J. Phys. Chem. A **2005,** *109,* 603−608

Carbodiimide Production from Cyanamide by UV Irradiation and Thermal Reaction on Amorphous Water Ice

Fabrice Duvernay, Thierry Chiavassa,* Fabien Borget, and Jean-Pierre Aycard

Physique des Interactions Ioniques et Moléculaires, UMR 6633, Université de Provence et CNRS,
Centre de St Jérôme, case 252, 13397 Marseille Cedex 20, France

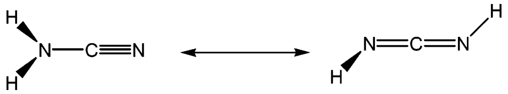
Received: September 9, 2004; In Final Form: October 27, 2004

Cyanamide (NH_2CN), an interstellar molecule, is a relevant molecule in prebiotic chemistry, because it can be converted into urea in liquid water. Carbodiimide (HNCNH), the most stable cyanamide isomer, is able to assemble amino acids into peptides. In this work, using FTIR spectroscopy, we show that carbodiimide can be formed from cyanamide at low temperature (10 K), by a photochemical process in argon matrix, in water matrix, or in solid film. We also report experimental evidence about the carbodiimide formation when cyanamide is condensed at low temperature (50−140 K) on an amorphous water ice surface, or when it is trapped in the water ice. The water ice acts as a catalyst. This isomerization reaction occurs at low temperature ($T < 100$ K), which agrees with those expected in the interstellar clouds composed of dust grains in which water is the most predominant compound. Finally, the hydrolysis reaction of cyanamide or carbodiimide leading to urea or isourea formation is not observed under our experimental conditions.

1. Introduction

The chemistry of interstellar clouds consists of thermal, photochemical, and cosmic-ray induced reactions taking place in the gas phase, at the surface, or in the dust grain bulk.[1] The surface of the cold dust grains (10−100 K) is mainly composed of amorphous water ice[2] and some other constituents such as NH_3, CO, and CO_2.[2] These icy mantles surround a silicate core.[2] Inside molecular clouds, UV radiation can induce chemical evolution of the grain surface, forming new species.[3] The icy mantle can play the role of a catalyst in reactions at low temperature ($T < 100$ K). For instance, H_2, the most predominant molecule in the interstellar medium (ISM), is only formed on the dust grain surface.[4] The new species formed in interstellar grains can sublimate in the hot region of interstellar clouds and enrich the gas phase in new organic species.[5] Cyanamide (NH_2-CN) has been detected in 1975 in the gas phase by spectral emissions coming from Sgr B2 molecular cloud at 80 504.5 and 100 629.5 MHz assigned to the $4_{13}-3_{12}$ and $5_{14}-4_{13}$ microwave transitions.[6] Actually, the origin of cyanamide in the interstellar medium is not well understood. Recent work has shown that cyanamide can be formed from UV irradiation of hexamethylenetetramine (HMT) in water matrix.[7] Cyanamide formation is also possible under the early Earth conditions from UV irradiation of diluted ammonium cyanide solution at room temperature.[8] Cyanamide is a relevant prebiotic molecule, which can be converted into urea (NH_2CONH_2) in liquid water.[9] In the gas phase, cyanamide is in prototropic equilibrium with carbodiimide[10] (HNCNH) ($P_{HNCNH}/P_{NH_2CN} = 1/115$ at 373 K), which is a condensing agent able to induce the formation of peptides from amino acids.[11] The thermal-induced isomerization observed in the gas phase can take place only through a bimolecular mechanism.[18] Considering the temperature range ($T < 100$ K) and the low density (10^3 parts·cm^{-3}) existing in interstellar clouds, the thermal-induced-isomerization reaction cannot take place in the gas phase. To the best of our knowledge, while the vibrational and spectral properties of cyanamide are well-known,[12−17] this is not the case for carbodiimide. It was isolated for the first time by the low-temperature matrix technique by King and Strope[17] in 1971. In this study, they have reported a partial infrared spectrum of carbodiimide in argon matrix.

SCHEME 1: Cyanamide−Carbodiimide Isomerization



A recent theoretical study suggests that water molecules can significantly lower the activation energy of the isomerization reaction cyanamide ↔ carbodiimide[18] (Scheme 1). The hydrolysis of carbodiimide leading to isourea, a urea tautomer, has also been discussed.[18,19]

In this work we show that carbodiimide can be formed from cyanamide at low temperature (10 K) by photoinduced reaction in argon or water matrix or in solid film. We also report experimental evidence about the carbodiimide formation when cyanamide is condensed at low temperature (80 K) on an amorphous water ice surface[20] or when it is trapped in water ice bulk. The goal of this work is to understand the interstellar behavior of cyanamide and the eventual formation of urea, which was recently assumed to be present in the interstellar medium (ISM).[21]

2. Experimental Details

The cyanamide (Aldrich, 99% purity) vapor pressure at room temperature is low;[10] thus this compound was sublimated (45−48 °C) in a glass tube connected to the cryostat and then carried by argon (Linde, 99.99% purity) toward a gold plated mirror cooled at 10 K at a rate of 0.7 mmol/min to obtain an argon matrix. Under these conditions, we cannot determine exactly the cyanamide concentration in argon; we can only state that

---

* Corresponding author. Telephone: +33 491-288-580. Fax: +33 491-636-510. E-mail: Thierry.chiavassa@up.univ-mrs.fr.

10.1021/jp0459256 CCC: $30.25

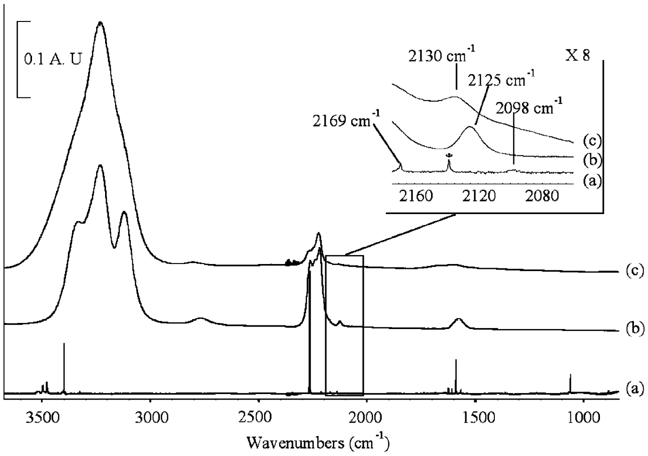


Figure 1. FTIR spectra of cyanamide deposited and recorded at 10 K (a) in Ar matrix, (b) in solid film, and (c) in water environment. *, CO impurity.

TABLE 1: Cyanamide Infrared Frequencies (cm^{-1}) in Different Environments Deposited and Recorded at 10 K[a]

assignment	Ar matrix (cm^{-1})	solid film (cm^{-1})	water matrix (cm^{-1})
$\nu_a(NH_2)$	3486	3342-3235	
$\nu_s(NH_2)$	3400		
$\nu(C{\equiv}N)$	2264	2265−2239−2220	2268−2244−2224
$\delta(NH_2)$	1589	1580	1590
$\nu(C-N)$	1060		
$\tau(NH_2)$	728		

[a] δ, bending; ν, stretching; τ, torsion.

TABLE 2: Carbodiimide Frequencies (cm^{-1}) in Different Environments at 10 K[a]

assignment	Ar matrix		solid film	water matrix
$\nu(NH)$	3425[b]			
$\tau(NH) + \nu_s(NCN)$	2169			
$\nu_a(NCN)$	2098	trapped in cyanamide	2125	2130
		aggregate	2095	2100
$\tau(NH)$	886			

[a] ν, stretching; τ, torsion. [b] Assigned from photolysis of cyanamide in Ar matrix experiment.

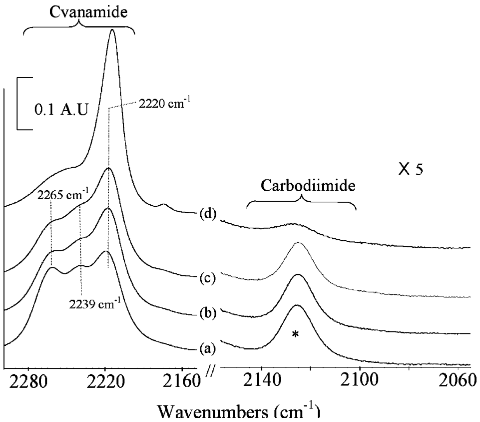


Figure 2. FTIR spectra of pure cyanamide deposited at 10 K and then recorded at (a) 10, (b) 80, (c) 120, and (d) 140 K. *, carbodiimide trapped in cyanamide (2125 cm^{-1}) coming from gas phase.

we work with a large excess of argon in the mixture (around 1/500). During the deposition, the cryostat is kept under a constant pressure of 10^{-7} mbar. To study the pure solid, cyanamide is deposited directly on the cold mirror without carrier gas at low temperature (10−80 K), and then the sample is warmed at a 0.5 K/min heating rate to study the solid phase change.

Doubly distilled water vapor is deposited with argon on the gold plated mirror at 80 K ($H_2O/Ar = 1/50$) at a rate of 4 mmol/min; these conditions are known to produce amorphous ice.[22] The film is then cooled at the temperature of deposition chosen for cyanamide. Cyanamide is carried by argon (Linde, 99.99% purity) or neon (Air Liquide, 99.99% purity) to prevent formation of aggregates on the water ice surface. The carrier gases are selected depending on the temperature of water ice film: neon for 50 K[23] and argon for 70 and 80 K.[23] The mixtures were deposited at a rate of 7×10^{-1} mmol/min. VUV irradiation is performed using a microwave discharge hydrogen flow lamp (Opthos instruments) mounted directly on the sample chamber (60 min of irradiation corresponds to about 10^6 years in the molecular clouds[24]). This radiation is transmitted to the substrate through a SiO_2 window in the range up to 160 nm. The infrared spectra of the samples were recorded in transmission-reflection mode between 4000 and 600 cm^{-1} with a Nicolet Magna 750 FTIR spectrometer equipped with a liquid N_2 cooled detector, a germanium coated KBr beam splitter, and a globar source. One hundred interferograms were recorded, and the resolution was set to 0.12 cm^{-1} in the case of rare gas matrix experiments and 1 cm^{-1} in the case of solid experiments.

3. Results and Discussion

3.a. Infrared Spectra of NH_2CN and HNCNH in Different Environments. The infrared spectrum of NH_2CN in Ar matrix (Figure 1a) recorded between 4000 and 600 cm^{-1} at 10 K (Table 1) is in good agreement with that previously reported.[17] The most intense band of NH_2CN monomer trapped in argon matrix is the C≡N stretching mode located at 2264 cm^{-1}. The multiple bands of antisymmetric NH stretching mode around 3480 cm^{-1} are due to multimer interactions and different matrix sites.[17] The symmetric NH mode at 3400 cm^{-1} is characterized by a narrow and strong band. The other modes observed in argon matrix are NH_2 bending, C−N stretching, and NH_2 twisting modes located at 1589, 1060, and 728 cm^{-1}, respectively. Weak bands are also observed at 883, 2098, and 2169 cm^{-1}, which are in agreement with those expected for carbodiimide[17] trapped in argon matrix (Table 2). These modes have been assigned to the NH torsional mode, NCN antisymmetric stretching mode, and combination between the NH torsional and NCN symmetric stretching modes, respectively. The carbodiimide formation results from cyanamide isomerization, occurring by a bimolecular process[18] in the gas mixture ($T > 20$ °C) before it was deposited on the gold plated mirror. The amount of carbodiimide is less than 1%.[10]

The spectrum of solid NH_2CN (Figure 1b) deposited at 10 K shows broad and intense bands related to the NH and CN stretching modes, which are located from 3350 to 3200 cm^{-1} and from 2270 to 2210 cm^{-1} (Figure 2a). These strongly downshifted frequencies with respect to the monomer values are due to the hydrogen bonding interactions between NH_2CN molecules. The $\nu(C-N)$ mode observed at 1060 cm^{-1} in argon matrix cannot be detected in the IR spectrum of the solid phase, but it is observed at 1145 cm^{-1} in the Raman spectrum.[16] Moreover, we observe the presence of carbodiimide isolated and trapped in an environment of solid NH_2CN. Then a band at 2125 cm^{-1} can be assigned to the antisymmetric NCN stretching mode, which is very characteristic for many carbodiimide derivatives.[25] By raising the temperature from 10 to 150 K (Figure 2), a change in the infrared spectrum is observed above 50 K. It can be understood in terms of a phase transition

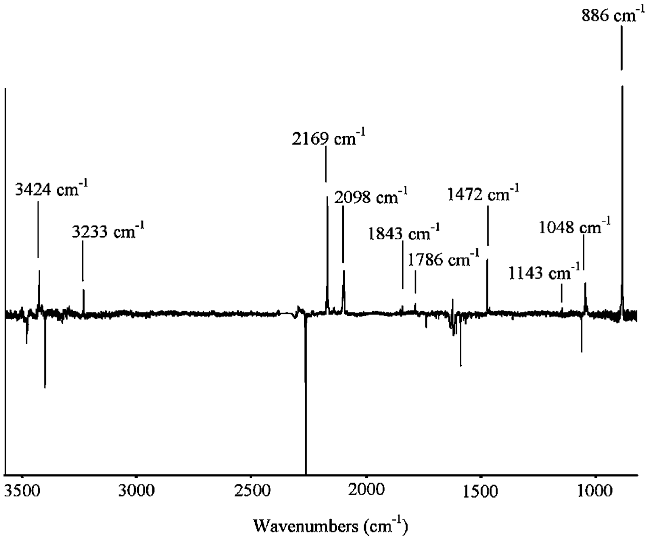


Figure 3. Infrared difference spectrum between the spectrum of cyanamide in Ar matrix deposited and recorded at 10 K and the spectrum after 120 min of VUV irradiation ($\lambda > 160$ nm) recorded at 10 K. Negative peaks, cyanamide; positive peaks, species formed during VUV irradiation.

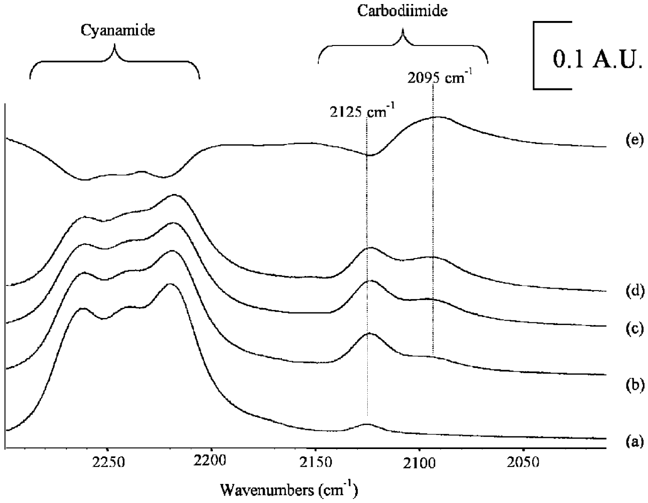


Figure 4. Spectra of solid film of cyanamide deposited and recorded at 10 K (a) before irradiation, (b) after 90 min of VUV irradiation, (c) after 240 min of VUV irradiation, and (d) after 420 min of VUV irradiation. (e) Spectrum resulting from the difference (d) − (c).

from an amorphous to a crystalline solid form of NH$_2$CN. In particular, in the region related to the C≡N stretching mode, the 2220 cm^{-1} feature becomes thinner and increases while the other components (2265, 2239 cm^{-1}) decrease. During this warmup, it is noticeable that the integrated absorption area of the C≡N stretching mode does not change (i.e., the amount of cyanamide does not change). The vibrational band at 2125 cm^{-1}, due to carbodiimide, decreases and disappears around 140 K. This disappearance of the carbodiimide feature between 130 and 140 K cannot be due to the carbodiimide−cyanamide isomerization; otherwise we should observe an increase of the amount of cyanamide. It could be rather due to carbodiimide sublimation, which occurs during the crystallization of cyanamide.

Trapped and diluted in a water ice film, the spectrum of the sample recorded at 10 K (Figure 1c) shows that the cyanamide ν(NH) modes are overlapped by the ν(OH) absorption band of water. Only the ν(NCN) mode of carbodiimide (generating in the gas phase) is observable (Figure 1c), slightly upshifted with respect to the observed values recorded in the pure solid (Tables 1 and 2). The band related to the ν(CN) mode of cyanamide (Figure 1c) shows a different behavior than in the pure solid (Figure 1b). This band has three components (Table 1), as in the pure solid spectrum, but the intensity of the third component, located at 2224 cm^{-1} (instead of at 2220 cm^{-1} in the pure solid), is more intense. This increase could be the result of a cyanamide−water interaction. For the study of the cyanamide reactivity adsorbed or trapped in water bulk, we will consider only the spectral range 2300−2000 cm^{-1}.

3.b. UV Irradiation of NH$_2$CN. The photolysis of the NH$_2$CN in Ar matrix, using a hydrogen lamp ($\lambda > 160$ nm), leads to the formation of carbodiimide.[26] Some other new species[26] are characterized by the emergence of new bands, which appear positive on the infrared difference spectrum (spectrum after 120 min minus that before irradiation) (Figure 3). During this process, because cyanamide is broken down, its bands decrease and appear negative, whereas those of carbodiimide increase and appear positive. A band at 3424 cm^{-1} not assigned by King et al.[17] in their vibrational analysis of HNCNH in argon matrix can be unambiguously assigned to the NH stretching mode from its correlated evolution with the other bands previously assigned to carbodiimide (Table 2).

This type of isomerization induced by UV irradiation has already been reported for HCN,[27] HC$_3$N,[28] and H$_3$CCC[29] producing CNH, C$_3$NH, and H$_2$CCCH, respectively.

Among the new species formed, we can identify several radicals previously observed such as HNCN,[30] HCNN,[26] and NCN,[31] characterized by the sets of bands at 1843, 1143 cm^{-1}, at 3233, 1786, 860 cm^{-1}, and at 1472 cm^{-1}, respectively. NH bond cleavage and the diffusion of H atoms into the argon matrix lead to the formation of HNCN and NCN radicals. After 180 min of irradiation, we observe a photostationary equilibrium between the cyanamide and the carbodiimide. This result indicates that carbodiimide may undergo a secondary photochemical process leading to the formation of cyanamide.

VUV photolysis at 10 K of cyanamide solid film (Figure 4) induces also the carbodiimide formation. The band located at 2125 cm^{-1}, related to carbodiimide monomer in cyanamide environment (coming from the gas phase) grows (Figure 4b) at the beginning of the UV irradiation and then decreases when the amount of carbodiimide becomes predominant in the sample (Figure 4e). At the same time we observe another band located at 2095 cm^{-1} related to carbodiimide aggregates. During UV irradiation the amount of carbodiimide increases and promotes carbodiimide aggregate formation (2095 cm^{-1}) while the contribution of monomer species (2125 cm^{-1}) decreases. Bernstein et al.[7] have previously assigned a band at 2098.8 cm^{-1} to carbodiimide in solid film environment yielded by photochemical decomposition of HMT.[7]

In water matrix (Figure 5), the irradiation process leads again to carbodiimide formation in two different environments characterized by two bands located at 2130 and 2100 cm^{-1} (Table 2). As for the cyanamide in water environment, these two bands are upshifted compared to the values observed in solid film (2130 cm^{-1} instead of 2125 cm^{-1} and 2100 cm^{-1} instead of 2095 cm^{-1}). The former is related to carbodiimide isolated in water−cyanamide environment, while the latter is linked to carbodiimide aggregates in water−cyanamide environment.

It is noticeable that the cyanamide−water component at 2224 cm^{-1} is more affected by UV irradiation than the two other components located at 2268 and 2244 cm^{-1} (Figure 5e). This is observable in the difference spectrum, where the 2224 cm^{-1}

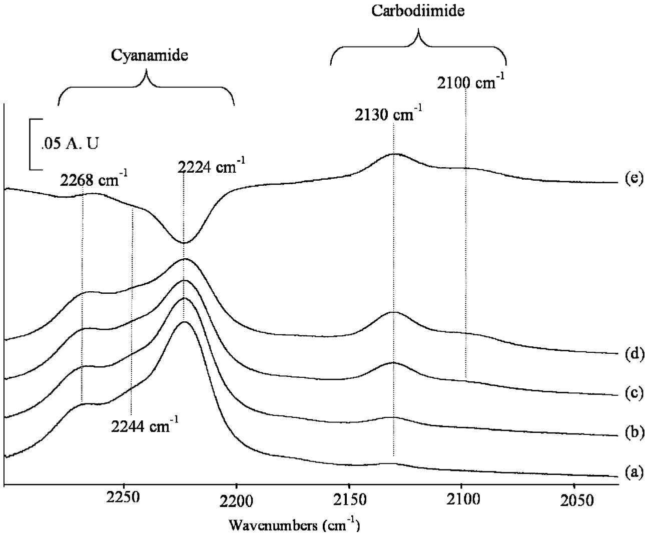


Figure 5. FTIR spectra of cyanamide in water matrix deposited and recorded at 10 K (a) after deposition, (b) after 30 min of VUV irradiation, (c) after 120 min of VUV irradiation, and (d) after 300 min of VUV irradiation. (e) Spectrum resulting from the difference (d) − (a).

band decreases more than the two other bands located at 2268 and 2244 cm^{-1}. This result indicates that water molecules play a role in the photoisomerization process. The hydrogen bonds between cyanamide and water molecules could help the NH bond cleavage of cyanamide and promote carbodiimide formation. The carbodiimide aggregate formation (2100 cm^{-1}) in water matrix is less efficient than in pure solid film of cyanamide (Figures 4d and 5d). In water matrix, cyanamide molecules are isolated, and then the aggregate formation becomes unfavorable. The vibrational band positions of carbodiimide observed in different environments can help in understanding the thermal isomerization process.

3.c. Thermal Process. The isomerization of cyanamide into carbodiimide by a thermal process occurs in the gas phase at room temperature. Theoretically, it was predicted that this reaction could be favored by surrounding water molecules.[18] Indeed when cyanamide was surrounded by one to five water molecules, activation energies were predicted to vary from 36.3 to 8.6 kcal·mol^{-1}, respectively. The strong lowering of the barrier indicates that this reaction can occur at low temperature in a water environment. We give, in this part, experimental evidence supporting these theoretical arguments, and we show the catalytic role of the water ice in the isomerization process of cyanamide into carbodiimide at low temperature. We have then studied the thermally induced production of cyanamide species adsorbed/mixed on/in water ice.

The IR spectrum of amorphous water ice film shown in Figure 6a can be divided into three regions.[32,33] In the highest wavenumber range, the OH stretching modes of ice bulk appear as a broad band centered at 3250 cm^{-1}, 500 cm^{-1} downshifted from the stretching modes of free water molecules. In the region near 1600 cm^{-1}, the band observed at 1640 cm^{-1} is assigned to the OH bending modes. In the lowest wavenumber region of the spectrum (ca. 800 cm^{-1}), we observed the libration modes of water molecules in the bulk. The most striking feature is a narrow and weak peak at 3695 cm^{-1}. This band is due to the dangling stretching mode of the OH groups,[34] which is a potential site for adsorption of proton acceptor molecules.[35,36] In the case of proton donor molecules, lone pair electrons on an oxygen atom, called the dangling O site, can provide another adsorption site.[37] Unfortunately, the band associated with the dangling O site is too weak and overlapped by the ν(OH) mode of the bulk to be observed under our experimental conditions.

We initially study the thermal behavior of isolated cyanamide deposited over an amorphous film of water ice. Cyanamide was deposited at 50 K with neon (Figure 6 b), and at 70 (Figure 6c) and 80 K (Figure 6d) with argon, over an amorphous ice. Neon or argon is added to minimize the formation of cyanamide aggregates in the gas phase. As shown by Tordini et al.,[18] NH_2-CN has both an acid and a basic character for water molecules. This acid character is even more strengthened when the number of water molecules is increased (from one to five). Thus, the dangling OH and the dangling O could be affected by the NH_2-CN adsorbed on the water ice surface. However, when the cyanamide is deposited below 70 K with carrier gas, it has no effect on the dangling OH (Figure 6). This is probably due to the cyanamide aggregate, which is formed on the water ice

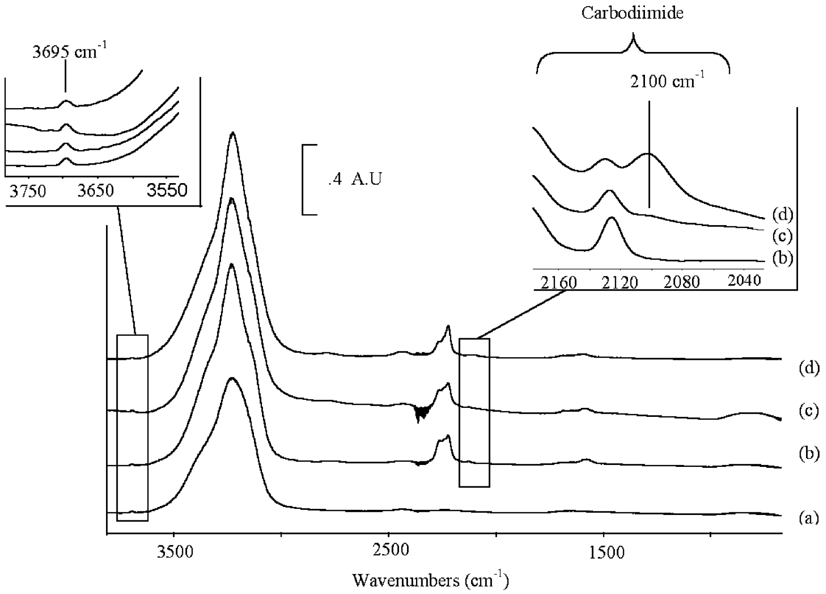


Figure 6. FTIR spectrum of (a) amorphous water ice film deposited and recorded at 80 K, (b) cyanamide/Ne deposited and recorded at 50 K on an amorphous water ice film, (c) cyanamide/Ar deposited and recorded at 70 K on an amorphous water ice film, and (d) cyanamide/Ar deposited and recorded at 80 K on an amorphous water ice film.

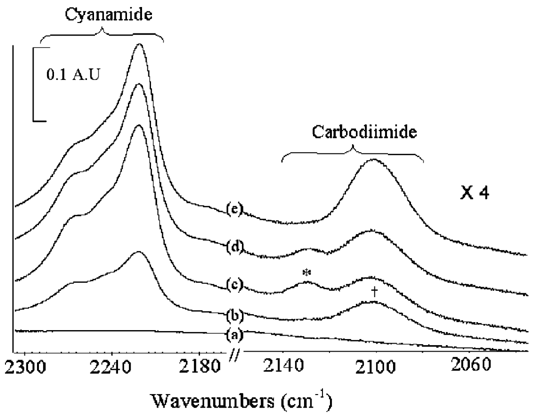


Figure 7. FTIR spectra of (a) water ice film at 80 K, (b) cyanamide/Ar (10^{-2} mol) deposited at 80 K on the water ice film, (c) cyanamide/Ar (5×10^{-2} mol) deposited at 80 K on the water ice film, (d) cyanamide/Ar (5×10^{-2} mol) deposited at 110 K on the water ice film, and (e) cyanamide/Ar (5×10^{-2} mol) deposited at 140 K on the water ice film. †, carbodiimide yield at the water ice surface (2100 cm^{-1}); *, carbodiimide trapped in cyanamide (2125 cm^{-1}) coming from gas phase.

surface after the sublimation of the carrier gas. As we have already reported in a previous study about the adsorption of HNCO on water ice,[38] hydrogen bonding interactions existing between the adsorbate molecules (NH_2CN) can contribute to preventing the dangling OH from being affected. Indeed, these hydrogen bonding interactions induce a distance increase between the nitrogen of cyanamide and the dangling OH and thus attenuate the interaction between them.[38]

When cyanamide is deposited at 80 K with argon, we observe the appearance of a new band located at 2100 cm^{-1} (Figure 6d); it increases until the surface is completely covered (Figure 7b). This band is not observed for deposition temperature lower than 70 K (Figure 6c). The presence of the band located at 2100 cm^{-1} shows that carbodiimide has been formed from an ice-catalyzed cyanamide isomerization. It also appears that the amount of carbodiimide yielded on the water ice surface is greater than for the carbodiimide coming from the equilibrium in the gas phase (Figure 7c). Thus, the water ice surface contributes also to improving the relative stability of carbodiimide. The position of this band (2100 cm^{-1}) is similar to that observed for carbodiimide aggregates in water environment. This result lets us suppose that carbodiimide molecules are in interaction between them on the water ice surface. The temperature threshold for the formation of carbodiimide on water ice surface is close to 70 K. After prolonged cyanamide deposition, we still observe the 2125 cm^{-1} feature related to carbodiimide trapped in cyanamide and coming from the isomerization reaction in the gas phase (Figure 7c).

Now when cyanamide is deposited without a rare gas, we noticed that it is less “reactive” (Figure 8b). We estimated that the amount of carbodiimide yielded on the water ice surface is 8 times higher when cyanamide is added with argon (Figure 8c) than without argon (Figure 8b). Indeed, cyanamide should be less reactive when it is associated by hydrogen bonding interaction with other cyanamide molecules. Moreover, maybe cyanamide aggregates could not cover the water ice surface completely, and the size of the aggregate avoids a full coverage inside the pores. The same result is observed when cyanamide is co-deposited with H_2O at 80 K (Figure 8a). The FTIR spectrum is similar to the one obtained for cyanamide aggregates in water environment. All these results confirm that isolated cyanamide is more reactive for water molecules than cyanamide aggregates (Figure 8).

Warming the sample deposited with argon from 80 to 140 K (Figure 7d,e) induces a water ice and cyanamide structure change and an intensity increase of the band at 2100 cm^{-1}. The formation of carbodiimide along with the rise of temperature should be due to a higher mobility of NH_2CN and H_2O molecules. At the same time, the carbodiimide behavior trapped in cyanamide is similar to that observed in the cyanamide film (Figure 7d,e). The cyanamide/carbodiimide ratio on the water ice surface is estimated to be close to 4% at 80 K and 13% at 140 K from the integrated area measurement of their respective bands.

These experimental results are in good agreement with the DFT and MP2 calculations performed on the isomerization of cyanamide into carbodiimide in the presence of water molecules.[18] According to these theoretical results, the reaction is strongly promoted by water molecules. Carbodiimide formation process via an ionic intermediate ($H_3O^+HNCN^-$) is predicted

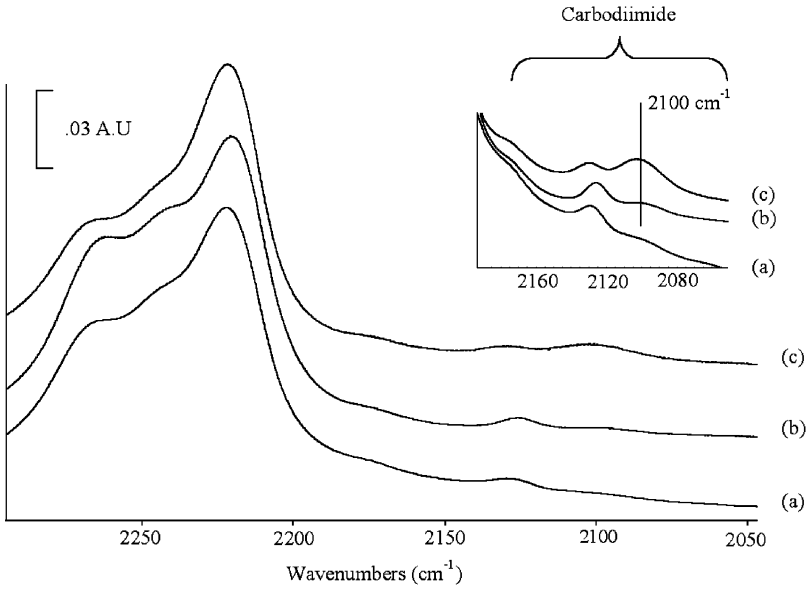


Figure 8. FTIR spectra in the ν(CN) mode of cyanamide and ν(NCN) mode of carbodiimide region of (a) cyanamide co-deposited with H_2O at 80 K, (b) cyanamide aggregates deposited on the water ice film at 80 K, and (c) cyanamide/Ar (5×10^{-2} mol) deposited at 80 K on the water ice film.

to be less stable than carbodiimide, about 15 kJ·mol^{-1} in an environment of five water molecules. Within the accuracy of our experiment, no trace of these species could be detected. According to the same calculations, the hydrolysis of carbodiimide leading to isourea is both thermodynamically and kinetically favorable in comparison with the hydrolysis of cyanamide. Thereby carbodiimide can be considered as a suitable stable intermediate in the hydrolysis of cyanamide. However, urea or isourea was not detected during all the thermal process, showing that the hydrolysis of cyanamide or carbodiimide is unfavorable in a solid water environment. This result indicates that urea formation from cyanamide or carbodiimide is unlikely in the interstellar medium following this reaction pathway.

4. Conclusion

The aim of this work was the isomerization of cyanamide into carbodiimide at low temperature to understand the interstellar behavior of cyanamide. We showed that carbodiimide formation takes place by both photochemically and thermally induced reaction from cyanamide at low temperature. The photochemical results obtained from matrix experiments let us suggest that an NH bond cleavage and the H atom migration are the origin of the carbodiimide formation at low temperature. Adsorption experiments of cyanamide on water ice surface show that cyanamide can be converted into carbodiimide at low temperature ($T > 70$ K) through an isomerization reaction, promoted by the water molecules which are able to mediate the proton transfer, playing the role of a catalyst. This observed reaction is in good agreement with previous ab initio and DFT calculations.[18] These authors also conclude that the hydrolysis of carbodiimide leading to isourea is both thermodynamically and kinetically favorable with respect to the cyanamide hydrolysis. Experimentally, we showed that the hydrolysis reaction of cyanamide or carbodiimide did not take place below 180 K in a water solid phase, and consequently under these conditions urea cannot be formed in ISM from these pathways.

These results have important implications for interstellar chemistry because they indicate that carbodiimide formation from cyanamide (which has been detected in the ISM) is possible by both thermal and photochemical processes in dust grains or in comets where water is the most predominant species. A vibrational band at 2100 cm^{-1}, related to carbodiimide, should be searched for in IR spectra obtained from interstellar sources.

Acknowledgment. The “Programme National de Physique et Chimie du Milieu Interstellaire” is gratefully acknowledged for the financial support of this work.

References and Notes

(1) Hartquist, T. W.; Williams, D. A. *The chemically controlled cosmos*; Cambridge University Press: New York, 1995.

(2) Greenberg, J. M. *Surf. Sci.* **2002**, *500*, 793.

(3) Gerakines, P. A.; Moore, M. H.; Hudson, R. L. *Icarus* **2004**, *170*, 202.

(4) Schmitt, B. *Molecules and grain in space*; AIP Press:Cambridge: New York, 1994; p 735.

(5) Hudson, R. L.; Moore, M. H. *Astrophys. J.* **2003**, *586*, 107.

(6) Turner, B. E.; Kislyakov, A. G.; Liszt, H. S.; Kaifu, N. *Astrophys. J.* **1975**, *201*, 149.

(7) Bernstein, M. P.; Sandford, S. A.; Allamandola, L. J.; Chang S. *J. Phys. Chem.* **1994**, *98*, 12206.

(8) Schimpl, A.; Lemmon, A.; Calvin, M. *Science* **1965**, *147*, 149.

(9) Kilpatrick, M. L. *J. Am. Chem. Soc.* **1947**, *69*, 40.

(10) Jabs, W.; Winnewisser, M.; Belov, S. P.; Lewen, F.; Maiwald, F.; Winnewisser, G. *Mol. Phys.* **1999**, *97*, 213.

(11) Hartmann, J.; Nawroth, T.; Dose, K. *Origins Life* **1984**, *14*, 213.

(12) Topping, M. G.; Lide, R. *J. Mol. Spectrosc.* **1962**, *8*, 153.

(13) Attanasio, A.; Bauder, A.; Günthard, Hs. H. *Chem. Phys.* **1974**, *6*, 373.

(14) Wagner, D.; Wagner, L. *J. Chem. Phys.* **1960**, *64*, 1480.

(15) Flecher, H.; Brown, B. *J. Chem. Phys.* **1963**, *39*, 2478.

(16) During, R.; Walker, M.; Baglin, G. *J. Chem. Phys.* **1968**, *48*, 4675.

(17) King, S. T.; Strope, J. H. *J. Chem. Phys.* **1971**, *54*, 1289.

(18) Tordini, F.; Bencini, A.; Bruschi, M.; De Gioia, L.; Zampella, G.; Fantucci, P. *J. Phys. Chem. A* **2003**, *107*, 1188.

(19) Lewis, M.; Glaser, R. *J. Am. Chem. Soc.* **1998**, *120*, 8541.

(20) Duvernay, F.; Chiavassa, T.; Borget, F.; Aycard, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 7772.

(21) Raunier, S.; Chiavassa, T.; Duvernay, F.; Borget, F.; Aycard, J. P.; Dartois, E.; d’Hendecourt, L. *Astron. Astrophys.* **2004**, *416*, 165.

(22) Mayer, E.; Pletzer, R. *Nature* **1986**, *319*, 298.

(23) Hallam, H. E. In *Vibrational spcetroscopy of trapped species*; Hallam, H. E., Ed.; Wiley: London, 1973; p 39.

(24) Greenberg, J. *Surf. Sci.* **2002**, *500*, 793.

(25) Meakins, G. D.; Moss, R. J. *J. Chem. Soc.* **1957**, 993.

(26) Maier, G.; Eckert, J.; Bothur, A.; Reisenauer, H. P.; Schmidt, C. *Liebigs Ann.* **1996**, 1041.

(27) Milligan, D.; Jacox, M. E. *J. Chem. Phys.* **1967**, *47*, 278.

(28) Guennoun, Z.; Couturier-Tamburelli, I.; Pietri, N.; Aycard, J. P. *Chem. Phys. Lett.* **2003**, *368*, 574.

(29) Jacox, M. E.; Milligan, D. E. *Chem. Phys.* **1974**, *4*, 45.

(30) Ogilvie, J. F. *Can. J. Chem.* **1968**, *46*, 2472.

(31) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1966**, *45*, 1387.

(32) Rowland, B.; Devlin, J. P. *J. Chem. Phys.* **1991**, *94*, 812.

(33) Buch, V.; Devlin, J. P. *J. Chem. Phys.* **1999**, *110*, 3437.

(34) Buch, V.; Devlin, J. P. *J. Chem. Phys.* **1991**, *94*, 4091.

(35) Couturier-Tamburelli, I.; Chiavassa, T.; Pourcin, J. *J. Phys. Chem. B* **1999**, *103*, 173.

(36) Borget, F.; Chiavassa, T.; Allouche, A.; Aycard, J. P. *J. Phys. Chem. B* **2001**, *105*, 449.

(37) Manca, C.; Martin, C.; Roubin, P. *J. Phys. Chem. B* **2003**, *107*, 8929.

(38) Raunier, S.; Chiavassa, T.; Allouche, A. Marinelli, F.; Aycard, J. P. *Chem. Phys.* **2003**, *288*, 197.