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Reactivity of HNCO with NH_3 at low temperature monitored by FTIR spectroscopy: formation of $NH_4^+OCN^-$

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Abstract

The reactivity of isocyanic acid (HNCO) with solid ammonia (NH_3) was first studied at 10 K, using FTIR spectroscopy. The ammonium isocyanate ($NH_4^+OCN^-$) is formed from a reaction between HNCO and NH_3. Vibrational band assignments for $NH_4^+OCN^-$ have been given. On the other hand, when HNCO is adsorbed on amorphous NH_3 film, the reaction does not occur. Warming up of this sample at 90 K induces the $NH_4^+OCN^-$ formation. Quantum calculations showed that the solvation of NH_3 directly bonded to HNCO by at least three NH_3 molecules plays a major role in the $NH_4^+OCN^-$ formation process and confirmed the spontaneous character of this reaction.

1. Introduction

HNCO has been detected in the interstellar medium, in gas phase [1–3] but never in the cold (10/100 K) interstellar dust grains. Space-based observations by the infrared space observatory (ISO) have revealed the presence of many species in these grains as H_2O, CO, CO_2, CH_3OH and NH_3 [4].

Laboratory studies, relative to the UV irradiation of CO/NH_3 and $CO/NH_3/H_2O$ mixtures [5] at 10 K, have shown that $NH_4^+OCN^-$ could be formed in the grains. The vibrational band assigned to the νOCN^- mode located about 2165 cm^{-1} is in excellent agreement with the one, known as 'XCN' band, observed on ISO spectra and located at 4.62 μm [6,7]. This assignment is supported by isotopic labeling experiments [8,9]. The $NH_4^+OCN^-$ formation can be explained from an acid–base reaction occurring between NH_3 and HNCO formed during the CO/NH_3 UV irradiation [9–11]. The reactions proposed by Grim et al. [12] are as follows:

$$NH_3 + h\nu \rightarrow NH_3^* \rightarrow NH_2 + H$$

$$NH_2 + CO \rightarrow H + HNCO$$

$$HNCO + NH_3 \rightarrow NH_4^+ + OCN^-$$

Here, using the tools of FTIR spectroscopy and quantum calculation, we focus on the conditions of $NH_4^+OCN^-$ formation and the ionization pro-

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cess when HNCO is co-deposited with NH_3 (1/10 mixture) or adsorbed on NH_3 ice film.

2. Experimental

Pure HNCO is synthesized from the thermal decomposition of cyanuric acid (Aldrich Chemical, 98%) at 650 °C, under a primary vacuum [13,14]. 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, $H_2O \geqslant 200$ ppmv).

To study the reactivity of HNCO into the NH_3 solid, the sample $HNCO/NH_3$ (1/10) was deposited at a rate of 2×10^{-2} mol/min from two separate inlets onto a gold-platted mirror held at a constant pressure of 10^{-7} mbar at 10 K. The concentration was estimated from standard manometric techniques. Previously, and under the same conditions, we undertook a study of pure HNCO and pure NH_3 spectra.

The thermal activation of the samples was achieved through gradual warming up of the mirror from 10 to 180 K, and using a heating rate of 1 K/min.

Infrared spectra were recorded with a FTIR Spectrometer (Nicolet series II Magna system 750) in the range 4000–500 cm^{-1}, with a resolution of 0.5 cm^{-1} and 100 scans.

3. Experimental results

Regarding NH_3 [15], the infrared spectrum of solid HNCO at low temperature (10–145 K) has already been reported [10]. The solid NH_3 infrared spectrum (Fig. 1a) can be characterized by four fundamental modes noted ν_1, ν_2, ν_3 and ν_4, whose frequencies are 3210, 1075, 3375 and 1625 cm^{-1} respectively. The HNCO infrared spectrum (Fig. 1b) displays six vibrational modes noted ν_1–ν_6 and the frequencies are listed in Table 1 with their corresponding assignments. The HNCO IR spectrum is characterized by an intense vibrational band located at 2252 cm^{-1} and a broad feature split into two bands at 3200–3365 cm^{-1}, which are relative to the ν_{as}NCO and νNH stretching modes.

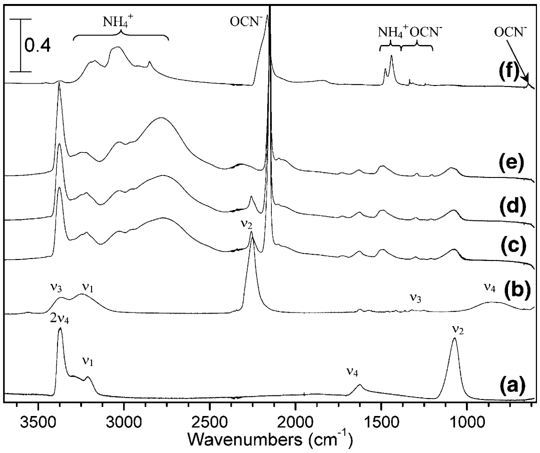


Fig. 1. Co-deposition of HNCO and NH_3 in a ratio 1/10 at 10 K: (a) NH_3 10 K; (b) HNCO 10 K; (c) $HNCO/NH_3$ 10 K; (d) 30 K; (e) 120 K; (f) 160 K.

When HNCO and NH_3 are co-deposited at 10 K. The HNCO IR spectrum shows three bands, which are slightly shifted, compared with the values observed for the solid HNCO or HNCO in an H_2O environment (Table 1). The most striking feature is the $NH_4^+OCN^-$ spontaneous formation due to an acid–base reaction in the bulk between HNCO and NH_3 (Fig. 1c). The absorption bands relative to $NH_4^+OCN^-$ species are reported in Table 2 with their assignments. OCN^- is characterized by an intense band at 2151 cm^{-1} which is well correlated with and two weaker bands at 1212 and 630 cm^{-1}, which are, respectively, relative to the asymmetric stretching and symmetric bending modes [16]. The band at 2151 cm^{-1} cannot be due to the CO formation because this latter can be characterized in NH_3 environment by a band at 2145 cm^{-1}. Moreover, Co is expected to sublimate near of 40 K whereas the 2151 cm^{-1} band is not reduced in intensity before the temperature of 200 K reached. The frequency (2151 cm^{-1}) of the OCN^- asymmetric stretching mode is different from that observed in a H_2O environment (2170 cm^{-1}) [17]. NH_4^+ can be characterized by a weak band at 1495 cm^{-1} assigned to NH bend and by a broad and intense band in the region near 3000 cm^{-1}, which is the superposition of bonded NH stretch and combination modes [18]. As the sample is heated above 30 K (Fig. 1d), due to a possible

Table 1
Experimental frequencies (cm^{-1}) of HNCO solid, in H_2O and in NH_3 environments at 10 K

Modes	Assignments	HNCO solid at 10 K	HNCO in H_2O solid at 10 K [28]	HNCO in NH_3 solid at 10 K
ν_1[a]	NH stretch	3365–3245	–	3218
ν_2	NCO asymmetric stretch	2252	2242	2259
ν_3[b]	NCO symmetric stretch	1322–1252	1321–1261	1313–1254
ν_4	HNC bend	862	–	–
ν_5	NCO in plane bend	597	–	–
ν_6	NCO out of plane bend	657	–	–

[a] Two components are observed for this mode. Such a splitting is due to hydrogen bond interaction.

[b] Fermi resonance of ν_3 and $2\nu_6$.

Table 2
Experimental frequencies (cm^{-1}) of $NH_4^+OCN^-$ at 10 K in NH_3 environment and $NH_4^+OCN^-$ solid at 160 K

		Assignments	$NH_4^+OCN^-$ in solid NH_3 at 10 K	$NH_4^+OCN^-$ solid at 160 K
	$\nu_1 + \nu_5$	Combination mode	3225	3200
	ν_3	NH stretch	–	3170
NH_4^+	$\nu_2 + \nu_4$	Combination mode	3030	3034
	$2\nu_4$	First overtone of NH bend	2800	2853
	$\nu_2 + \nu_6$	Combination mode	2080	2080
	ν_2	NH bend	1630	
	ν_4	NH bend	1495	1477–1441[a]
	ν_3	OCN asymmetric stretch	2151	2165
OCN^-	$2\nu_2$	First overtone of OCN bend	1300	1335–1317[a]
	ν_1	OCN symmetric stretch	1212	1244–1227[a]
	ν_2	OCN bend	630	645

[a] Splitting probably due to a crystallization effect.

excessive NH_3 diffusion in the mixture, the reaction continues up to 120 K with HNCO, which has not yet reacted in the solid (Fig. 1e). After NH_3 sublimation at 125 K, we observe only $NH_4^+OCN^-$ which displays a vibrational spectrum (Table 2, Fig. 1f) different from the one previously recorded at 10 K. This change shows that NH_3 presence ($T < 120$ K) significantly disturbs the $NH_4^+OCN^-$ environment, which in its crystalline form displays NH_4^+ cation surrounded by eight NCO^- anion [19]. The frequency of the asymmetric OCN^- stretching mode is 2163 cm^{-1} at 160 K. This value is consistent with the experimental data obtained from UV irradiation of CO/NH_3 (1/1) ice and heated up to 100 K [8].

We shall now compare these results with those obtained from HNCO adsorbed on NH_3 solid. The NH_3 film prepared at 10 K is an amorphous film [20]. The ν_2 and ν_3 bands are broad and not split into two components as in the metastable (77 K) or cubic (150 K) phases [20] (Fig. 2b). Moreover, the lattice band at 530 cm^{-1} expected for the metastable or cubic phase is not present. X-ray study of solid ammonia at −102 °C shows that the lone electron pair of NH_3 is used and that each NH_3 molecule is involved in six hydrogen bonds [21]. When HNCO is adsorbed on NH_3 ice (Fig. 2a), no reaction occurs at 10 K. A warming-up the sample to a temperature circa 70 K induces a solid NH_3 transformation, probably from amorphous to a metastable phase. Thus, a splitting into two components of the ν_2 and ν_3 modes and, at 530 cm^{-1}, emergence of a lattice band not observed in the amorphous film, are now observed for solid NH_3. At 90 K (Fig. 2c), however, a new weak band is observed at 2163 cm^{-1}, which is assigned to the $\nu_{as}OCN^-$ stretching mode. After sublimation of NH_3 at 125 K, the IR spectrum shows (Fig. 2d)

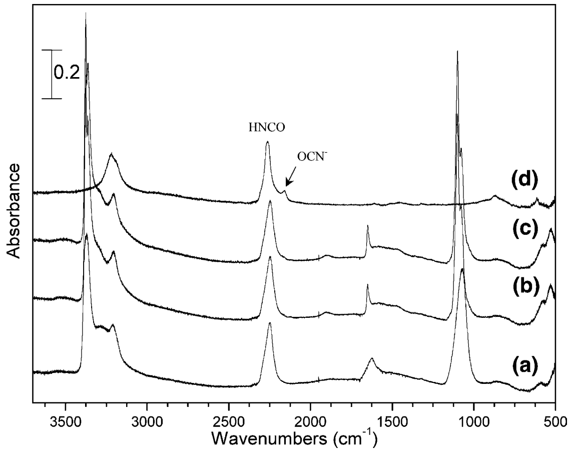


Fig. 2. Adsorbtion of HNCO on NH_3 surface: (a) 10 K; (b) 70 K; (c) 90 K; (d) 130 K.

similar features to those observed for $NH_4^+OCN^-$ in the co-deposition experiment (Fig. 1f). The small amount of $NH_4^+OCN^-$ detected can be explained because it is only formed at the solid interface HNCO/NH_3.

Since no reaction occurs at 10 K when HNCO is adsorbed on NH_3 ice film but only when HNCO is co-deposited with NH_3, we suggest that $NH_4^+OCN^-$ is produced by solvation-induced dissociative ionization process. In order to confirm this hypothesis, we performed calculations on HNCO ionization in direct interaction with NH_3 molecules.

4. Computational section

To explain the formation of $NH_4^+OCN^-$, we investigated the interaction between HNCO and the reactive NH_3, and then the solvation of HNCO by one, two and three NH_3 molecules. These systems are noted $HNCO{:}(NH_3)(NH_3)_n$ ($n = 0$–3) and were optimized at B3LYP/6-31G** basis set level of theory [22]. The quantum calculations were carried out using GAUSSIAN 98 [23]. The interaction energy of the different system, ΔE, was calculated using the following equation:

$$\Delta E(n) = E\left[\mathrm{HNCO(NH_3)}_{n+1}\right] - E[\mathrm{HNCO}] - E\left[(\mathrm{NH_3})_{n+1}\right] \qquad (1)$$

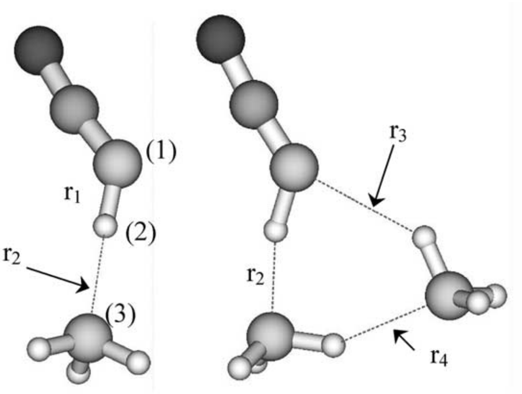
Each term is evaluated using the entire orbital set as usual in the Boy's counterpoise method (BSSE correction) [24].

With one NH_3 only ($n = 0$), HNCO is bonded to NH_3. The system features a strong hydrogen bond (H-bond) ($r_2 = 1.825$ Å in Fig. 3a), between the hydrogen of HNCO and the nitrogen of NH_3, forming an angle (N–H…N) of 177.2°. The stabilizing energy of the system is −46 kJ/mol. In this configuration, HNCO displays a proton donor character and the covalent bond length NH (r_1) of HNCO (H–NCO) is 1.040 Å (1.008 Å for isolated HNCO).

(1) $n = 1$. The optimized structure (Fig. 3b) presents three H-bonds, forming a quasi-planar cycle. In this configuration, HNCO is in the time proton donor to the first NH_3 and proton acceptor by its lone electron pair with the second NH_3. The H-bond (r_2) length is now 1.721 Å, indicating a strong reinforcement. Simultaneously, r_1 increases to 1.060 Å. The H-bond (r_3), between the nitrogen of HNCO and hydrogen of NH_3 is 2.405 Å, which denotes a rather weak H-bond. The bond length (r_4), between the two NH_3, is 2.076 Å. The stabilizing energy is now −67 kJ/mol, the gain between the systems (3a) and (3b) is about −21 kJ/mol. Adding extra solvent molecules reinforces r_2 (1.825–1.721 Å). One consequence is to weaken the involved covalent bond r_1 (1.040–1.060 Å) as already frequently reported [25,26].

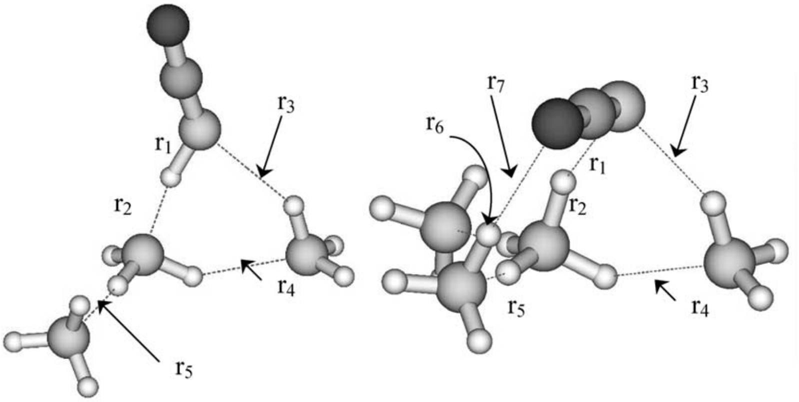
(2) $n = 2$. The new additional NH_3 presents a H-bond ($r_5 = 2.094$ Å in Fig. 3c) with the $HNCO{:}(NH_3)(NH_3)$ system. The other H-bonds are altered, (r_3) decreased to 2.366 Å and (r_4) increased to 2.169 Å. The position of the third NH_3 is out of plane and does not involve any interaction with HNCO. The stabilizing energy increases to −89 kJ/mol. The new NH_3 contributes, by hyperconjugation, to weakening r_1 down to 1.088 Å and reinforcing r_2 to 1.617 Å, without interacting with HNCO.

(3) $n = 3$. After optimization, the $HNCO{:}NH_3(NH_3)_3$ system spontaneously developed into $OCN^-{:}(NH_4^+)(NH_3)_3$ (Fig. 3d). There was formation of NH_4^+ and OCN^- ions by proton transfer from HNCO to NH_3 ($r_1 = 1.715$ Å). The different NH bonds of NH_4^+ are bonded directly to three NH_3 and OCN^- molecules via hydrogen bonding.



(a)
n=0
ΔE(BSSE) = -46.14
(r_1=1.040/r_2=1.825)

(b)
n=1
ΔE(BSSE) = -67.46
(r_1=1.060/ r_2=1.721)



(c)
n=2
ΔE(BSSE) = -89.12
(r_1=1.088/ r_2=1.617)

(d)
n=3
(r_1=1.715/ r_2=1.070)

Fig. 3. Optimized structures of HNCO:$(NH_3)(NH_3)_n$ for $n = 0$–3, with interaction energies ΔE(BSSE) given in kJ/mol. r_1 and r_2 are distances between N(1) and H(2), and between H(2) and N(3) given in Å (values in parentheses).

The isocyanate displays three H-bonds, r_1, r_3 and r_7, with 2.137, 1.715 and 2.046 Å, respectively. The lengths of the different H-bonds, r_4, r_5 and r_6, between the NH_3 and NH_4^+ are 1.952, 1.892 and 1.945 Å.

The stabilization effect of the system increases with the number of NH_3. The gain between every addition of NH_3 is about 20 kJ/mol from $n = 0$ to 2 [27]. 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 solvation contribution and the resulting system is energetically stable. These results are consistent with the calculations of Daigoku et al. [27] and Wang et al. [28]. Both found a stabilization effect of NH_4^+ with full solvation of NH bonds in a symmetry T_d for $NH_4^+(NH_3)_4$. The bond lengths of NH in NH_4^+

decreased while the H-bond distances NH...N with the NH_3 solvents increased, continuously from $NH_4^+(NH_3)$ to $NH_4^+(NH_3)_4$ [28]. In this case, the H-bond distances with all NH_3 are 1.920 Å. This is good agreement with our values 1.952, 1.892 and 1.945 Å for the system ($n = 3$), where the symmetry is broken.

Quantum calculations confirm the spontaneous character of the reaction between HNCO and NH_3 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 lone electron pair, and if this NH_3 is solvated enough. Three NH_3 molecules are at least required to induce the proton transfer.

5. Discussion and conclusion

We showed that when HNCO is co-deposited with the NH_3 (1/10) mixture, an acid–base reaction occurs between HNCO and NH_3 as soon as 10 K to produce $NH_4^+OCN^-$. The more typical vibrational bands of $NH_4^+OCN^-$, which serve in probing its identification, at 2151 and 1495 cm^{-1} are in excellent agreement with the values reported for $NH_4^+OCN^-$ induced during the photolysis of CO/NH_3 ices [29]. However, the behavior of HNCO is different when it is co-deposited with NH_3 and when it is adsorbed on NH_3 amorphous films at 10 K. In the latter case, the system is not reactive. Nevertheless, upon sample warm-up at a temperature of 90 K, $NH_4^+OCN^-$ can be formed but in a weak proportion because it is only formed at the interface of the two solid phases. The $NH_4^+OCN^-$ formation can be explained from a dynamical reconstruction of the NH_3 film. The changes observed on the NH_3 infrared spectrum at 70 K suggest a transformation from an amorphous to metastable phase [20]. This transformation is favorable to solvation of HNCO by NH_3 molecules and it follows the emergence of a reaction as confirmed by the quantum calculations.

Some other observations providing useful information on the identification of the species in the interstellar medium can be obtained from the position of the vibrational bands of OCN^-, NH_4^+ and HNCO. The more typical OCN^- (2165 cm^{-1}) and NH_4^+ (1495 cm^{-1}) IR absorptions are shifted versus those recorded by the ISO spectra of protostellar objects.

Thus, the two bands assigned to $NH_4^+OCN^-$ in the ISO spectra are generally reported at 2165 cm^{-1} (νOCN^-) and 1460 cm^{-1} (δNH_4^+) [17]. We think that these differences could be explained from the environment of $NH_4^+OCN^-$. In this study we did not consider H_2O, which is the major constituent of the interstellar grains. NH_3/H_2O ice could modify the frequency of the ions, we also consider studying the behavior of HNCO co-deposited with such a mixture. For example, the νOCN^- frequency changes from 2151 cm^{-1} in an NH_3 environment to 2170 cm^{-1} in an H_2O environment. The solid $NH_4^+OCN^-$ frequencies at $T = 160$ K are also very much altered modified compared to $NH_4^+OCN^-$ frequencies in an NH_3 environment ($T < 125$ K).

In the same way, the νNCO frequency of HNCO changes significantly according to its environment: from 2259 cm^{-1} in the HNCO/NH_3 system to 2242 cm^{-1} in the HNCO/H_2O [17] system compared with the 2252 cm^{-1} expected for HNCO solid at 10 K. We believe that the non-detection of HNCO in the interstellar grain, nevertheless produced in laboratory during the photolysis of CO/NH_3 or CO/NH_3/H_2O mixtures [5], can be due both to its great reactivity to NH_3 and to its fast photodecomposition [30].

Further study concerning HNCO adsorbed on solid NH_3 and HNCO in NH_3/H_2O ices must be envisaged.

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