCO interacting with the lone pair of NH_3 is itself solvated by two H_2O molecules.

From an astrophysical point of view, we confirm that the HNCO can react with $\text{NH}_3/\text{H}_2\text{O}$ mixtures in order to form OCN^- . The non-detection of HNCO in these interstellar solids can be due to its high reactivity. Although, it put in evidence it is formed in solid phase upon UV irradiation of the CO/NH_3 mixture.

In our experiment, however, at 10 K we can observe the presence of HNCO because the latter is mainly deposited in the form of aggregates.

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