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Experimental investigation of nitrile formation from VUV photochemistry of interstellar ices analogs: acetonitrile and amino acetonitrile

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ABSTRACT

Context. The study of the chemical reactivity in interstellar ices in astrophysical environments is an important tool for understanding the origin of the organic matter in molecular clouds, in protoplanetary disks, and possibly, as a final destination, in our solar system. The laboratory simulations of the reactivity in ice analogs provide important information for understanding the reactivity in these environments. Here, we used these experimental simulations to trace some formation pathways of two nitriles, acetonitrile and amino acetonitrile, which are two potential precursors of amino acids in astrophysical environments.
Aims. The purpose of this work is to present the first experimental approach for the formation of acetonitrile and amino acetonitrile in interstellar-like conditions.
Methods. We use Fourier Transform InfraRed (FTIR) spectroscopy and mass spectrometry to study the formation at 20 K of acetonitrile CH_3CN from VUV irradiation of ethylamine and of amino acetonitrile NH_2CH_2CN from VUV irradiation of ammonia: acetonitrile mixture. Isotopic substitutions are used to confirm identifications.
Results. We demonstrate that acetonitrile can be formed at 20 K from the VUV irradiation of ethylamine with a yield of 4%. Furthermore, in presence of ammonia, at 20 K and under VUV irradiation, the acetonitrile can lead to the amino acetonitrile formation. These results suggest that acetonitrile and amino acetonitrile can be formed in astrophysical environments that are submitted to VUV irradiations.

Key words. astrochemistry – ISM: molecules – methods: laboratory

1. Introduction

The evolution of labile and functionalized organic matter starts in dense molecular clouds. These cold (10–50 K) clouds are composed of interstellar grains that show large amounts of dirty ices in astronomical infrared vibrational spectra, which are mainly composed of water but also of other molecules such as CO, CO_2, CH_3OH, NH_3, etc. (Dartois 2005). During the grain evolution, this material will undergo numerous chemical modifications caused by ionic and VUV irradiations as well as thermal effects. In the laboratory, where templates can be studied more precisely, this evolution ultimately leads to the formation of a complex semi-refractory organic residue that may well exist in molecular clouds and in the early phases of planetary systems formation. Areas of the initial molecular cloud collapse to form in proto-stars, which evolve into solar nebulae that potentially lead to a planetary system like ours. During this evolution, interstellar grains agglomerate and lead to small objects such as comets or asteroids that include organic matter, some of which may then have been preserved from their original InterStellar Medium (ISM) state. Later on, these small bodies may serve as reservoirs of organic material for the development of a prebiotic chemistry at the surface of telluric planets. Thereby, the understanding of the constitution and of the molecular evolution of interstellar matter provides clues about the organic matter that has been delivered onto the primitive Earth or onto any telluric planet. In this contribution, we experimentally investigate the formation of several nitrile derivatives in environments relevant to interstellar ices or comets. Nitriles are compounds of interest in astrochemistry because they are easily detected in the gas phase in interstellar and planetary media (Belloche et al. 2008; Olmi et al. 1993; Remijan et al. 2004; Whittet et al. 2001). Nitrile derivatives are considered as potential amino acid precursors in astrophysical environments (Bernstein et al. 2002; Elsila et al. 2007; Hudson et al. 2008). However, amino acids have not been detected in the ISM, which may support experimental results showing that nitriles are more stable under VUV irradiation than their amino acids homologs (Bernstein et al. 2004). In addition, amino acid formation from nitriles requires an acid hydrolysis step that is not possible in interstellar grains (Rimola et al. 2010). Thus, their relevance as biomolecule precursors in prebiotic chemistry have very probably been important after their delivery onto the primitive Earth through an early bombardment by comets or asteroids (Oro 1961). We therefore focused our investigation on the smallest alkyl nitriles detected in astrophysical environments, acetonitrile and amino acetonitrile. Acetonitrile

(CH$_3$CN) was detected in comets (Huebner et al. 1974; Snyder & Buhl 1971), Titan's atmosphere (Lara et al. 1996), in hot cores (Belloche et al. 2009; Remijan et al. 2004) and in protostellar objects (Codella et al. 2009). Experiments simulating interstellar ices have suggested that in some conditions, acetonitrile could be considered as an amino acid precursor (Hudson et al. 2008). Indeed, when a refractory residue that comes from an irradiated ice mixture of acetonitrile and water is hydrolysed under acidic conditions, several amino acids are detected. However, acetonitrile has not been detected in the solid phase of the interstellar medium and its formation pathway is not yet explained. Experiments suggest that acetonitrile could be formed in the ISM from the photochemistry of acetamide, which is detected in hot cores (Hollis et al. 2006), and whose photodegradation leads to acetonitrile and water in the gas or solid phases (Duvernay et al. 2007; Spall & Steaciel 1957).

Amino acetonitrile (NH$_2$CH$_2$CN) has been observed with radio astronomy in the hot core Sgr B2(N) (Belloche et al. 2008), but not in the solid phase. It is considered as a potential glycine precursor through the Strecker reaction in extraterrestrial objects such as in meteorites and comets (Bernstein et al. 2002; Elsila et al. 2007; Elsila et al. 2009; Koch et al. 2008). Only theoretical studies were done on the formation of amino acetonitrile. Some authors have proposed that it could be formed at the surface of interstellar dust grains or in the gas phase from methanimine and hydrogen cyanide or hydrogen isocyanide in a water environment (Basiuk et al. 2002a,b; Koch et al. 2008; Woon 2002; Xu & Wang 2007). The purpose of this work is to present the first experimental approach for the formation of acetonitrile and amino acetonitrile in interstellar-ice-like conditions. We test here the possibility to form acetonitrile from one of the simplest amines, ethylamine (C$_2$H$_5$NH$_2$), under VUV irradiation at 20 K and the formation of amino acetonitrile from a mixture of acetonitrile and ammonia under VUV irradiation at 20 K. We present the astrophysical implications of our results in Sect. 3.3.

2. Experimental details

For this study, the following reagents were used: Acetonitrile (Acros Organics, 99% purity), acetonitrile ^{15}N (Sigma Aldrich, 98% purity), amino acetonitrile (Sigma Aldrich, 97% purity), ethylamine (Fluka, 99% purity), ethylamine ^{15}N (Isotech Aldrich, 98% purity) and ammonia (Air Liquide, 99.9% purity). Reagents were mixed in different ratios in a pyrex line using standard manometric techniques. Liquid reagents (acetonitrile, aminoacetonitrile) were vacuum transferred away from their liquid state by evaporation and if necessary, their resulting vapors were mixed in a glass bulb with other reagents. The gaseous mixture was deposited at a 6×10^{-1} mol min^{-1} rate on a gold platted surface kept at 20 K with the help of a model 21 CTI cold head. The warming up of the sample was realized at a 4 K min^{-1} heating rate using a resistive heater along with a Lakeshore model 331 temperature controller. The VUV irradiation ($\lambda > 120$ nm) was realized using a microwave discharge hydrogen flow lamp (Opthos Instruments). The flux of photons is estimated to be in the range 10^{14}–10^{15} photons cm^{-2} s^{-1}. The infrared spectra of the samples were recorded in a reflection mode between 4000 and 600 cm^{-1} using a Nicolet Magna 750 FTIR spectrometer with a MCT detector. Each spectrum was averaged over one hundred scans and has a 1 cm^{-1} resolution. The mass spectra were monitored using a RGA quadrupole mass spectrometer (MKS Microvision-IP plus) while the products are desorbed during the controlled temperature ramp. The ionisation source is a 70 eV impact electronic source and the mass spectra are recorded
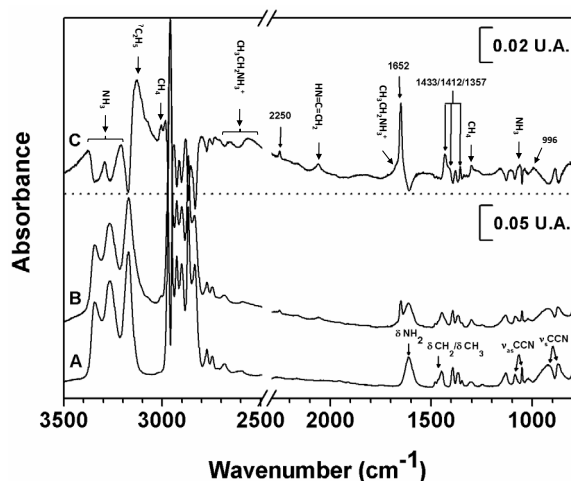
Fig. 1. Infrared spectra of pure ethylamine ice (A), pure ethylamine after 240 min of VUV irradiation at 20 K (B) and difference spectrum (C) of (A) and (B). All spectra were recorded at 20 K.

between 1 and 200 amu. The photochemical yield of the photoproducts was obtained with the method already described in Bossa et al. (2009a).

3. Results and discussion

3.1. From ethylamine to acetonitrile through photolysis

In this section, we investigate the formation of acetonitrile from the photolysis of ethylamine. The infrared spectra of pure ethylamine before (Fig. 1A) and after 240 min of irradiation (Fig. 1B) at a temperature of 20 K are displayed in Fig. 1 along with vibrational assignments. Solid ethylamine can be trapped at low temperature under trans- and left-conformers as shown by the presence of the two bands at 1084 cm^{-1}, and 1150 cm^{-1} which are related to the CCN stretching modes (Durig et al. 2006; Zeroka et al. 1999). The comparison of the two spectra in Figs. 1A and B shows the appearance of new infra-red bands. The new features of these photoproducts can be more easily observed by subtracting those two spectra (Fig. 1C).

The most intense band appears at 1652 cm^{-1}. This band corresponds to the C=N or C=C stretching mode. The presence of an unsaturated compound is consistent with the elimination of molecular hydrogen (H$_2$) induced by ultra-violet photons. But at this stage, from the 1652 cm^{-1} band alone, we cannot conclude about the photoproduct formed during this process since this molecular hydrogen could be lost as well from the C–N bond to give ethanimine (Hashiguchi et al. 1984; Stolkini et al. 1977) or from the C–C bond to produce ethenamine (Hamada et al. 1984) (Eqs. (1) and (2)). These two photoproducts have, unfortunately, a very close absorption band in this region.

$$CH_3CH_2NH_2 + h\nu \rightarrow CH_3CH=NH + H_2 \qquad (1)$$

$$CH_3CH_2NH_2 + h\nu \rightarrow CH_2=CHNH_2 + H_2. \qquad (2)$$
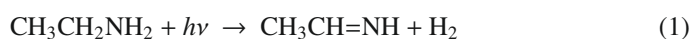
Next to the 1652 cm^{-1} band, some other bands can be assigned to ethanimine. The bands at 1433 cm^{-1} and 1412 cm^{-1} are close to the anti-symmetric and symmetric modes of the methyl deformation in ethanimine (CH$_3$CH=NH) (Stolkini et al. 1977). Other bands at 1357 cm^{-1} and between 1100–1000 cm^{-1} could also be consistent with the mixed and the deformation modes of this species (Stolkini et al. 1977; Hashiguchi et al. 1984). For removing any ambiguity with these assignments, the isotopomer

Table 1. Positions and attributions of infrared absorption bands after a 240 min photolysis at 20 K of a pure ethylamine ($C_2H_5NH_2$) ice and of its pure isotopomer ($C_2H_5{}^{15}NH_2$).

Ice ($\lambda > 120$ nm)	Wavenumber (cm^{-1})	Attribution	Identification	Ref.
$C_2H_5NH_2$	3380	NH_3	(ν_3) (ν_{as}) NH_3	(d'Hendecourt et al. 1986; Ferraro et al. 1980)
(pure, 20 K)	3294	NH_3	(2 ν_4) harmonic	(d'Hendecourt et al. 1986; Ferraro et al. 1980)
	3209	NH_3	(ν_1) (ν_s) NH_3	(d'Hendecourt et al. 1986; Ferraro et al. 1980)
	3127	C_2H_5	ν_{as} CH_2	(Sogoshi et al. 1997)
	3008	CH_4	νCH_4	(d'Hendecourt et al. 1986; Gerakines et al. 1996)
	2655	$[CH_3CH_2NH_3^+]$	Fermi res.	(Hagemann & Bill 1984)
	2566	$[CH_3CH_2NH_3^+]$	Fermi res.	(Hagemann & Bill 1984)
	2250	$CH_3C\equiv N$	ν $C\equiv N$	(d'Hendecourt et al. 1986; Hudson & Moore 2004)
	2165	CH_3–NC?	ν NC?	(Hudson & Moore 2004)
	2080	[CN]	ν C-N	(Gerakines et al. 2004; Moore & Hudson 2003)
	2058	CH_2=C=NH	ν_{as} C=C=N	(Hudson & Moore 2004; Jacox & Milligan 1963)
	1670	$[CH_3CH_2NH_3^+]$	δ_{as} NH_3^+	(Hagemann & Bill 1984; Zeroka et al. 1999)
	1652	CH_3CH=NH	ν C=N	(Hashiguchi et al. 1984; Stolkini et al. 1977)
	1433	CH_3CH=NH	δ_{as} CH_3	(Stolkini et al. 1977)
	1412	CH_3CH=NH	δ_s CH_3	(Stolkini et al. 1977)
	1357	CH_3CH=NH	mixed mode	(Hashiguchi et al. 1984; Stolkini et al. 1977)
	1301	CH_4	dd CH_4	(d'Hendecourt et al. 1986; Gerakines et al. 1996)
	1062	NH_3	(ν_2) umbrella mode	(d'Hendecourt et al. 1986; Ferraro et al. 1980)
	996	CH_2=C=NH	δ CNH	(Jacox & Milligan 1963)
$C_2H_5{}^{15}NH_2$	3202	$^{15}NH_3$	(ν_1) (ν_s) $^{15}NH_3$	
(pure, 20K)	2224	$CH_3C\equiv{}^{15}N$	ν $C\equiv{}^{15}N$	
	2136	CH_3–^{15}NC?	ν ^{15}NC	
	2071	$[C^{15}N]$	ν C–^{15}N	(Gerakines et al. 2004; Moore & Hudson 2003)
	2031	CH_2=C=^{15}NH	ν C=^{15}N	
	1634	CH_3CH=^{15}NH	ν C=^{15}N	
	1433	CH_3CH=^{15}NH	δ_{as} CH_3	(Stolkini et al. 1977)
	1412	CH_3CH=^{15}NH	δ_s CH_3	(Stolkini et al. 1977)

Notes. Vibration mode: stretching (ν), bending (δ), rocking (ρ), torsion (τ), wagging (w). Type of vibration mode: asymmetric (as), symmetric (s).
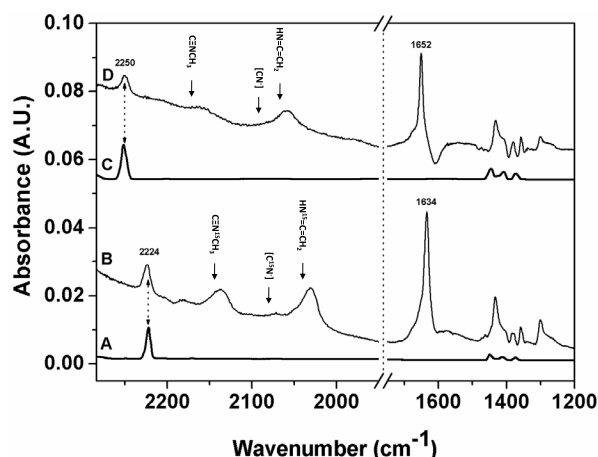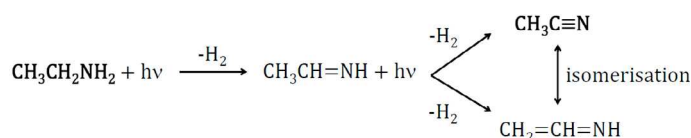

Fig. 2. Infrared spectra of pure acetonitrile ^{15}N ice (A) and difference spectrum between pure ethylamine ^{15}N and ethylamine ^{15}N after 240 min of VUV irradiation at 20 K (B). Spectra (C) and (D) are identical to (A) and (B) with the isotopomer ^{14}N. All spectra were recorded at 20 K.

^{15}N photolysis of ethylamine at 20 K was compared to the normal isotopomer (Fig. 2). This comparison shows a clear shift of the wavenumber attributed to C=N vibration, which shifts from 1652 cm^{-1} for ^{14}N to 1634 cm^{-1} for ^{15}N. This variation is consistent with the presence of the nitrogen in the C=N group because of the increase of the reduced mass of the vibrator. Furthermore,

the methyl deformations at 1433 cm^{-1} and 1412 cm^{-1} are not shifted in the ^{15}N photolysis. It appears from these results that the primary product formed during the photolysis of ethylamine is ethanimine (CH_3CH=NH).

Another interesting feature is the band at 2250 cm^{-1} (Fig. 1C and Table 1). This band is characteristic of a $C\equiv N$ stretching mode in an aliphatic nitrile. To check if this band could correspond to a vibration mode of acetonitrile, the smallest nitrile that could be formed in these conditions, the spectrum of solid acetonitrile, was compared to the photolysis spectra of solid ethylamine at 20 K (Fig. 2). Evidently the band due to the $C\equiv N$ stretching mode of acetonitrile (2250 cm^{-1}) has the same position as the nitrile band observed on the photolysis spectrum (Figs. 2C and D). This implies that acetonitrile is present after the photolysis of a pure ice of ethylamine. To strengthen this identification, the spectrum of the $CH_3C\equiv{}^{15}N$ acetonitrile isotopomer was also compared to the one obtained after photolysis of ethylamine ^{15}N (Figs. 2A and B). The band at 2250 cm^{-1} is not observed in the ^{15}N spectrum recorded after VUV photolysis, which is consistent with the attribution to a nitrile function. Moreover, a new band is present at 2224 cm^{-1}. This band has the same position as the one of the stretching vibration mode of $C\equiv{}^{15}N$ in $CH_3C\equiv{}^{15}N$. From these results, we can conclude that acetonitrile is formed during the photolysis of ethylamine ice at 20 K. The photochemical yield of the acetonitrile formation is estimated from the amount of ethylamine consumed and the amount of acetonitrile observed after irradiation. We used the band strengths of the methylamine: NH_2 ($A = 4.3 \times 10^{-18}$ cm molecule^{-1}) and CH_3 ($A = 1.5 \times 10^{-18}$ cm molecule^{-1})

$$CH_3CH_2NH_2 + h\nu \xrightarrow{\text{-}H_2} CH_3CH=NH + h\nu \begin{array}{c} \xrightarrow{\text{-}H_2} CH_3C\equiv N \\ \Big\updownarrow \text{ isomerisation} \\ \xrightarrow{\text{-}H_2} CH_2=CH=NH \end{array}$$

Fig. 3. Pathways for acetonitrile formation from ethylamine.

vibrators (Holtom et al. 2005), at 1612 cm^{-1} and at 1131 cm^{-1} respectively to determine the amount of ethylamine consumed after VUV irradiation because the corresponding values are not known for this compound. Using the above approximation and the column density of acetonitrile at 2250 cm^{-1} (A = 2.2 × 10^{-18} cm molecule^{-1}) (d'Hendecourt et al. 1986), the branching ratio of formed acetonitrile/consumed ethylamine is estimated to be around 32% at 20 K and after 240 min of VUV irradiation. Given that 14% of the ethylamine was consumed, the photochemical yield of acetonitrile is estimated to be about 4%. Other molecular compounds were identified and are listed in Table 1, and displayed in Figs. 1 and 2. Among them, we note isoacetonitrile (CH$_3$N≡C) because the N≡C vibrator of this isonitrile can be assigned to the 2165 cm^{-1} feature (Fig. 2D) (Hudson Moore 2004), which is confirmed by the ^{15}N experiment (Fig. 2B). This compound is known for being an acetonitrile photoproduct formed by acetonitrile isomerisation. Another interesting species is ketenimine (CH$_2$=C=NH), which is identified by the bands at 2058 cm^{-1} and 996 cm^{-1} (Figs. 2B and D) (Hudson & Moore 2004; Jacox & Milligan 1963).

Ketenimine could be formed from the acetonitrile isomerisation or from the dehydrogenation of the ethanimine. The photochemical yield of formation of ketemine and isoacetonitrile were estimated using the band strengths given by Hudson et al. (Hudson & Moore 2004). The corresponding yields are 0.4%, and 1.3% respectively. Unfortunately, we could not estimate the photochemical yield for the formation of ethanimine because we lacked the band strength for this compound. Methane was also detected from the bands at 3008 cm^{-1} and 1301 cm^{-1}, which remain unchanged in frequency after the VUV photolysis of C$_2$H$_5$^{15}NH$_2$. This methane formation could be induced by the acetonitrile photolysis through the reaction (Hudson & Moore 2004):

$$CH_3C\equiv N + h\nu \rightarrow CH_4 + HCN. \tag{3}$$

Cyanhydric acid is not detected since it probably reacts with the excess of ethylamine to give the following salt [CH$_3$CH$_2$NH$_3^+$ CN$^-$], which is confirmed by the band at 2655 cm^{-1} and at 1670 cm^{-1} consistent with the ion CH$_3$CH$_2$NH$_3^+$ (Hagemann & Bill 1984) and the shoulder at 2080 cm^{-1} consistent with the CN$^-$ ion (Gerakines et al. 2004; Moore & Hudson 2003). Finally, ammonia was identified from the infrared bands at 3380 cm^{-1}, 3294 cm^{-1}, 3209 cm^{-1} and 1062 cm^{-1}. Ammonia was formed from the reaction between ˙NH$_2$ and ˙H coming from ethylamine photodissociation. This is also confirmed by the presence of the radical ˙C$_2$H$_5$, identified by the band at 3127 cm^{-1} (Sogoshi et al. 1997).
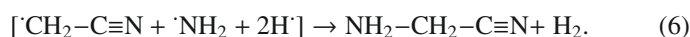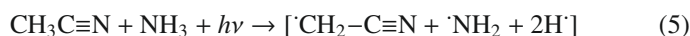
From these results, we can conclude that photochemistry of a pure ice at 20 K leads to the formation of acetonitrile. The process involves a first elimination of molecular hydrogen that leads to ethanimine. Then, from ethanimine a second elimination of molecular hydrogen probably leads to acetonitrile formation. However, we cannot exclude that acetonitrile could be formed by ketenimine isomerisation, which can also be synthesized from ethanamine by elimination of molecular hydrogen (Fig. 3).

3.2. Amino acetonitrile synthesis from photochemistry of an acetonitrile/ammonia mixture

In this section, we take a closer look at the amino acetonitrile formation from photochemical reactions of an acetonitrile/ammonia ice mixture. The VUV photochemistry ($\lambda > 120$ nm) of a pure solid of acetonitrile has already been investigated (12 to 25 K) (Hudson & Moore 2004). Hudson et al. (2004) have shown, as we did in the previous section, three main photoproducts: ketenimine (CH$_2$=C=NH), isoacetonitrile (CH$_3$–N≡C) and hydrogen cyanide with methane. Ketenimine is one of the major compounds formed during photolysis, which results from an intramolecular rearrangement (Hudson & Moore 2004) through the pathway.

$$CH_3C\equiv N + h\nu \rightarrow [^\cdot CH_2\!-\!C\equiv N + ^\cdot H] \rightarrow CH_2 = C\!=\!NH. \tag{4}$$

The radical intermediate ˙CH$_2$–CN could be a useful starting point to form the amino acetonitrile because, it could react with the ˙NH$_2$ radical coming from ammonia photolysis,

$$CH_3C\equiv N + NH_3 + h\nu \rightarrow [^\cdot CH_2\!-\!C\equiv N + ^\cdot NH_2 + 2H^\cdot] \tag{5}$$

$$[^\cdot CH_2\!-\!C\equiv N + ^\cdot NH_2 + 2H^\cdot] \rightarrow NH_2\!-\!CH_2\!-\!C\equiv N + H_2. \tag{6}$$

In order to test this hypothesis, a mixture of acetonitrile/ammonia was photolysed with VUV photons ($\lambda > 120$ nm). A comparison between an infrared spectrum of amino acetonitrile and a spectrum of an acetonitrile/ammonia mixture rapidly shows that infrared spectroscopy is not the most easy and convenient method to identify the formation of amino acetonitrile. Indeed, the NH$_2$ vibration modes of ammonia hide those of amino acetonitrile, while the C≡N vibration mode of acetonitrile masks the amino acetonitriles one. However, the sublimation temperature provides a way to distinguish between acetonitrile and amino acetonitrile, since the acetonitrile sublimation occurs at around 158 K, while that of amino acetonitrile occurs at higher temperatures, at around 200 K. Unfortunately, infrared spectroscopy is not sensitive enough to provide a secure detection of amino acetonitrile. The only way to follow the amino acetonitrile formation is to use a mass spectrometer. Consequently, the characterization of amino acetonitrile formed during the photolysis of an acetonitrile/ammonia mixture was conducted by monitoring the partial pressure of the ion at m/z 55 and 56 as a function of temperature.

This is shown in Figs. 4A and B, which display the mass spectra of acetonitrile and that of amino acetonitrile respectively. This last one can be identified without any ambiguity by its molecular ion at m/z 56 and the fragment ion m/z 55 (Fig. 4B). An ice mixture composed of acetonitrile/ammonia with a 5:1 ratio was photolysed ($\lambda > 120$ nm) during 190 min at 20 K. After this photolysis, the mixture was warmed from 20 K to 300 K at 4 K min^{-1} while the partial pressure of the ions at m/z 56 (Fig. 5A) and m/z 55 (Fig. 5B) was recorded. Figure 5 displays the evolution of the partial pressures of the mentioned ions.

The spectrum profiles obtained after irradiation (Figs. 5A and B) were also compared with the spectrum of the same ions resulting in the warming up of the same acetonitrile/ammonia mixture without VUV irradiation (Figs. 5C and D). For the irradiated sample (Figs. 5A and B), above 190 K, the partial pressure of the ion at m/z 55 increases to a maximum at 205 K and slows down to reach the baseline at 220 K, whereas with the non-irradiated sample the profile stays flat. The same profile is observed for the ion at m/z 56. Even if this variation is weak compared to the noise, these two intensities rise in the temperature range 190–220 K associated to a higher intensity for the
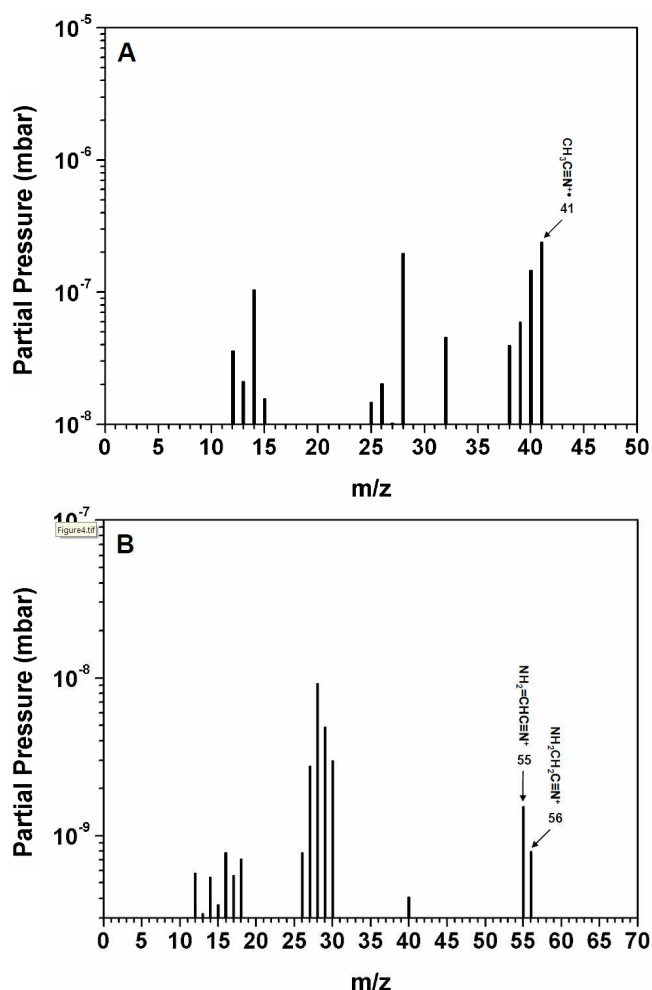
Fig. 4. Mass spectrum of evaporating acetonitrile at 158 K after warming up of the pure ice of this molecule (electronic ionization 70 eV) (A) and evaporating amino acetonitrile at 200 K after warming up of the pure ice of this molecule (electronic ionization 70 eV) (B).

m/z 55 ion compared with the ion of m/z 56 ion (Figs. 4A and B), which confirms the sublimation of amino acetonitrile. The signal at m/z 55 is then attributed to the $H_2N=CHC\equiv N^+$ fragment ion, which comes from the fragmentation of the $H_2NCH_2C\equiv N^{+\cdot}$ molecular ion represented by the signal at m/z 56.

3.3. Astrophysical discussion

All species used in our experiments have been detected in extraterrestrial environments in either the gas or in the solid phases. In particular, ethylamine has been identified in the comet-exposed materials from stardust (Glavin et al. 2008). Different pathways for ethylamine formation were already suggested for these environments. For example, the formation of ethylamine in the gas phase from a neutral-neutral reaction between the methyl radical and the methanimine followed by hydrogenation of the resulting product was proposed for its formation at the surface of interstellar or cometary grains (Bernstein et al. 1995). Other authors proposed ethylamine formation from the photochemistry of a mixture of ethylene and ammonia. Ethylene can be formed from methane (Atreya 1992; Gerakines et al. 1996) (Eqs. (7) and (8)) which represents 1% to 4% (with respect to water) of the composition of interstellar ices (Dartois 2005),

$$2CH_4 + h\nu \rightarrow 2CH_3^{\cdot} + 2H^{\cdot} \rightarrow C_2H_6 + H_2 \qquad (7)$$
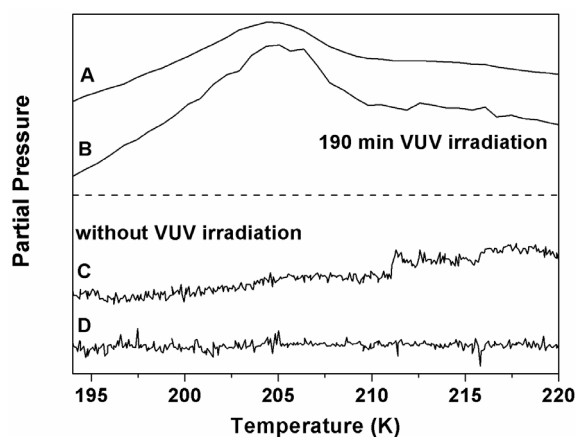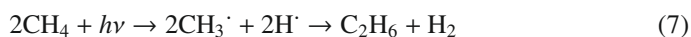
Fig. 5. Partial pressure for ions m/z 56 (A and C) and 55 (B and D) as a function of temperature during the warm-up of an ice mixture of acetonitrile:ammonia (5:1) (A and B) previously irradiated at 20 K during 190 min or (C and D) without irradiation.

$$C_2H_6 + H_2 + h\nu \rightarrow C_2H_4 + H_2. \qquad (8)$$
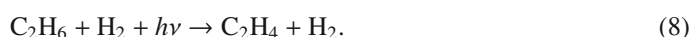
Then, ammonia is dissociated to give the aminyl radical $^{\cdot}NH_2$ (Gerakines et al. 1996) (Eq. (9)), which reacts further with the ethyl radical that can originate from the partial hydrogenation of ethylene (Eq. (10)) or by the partial photolysis of ethane (Eq. (11)) to yield ethylamine (Eq. (12)),

$$NH_3 + h\nu \rightarrow {}^{\cdot}NH_2 + {}^{\cdot}H \qquad (9)$$

$$C_2H_4 + {}^{\cdot}H \rightarrow {}^{\cdot}C_2H_5 \qquad (10)$$

$$C_2H_6 + h\nu \rightarrow {}^{\cdot}C_2H_5 + {}^{\cdot}H \qquad (11)$$

$${}^{\cdot}C_2H_5 + {}^{\cdot}NH_2 \rightarrow C_2H_5NH_2. \qquad (12)$$

Once formed, ethylamine can adsorb on the surface of interstellar or cometary grains, where it will undergo solid phase reactivity. Its presence in interstellar ices is strengthened by its detection in volatile compounds coming from cometary surface (Glavin et al. 2008). Consequently, by taking into account the above arguments and the results obtained in this work, we suggest that acetonitrile can be synthesized at the surface of interstellar or cometary grains following a two step dehydrogenation of ethylamine under VUV irradiation. In pure ethylamine the photochemical yield of acetonitrile after 240 min is 4%. This yield in acetonitrile needs to be lowered in real astrophysical environments, because the proportion of water could shield ethylamine from VUV photons, which should decrease this yield. Additionally, from recent experimental results, we can draw up another acetonitrile formation pathway. Our group have shown that it is possible to form in the solid phase amino alcohols ($NH_2CH(R)OH$) with the first step of the Strecker synthesis from the thermal reaction between an aldehyde or a ketone and ammonia (Bossa et al. 2009b; Duvernay et al. 2010). From the specific reaction between acetaldehyde and ammonia, the amino ethanol was synthesized and its VUV irradiation leads to acetamide. Acetamide under VUV irradiation then provides acetonitrile and water (Duvernay et al. 2007). Once formed, acetonitrile could be a precursor of another nitrile, the amino acetonitrile. Since at the surface of grains acetonitrile can co-exist with ammonia, which represents up to 10% (upper limit relative to water) (Dartois & d'Hendecourt 2001) of the interstellar ice composition, it will react through a photochemical reaction leading to amino acetonitrile. Others ways of synthesis of amino acetonitrile have been proposed through theoretical studies. Some authors suggest a

reaction similar to the third step of the Strecker reaction between methanimine and hydrogen cyanide or hydrogen isocyanide at the surface of interstellar grains (Koch et al. 2008), where the methanimine could be formed from the hydrogenation of hydrogen cyanide or from the dehydrogenation of methylamine.

4. Conclusion

In this contribution, we investigated the formation of two nitrile derivatives, acetonitrile and amino acetonitrile, under VUV photons irradiation of interstellar/pre-cometary ice analogs. From infrared spectroscopy data, acetonitrile is formed from VUV irradiation of ethylamine at 20 K through a two step dehydrogenation process. Once formed, acetonitrile can then react under VUV irradiation in solid phase with ammonia leading to the formation of amino acetonitrile. Acetonitrile synthesis from ethylamine can be suggested as a possible pathway for its formation on interstellar or cometary grains. We emphasize that this scenario is at present the only one demonstrated in the laboratory and astrophysically relevant environments. Other formation pathways, in particular those related to solid/gas phases reactivity, which are possible in evaporating comets, can be proposed as alternative pathways. Finally these studies clearly show the vast complexity of photo and thermochemistry that may happen on astrophysical ices in various environments. They also clearly demonstrate the necessity of laboratory simulations whose diagnostics provide other information than a simple comparison with astrophysical data. These results have then to be discussed within scenarios proposed for the general evolution of interstellar/cometary dirty ices.

References

Atreya, S. K. 1992, Adv. Space Res., 12, 1
Basiuk, V. A., & Bogillo, V. I. 2002a, Adv. Space Res., 30, 1439
Basiuk, V. A., & Bogillo, V. I. 2002b, Adv. Space Res., 30, 1445
Belloche, A., Menten, K. M., Comito, C., et al. 2008, A&A, 482, 179
Belloche, A., Garrod, R. T., Muller, H. S. P., et al. 2009, A&A, 499, 215
Bernstein, D. I., Sandford, S. A., Allamandola, L. J., & Chang, S. 1995, ApJ, 454, 327
Bernstein, M. P., Dworkin, J. P., Sandford, S. A., Cooper, G. W., & Allamandola, L. J. 2002, Nature, 416, 401
Bernstein, M. P., Ashbourn, S. F. M., Sandford, S. A., & Allamandola, L. J. 2004, ApJ, 601, 365

Bossa, J. B., Duvernay, F., Theulé, P., et al. 2009a, A&A, 506, 601
Bossa, J. B., Theulé, P., Duvernay, F., & Chiavassa, T. 2009b, ApJ, 707, 1524
Codella, C., Benedettini, M. T. B. M., Gueth, F., et al. 2009, A&A, 507, L25
d'Hendecourt, L. B., & Allamandola, L. J. 1986, A&ASS, 64, 453
Dartois, E. 2005, Space Sci. Rev., 119, 293
Dartois, E., & d'Hendecourt, L. 2001, A&A, 365, 144
Durig, J. R., Zheng, C., Gounev, T. K., Herrebout, W. A., & van der Veken, J. 2006, J. Phys. Chem. A, 110, 5674
Duvernay, F., Chatron-Michaud, P., Borget, F., Birney, D. M., & Chiavassa, T. 2007, Phys. Chem. Chem. Phys., 9, 1099
Duvernay, F., Dufauret, V., Danger, G., et al. 2010, A&A, 523, A79
Elsila, J. E., Dworkin, J. P., Bernstein, M. P., Martin, M. P., & Sandford, S. A. 2007, ApJ, 660, 911
Elsila, J. E., Glavin, D. P., & Dworkin, J. P. 2009, Meteor. Planetary Sci., 44, 1323
Ferraro, J. R., Sill, G., & Fink, U. 1980, Appl. Spectrosc., 34, 525
Gerakines, P. A., Schutte, W. A., & Ehrenfreund, P. 1996, A&A, 312, 289
Gerakines, P. A., Moore, M. H., & Hudson, R. L. 2004, Icarus, 170, 202
Glavin, D. P., Dworkin, J. P., & Sandford, S. A. 2008, Meteor. Planetary Sci., 43, 399
Hagemann, H., & Bill, H. 1984, J. Chem. Phys., 80, 111
Hamada, Y., Hashiguchi, K., Tsuboi, M., Koga, Y., & Kondo, S. 1984, J. Mol. Spectrosc., 105, 93
Hashiguchi, K., Hamada, Y., Tsuboi, M., Koga, Y., & Kondo, S. 1984, J. Mol. Spectrosc., 105, 81
Hollis, J. M., Lovas, F. J., Remijan, A. J., et al. 2006, ApJ, 643, L25
Holtom, P. D., Bennett, C. J., Osamura, Y., Mason, N. J., & Kaiser, R. I. 2005, ApJ, 626, 940
Hudson, R. L., & Moore, M. H. 2004, Icarus, 172, 466
Hudson, R. L., Moore, M. H., Dworkin, J. P., Martin, M., & Pozun, Z. D. 2008, Astrobiology, 8, 771
Huebner, W. B., Snyder, L. E., & Buhl, D. 1974, Icarus, 23, 580
Jacox, M. E., & Milligan, D. E. 1963, J. Am. Chem. Soc., 85, 278
Koch, D. M., Toubin, C., Peslherbe, G. H., & Hynes, J. T. 2008, J. Phys. Chem. C, 112, 2972
Lara, L. M., Lellouch, E., Lopez-Moreno, J. J., & Rodrigo, R. 1996, J. Geophys. Res., 101, 23261
Moore, M. H., & Hudson, R. L. 2003, Icarus, 161, 486
Olmi, L., Cesaroni, R., & Walmsley, C. M. 1993, A&A, 276, 489
Oro, J. 1961, Nature, 190, 389
Remijan, A. J., Sutton, E. C., Snyder, L. E., et al. 2004, ApJ, 606, 917
Remijan, A. J., Milam, S. N., Womack, M., et al. 2008, ApJ, 689, 613
Rimola, A., Sodupe, M., & Ugliengo, P. 2010, Phys. Chem. Chem. Phys., 12, 5285
Snyder, L. E., & Buhl, D. 1971, ApJ, 163, L47
Sogoshi, N., Wakabayashi, T., Momose, T., & Shida, T. 1997, J. Phys. Chem. A, 101, 522
Spall, B. C., & Steacie, E. W. R. 1957, Proc. R. Soc. London, Ser. A, 239, 1
Stolkin, I., Ha, T.-K., & Gunthard, H. H. 1977, Chem. Phys., 21, 327
Venkateswarlu, P. 1951, J. Chem. Phys., 19, 293
Whittet, D. C. B., Gibb, E. L., & Nummelin, A. 2001, Origins Life Evol. Biosphere, 31, 157
Woon, D. E. 2002, ApJ, 571, L177
Xu, S. C., & Wang, N. 2007, Acta Phys. Chim. Sin., 23, 212
Zeroka, D., Jensen, J. O., & Samuels, A. C. 1999, J. Mol. Struct. TheoChem, 465, 119