Determination of [CH 3 NC]/[H 2 C C NH] Abundance Ratios from N + CH 3 CN Solid Phase Reaction in the Temperature Range from 10 to 40 K: Application to the Complex Chemistry in Star-Forming Regions

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Determination of [CH$_3$NC]/[H$_2$C=C=NH] abundance ratios from N + CH$_3$CN solid phase reaction in the temperature range from 10 to 40 K: Application to the complex chemistry in star forming regions

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ABSTRACT:

The interstellar detection of CH$_3$CN metastable isomers would suggest that CH$_3$NC and H$_2$C=C=NH formed in star forming regions through energetic processing provoked by shocks or others energy sources. In this context laboratory simulations have been carried out to investigate the chemical transformation of CH$_3$CN into CH$_3$NC and H$_2$C=C=NH induced by UV photolysis and high energy particle irradiation. In the present study we have carried out the CH$_3$CN + N solid state reaction in the 10-40 K temperature range in order to examine the behavior of acetonitrile interacting with nitrogen atoms in icy interstellar grains. We show that CH$_3$CN + N is efficient in the solid phase but only in a very specific temperature range which combines high mobility and relatively long surface residence time of N atoms to allow the CH$_3$CN activation. By focusing in the behavior of [CH$_3$NC]/[H$_2$C=C=NH] abundance ratios versus temperature, we have measured abundance ratios around 10.4 at 10 K which decreases to 6.8 when the temperature of the reaction increases. These ratios are of the same order of magnitude as those reported from the acetonitrile isomers detection towards Sagittarius B2(N). While in previous studies involving energetic processing of solid CH$_3$CN, CH$_3$NC and CH$_2$CNH have been formed with [CH$_3$NC]/[CH$_2$CNH] ratios ranged between 0.3 and 1.7. Additionally, the analysis of CH$_3$NC and H$_2$C=C=NH column densities shows that at low temperatures the less stable isomer is favored against the most stable one. These results are compared to the puzzling behavior of CN-containing isomers such as HNC, HCN, HCNO and HOCN in molecular clouds.

KEYWORDS: Infrared spectroscopy, Star Forming Regions, interstellar ices, Complex organic molecules, Acetonitrile, Isocyanomethane, Ketenimine, Nitrogen atom.

1. INTRODUCTION

The three CN bearing isomers CH_3CN, CH_3NC and $H_2C=C=NH$ are considered as prebiotic molecules in star-forming regions and they have naturally been topics of many laboratory investigations and astronomical observations. The most stable isomer, CH_3CN was the first alkyl cyanide[1] detected in the interstellar medium in 1971 while its deuterated isotopologue[2] CDH_2CN was detected towards OMC1 hot cores in 1992 by Gerin et al. and very recently[3] through Sgr B2(N2) by Belloche et al. Conversely, the two other isomers CH_3NC, $H_2C=C=NH$ seem to be less abundant in the ISM. The first tentative detection of CH_3NC with an $[CH_3CN]/[CH_3NC]$ abundance ratio around 30 has been performed[4] by Cernicharo et al. in 1988 toward Sgr B2(OH). More lately, CH_3NC has been detected in Sgr B2(N) molecular cloud[5] and identified for the first[6] time in 2018 in a solar-type protostar, IRAS 16293–2422 B with an $[CH_3CN]/[CH_3NC]$ abundance ratio of 200. While $H_2C=C=NH$, which is slightly almost more stable than CH_3NC, has been detected by Lovas et al. toward the star-forming region[7] Sagittarius B2(N) hot cores with an $[CH_3CN]/[CH_2CNH]$ ratio around 100. Lovas et al. suggested that one of the routes to form $H_2C=C=NH$ went through either CH_3CN ionization or UV induced isomerization. The CH_3CN ionization might occur in diffuse clouds to form CH_3CN^+ which in turn would lead to CH_2CNH^+ through low barrier energy of 70 kJ mol. The neutral $H_2C=C=NH$ could then be a product resulting from the $CH_2CNH^+ + e$ electron capture reaction. While the UV induced $CH_3CN \rightarrow H_2C=C=NH$ tautomerization which shows an energy barrier[8] of 370 kJ/mol would be more probable in the SgrB2(N) region which contains widespread shocks to provide enough energy to the reaction to occur. However, these two reaction pathways leading to the formation of $H_2C=C=NH$ from its more abundant isomer CH_3CN exclude all the processes which may occur in dark regions not exposed to external energy sources. Additionally, CH_3CN has been also detected in comets, in atmospheres of moons and planets[9-15], but no trace of $H_2C=C=NH$ and CH_3NC which may also be present with a kind of $[CH_3CN]/[H_2C=C=NH]/[CH_3NC]$ abundance ratios which may inform about the existing links between these three isomers. In order to answer the question how CH_3CN, CH_3NC, $H_2C=C=NH$ form and how they evolve in space, many groups have investigated reactions involving CH_3CN as precursor through energetic processing to mimic the chemistry involved in the ISM and atmospheres of moons and planets. As reactions occurring in solid phase at cryogenic temperatures are known to be one of the main sources of the chemical complexity of the Universe, many laboratory studies have been focused in solid state reactions on interstellar, cometary and atmospheric ice analogues in the 10-200 K

temperature range. In this context, Hudson et al. have already shown that the bombardment[16] by 0.8 MeV H^+ ion of CH_3CN ices formed at 10 K led to CH_3NC, H_2CCNH, HCN, and CH_4. Similarly, Abdulgalil et al. showed that the irradiation[17] of CH_3CN ices by 200 keV H^+ particles formed CH_3NC, H_2CCNH, HCN, HCCCN and CH_4. These two studies have shown the chemical transformation of CH_3CN into CH_3NC and $H_2C=C=NH$ through energetic processing in solid phase to prove that CH_3CN isomerization would take place only in regions of space containing shocks or other energy sources. However, in order to examine the behavior of CH_3CN interacting with particles less energetic than 0.8 MeV H^+ ion or 200 keV H^+, we have recently investigated[18] the CH_3CN + N solid state reaction in the 3-10 K temperature range to underline the role of the nitrogen atoms in icy interstellar grains. Our study showed for the first time that by monitoring the mobility of ground state nitrogen atoms between 3 and 10 K, we form N_2^* long lived metastable species known as $N_2(A)$ excited molecular nitrogen which while interacting with CH_3CN induced its isomerization into CH_3NC and CH_2CNH through energy transfer process as follows:

$N + N \rightarrow N_2^*$

$N_2^* + CH_3CN \rightarrow N_2 + CH_3CN^* \rightarrow N_2 + CH_3NC$ or CH_2CNH

In the context of the present work we have studied the influence of the temperature on the CH_3CN + N solid state reaction from 10 to 40 K, a temperature range relevant to star forming regions, by focusing in the evolution of [CH_3CN]/[$H_2C=C=NH$]/[CH_3NC] abundance ratios versus temperature and also versus the environment where these three isomers are formed.

2. EXPERIMENTAL METHODS

Molecular nitrogen has been purchased from Messer, with a purity of 99.9995%. Natural CH_3CN, purchased from Sigma-Aldrich with a purity of 99.9% was degassed under vacuum. Our samples were prepared under ultrahigh vacuum of 10^{-10} mbar by co-depositing pure CH_3CN and N/N_2 mixture on a Rh-plated copper mirror maintained at temperatures ranged between 10 and 40 K, using a closed-cycle helium cryogenerator (Sumitomo cryogenics F-70). The N atoms were generated with a flux of about 10^{15} atoms cm^{-2} s^{-1} using a microwave discharge (SPECS, PCS-ECR) into N_2 gas. We have measured the yield dissociation of N_2 molecules around 4 %, using a Quadrupole Mass Spectrometer (QMS - Hidden Analytical). Samples were analyzed using Bruker Vertex 80v Fourier infrared (FTIR) spectrometer in

transmission–reflection mode, between 5000 and 500 cm^{-1} with a spectral resolution of 0.5 cm^{-1}. The sample holder, consisting of six mirrors optically polished mounted on a hexagonal face copper block which allows as mentioned earlier the simultaneous study of the CH_3CN + N reaction by two methods of CH_3CN + N/N_2 ice co-depositions as shown in figure 1.
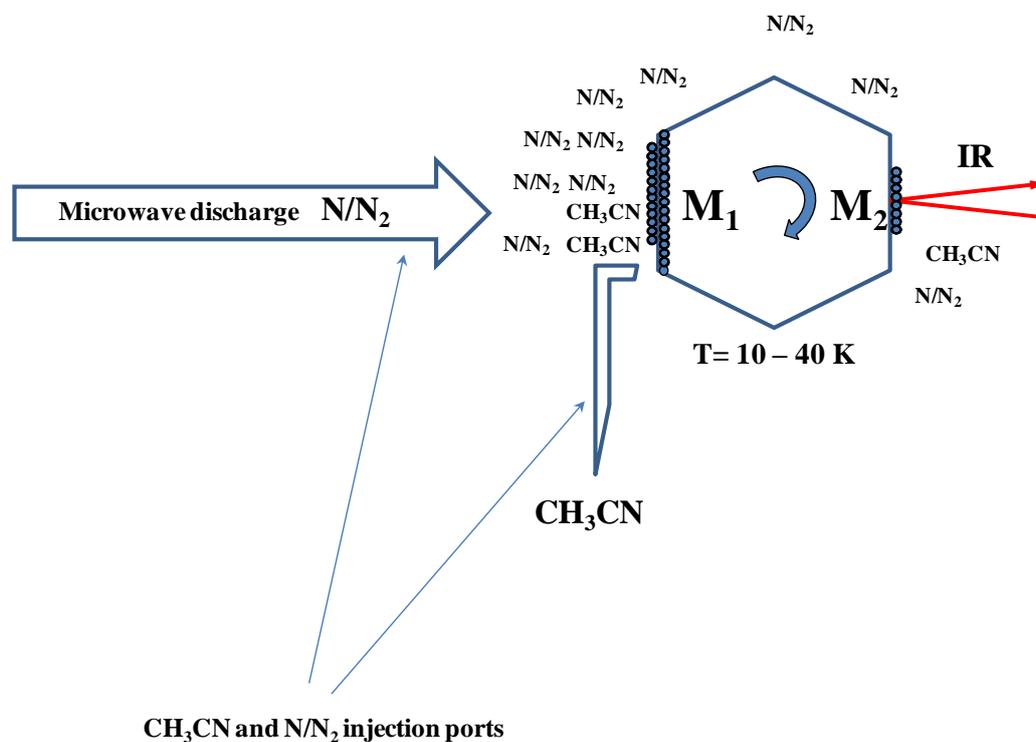
Figure 1: Direct and indirect CH_3CN + N/N_2 co-deposition on mirror M1 and M2, respectively.

a/ Direct deposition: It consists of forming icy samples through a direct co-injection of the reactants CH_3CN + N/N_2 on the surface of a cryogenic mirror located just front of the injection ports. Pure CH_3CN vapor gas was injected into the high vacuum chamber at a pressure of 10^{-8} mbar. Simultaneously, N/N_2 mixture generated from the microwave discharge was injected at a pressure of 10^{-5} mbar. The CH_3CN + N/N_2 co-deposition lasted 30 minutes. This co-injection method is a traditional one used by many groups to study solid sate reactions at cryogenic temperatures. With such a method, the icy samples are mainly made of reactants with high abundances, including a few amounts of the reaction products which depend in the efficiency of the reaction during the sample deposition. Additionally, using spectroscopy ground methods to probe the solid samples results in an overlapping between the huge signals due to the reactants with those due to the reaction products, generally very low.

b/ Indirect deposition: It is a background dosing which consists of forming icy samples through simultaneous condensation of CH_3CN + N/N_2 mixture gas suspended in the vacuum chamber. As, the condensation of the species (CH_3CN, N, N_2) suspended in the vacuum chamber depends on their masses ($M_{CH3CN} > M_{N2} > M_N$) the solid samples should contain more N atoms than N_2 and CH_3CN molecules. We have managed using this method, as it will be discussed bellow, to create icy samples containing amounts of reaction products twice higher than those of the reactants.

3. RESULTS AND DISCUSSIONS

In order to characterize the CH_3CN + N reaction in the 10-40 K temperature range, figure 2 shows the IR spectra resulting from the co-injections of CH_3CN + N_2 and CH_3CN + N/N_2, respectively, carried out at 20 K. The assignments of all vibrational modes[19] of CH_3CN ice are directly reported in spectrum 2b. The comparison between the two IR spectra permits discrimination of the IR signals derived from CH_3CN + N reaction products. We notice that the only new IR signals clearly visible and not hidden by those of the reactants and which would be assigned to the CH_3CN + N reaction products are located in the 2200-1900 cm^{-1} spectral region.
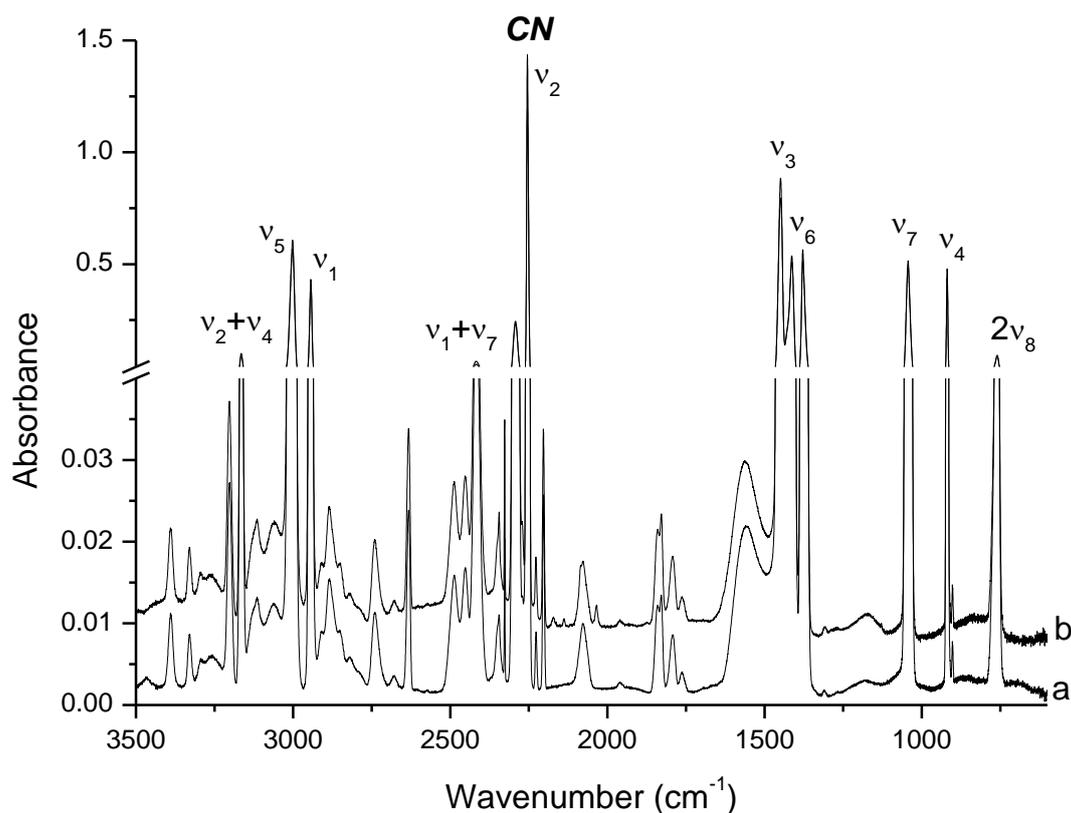
Figure 2: CH$_3$CN + N solid sate reaction at 20 K. a) CH$_3$CN + N$_2$ co-deposition. b) CH$_3$CN + N/N$_2$ co-deposition.

The expansion of spectra 2a and 2b in 2200-1840 cm^{-1} spectral region are shown in figure 3 where new IR signals related to CH$_3$CN + N solid sate reaction carried out at 20 K are observed at 2038, 2086 and 2167 cm^{-1} and which have been assigned to CH$_2$CNH, CN$^-$ and CH$_3$NC reaction products, respectively. We have already discussed these IR signal attributions in a previous study performed in the 3-10 K temperature range, showing that atomic nitrogen interacting with acetonitrile leads to the formation of CH$_3$NC, CH$_2$CNH and CN$^-$. These reactions products are similar to those obtained through energetic particle irradiation of CH$_3$CN ices. In the present study, we will focus only in the three CH$_3$CN, H$_2$C=C=NH, CH$_3$NC isomers. The main conclusion of our previous study, is that although the CH$_3$CN + N(^{4}S) reaction taken in the ground state is endothermic and would need an energy supply to occur, it takes place in solid phase because N(^{4}S)-N(^{4}S) recombination is more favourable in the solid state than in the gas phase. The N(^{4}S)-N(^{4}S) recombination is an exothermic process leading either to 945.6 kJ/mol energy release or to the formation of a reactive metastable molecular nitrogen N$_2$(A) which contains 665.7 kJ/mol of energy[20,21]. The

solid phase formation of such a long-lived metastable[22,23] allows CH$_3$CN isomerisation into CH$_3$NC and CH$_2$CNH through N$_2$(A) $\leftrightarrow$ CH$_3$CN energy transfer. It is important to notice that the two reaction pathways[8] leading to CH$_3$NC and CH$_2$CNH from CH$_3$CN are endothermic by 97.5 and 91.5 kJ/mol, respectively and have 261.5 and 368.6 kJ/mol as energy barriers, respectively. Even though CH$_2$CNH is slightly more stable by 6 kJ/mol than CH$_3$NC, it shows the highest barrier in the CH$_3$CN isomerization reaction and consequently among the three isomers it should be the less abundant.
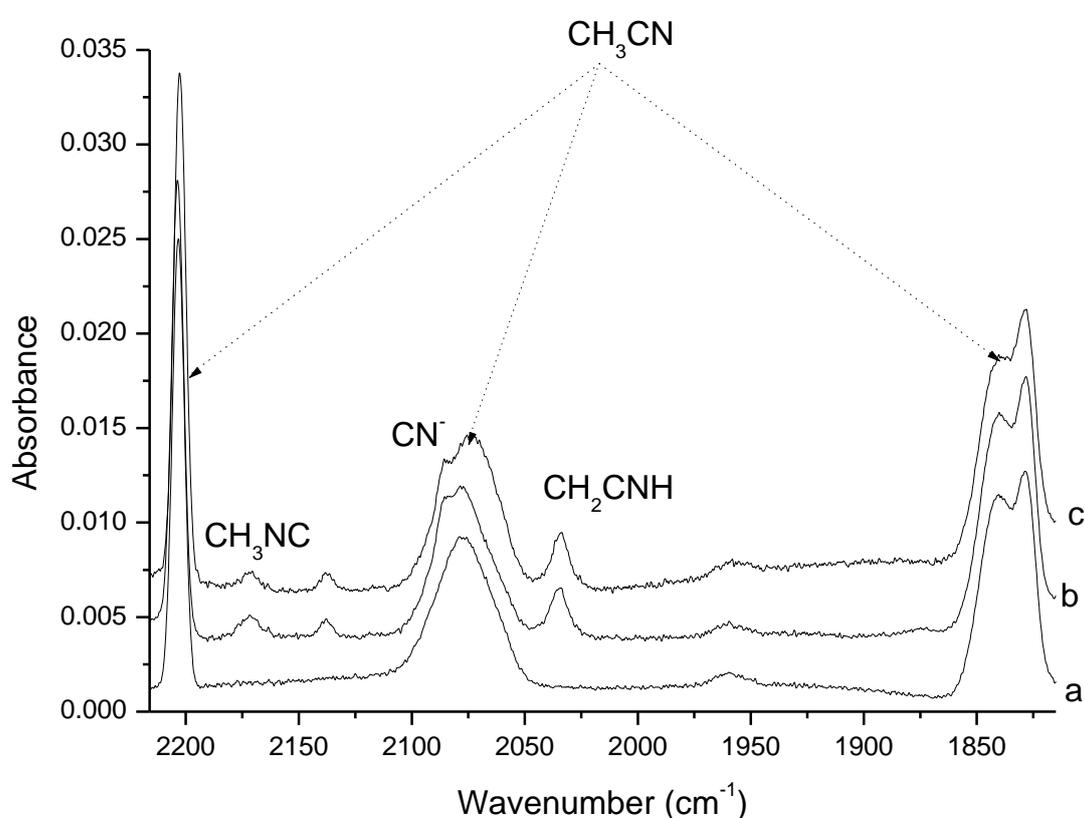
Figure 3: Zoom of figure 1 in 2200-1840 cm^{-1} spectral region. a) CH$_3$CN + N$_2$ co-deposition at 20 K. b) CH$_3$CN + N/N$_2$ co-deposition at 20 K. c) CH$_3$CN + N/N$_2$ co-deposition at 20 K, followed by a sample heating to 40 K. The band at 2138 cm^{-1} is due to CO molecule, a sample impurity usually detected in experiments using atom-bombardment.

The goal of the present work is to investigate the behavior of CH$_3$CN + N(^{4}S) solid state reaction between 10 and 40 K where the N(^{4}S)-N(^{4}S) recombination would be much more efficient than in the 3-10 K temperature range. Spectrum 3c shows the results of CH$_3$CN +

N/N$_2$ co-deposition at 20 K, followed by a sample heating to 40 K. We notice, by comparing spectra 3b and 3c, that the intensities of the IR signals of the reaction products do not change after sample heating to 40 K. There is then no reaction taking place during the sample heating from 20 to 40 K and this could be linked to the amount of N-atoms in the CH$_3$CN + N/N$_2$ ices formed at 20 K. As at 20 K the mobility of N-atoms is very efficient[24], the CH$_3$CN + N reaction occurring during the sample deposition is totally complete. As all N-atoms have already recombined during the sample deposition, there are no more nitrogen atoms left in a sample prepared at 20 K and consequently, the sample heating from 20 to 40 K cannot induce the N(^{4}S)-N(^{4}S) recombination essential for the chemical transformation of CH$_3$CN in the solid phase.

The CH$_3$CN + N$_2$/N co-deposition carried out at 10 K, followed by a sample heating to 40 K is shown in figure 4. We note that the IR signals of the reaction products due to CH$_3$CN interacting with N-atoms, namely CH$_3$NC, CH$_2$CNH, and CN$^-$ are present in the IR spectrum recorded just after the sample deposition at 10 K (spectrum 4a). This proves that at 10 K, the mobility of the N-atoms is efficient enough to provoke N(^{4}S)-N(^{4}S) recombination and to allow the CH$_3$CN + N reaction to partially occur during the CH$_3$CN + N/N$_2$ co-deposition. As shown in spectrum 4b, counter to the CH$_3$CN + N/N$_2$ co-deposition carried out at 20 K, the heating of the sample formed at 10 K, to 40 K leads to an increase of the IR signals of the reaction products. Thus, just after the sample deposition at 10 K, there are still free N-atoms trapped in the mixed CH$_3$CN-N$_2$ ice which start recombining and transforming CH$_3$CN when the temperature of sample increases. However, comparison between spectra 4a and 4b shows that the IR signals of CH$_3$NC and CH$_2$CNH behave differently when the temperature of the sample increases. The heating of the sample from 10 to 40 K shows that the absorption band areas of CH$_3$NC and CH$_2$CNH increase from 0.005 to 0.010 cm^{-1} and from 0.016 to 0.049 cm^{-1}, respectively. In the N$_2$(A) + CH$_3$CN → N$_2$ + CH$_3$CN* → N$_2$ + CH$_3$NC or CH$_2$CNH processing, CH$_2$CNH the isomer with the highest energy barrier forms more efficiently in the solid phase during sample heating from 10 to 40 K. Converted into column densities (molecules cm^{-2}) by taking the band strengths[25] of CH$_2$CNH, A(=C=NH) and organic nitriles CH$_3$CN and CH$_3$NC, A(C≡N) around 7.2×10^{-17} and 2.2×10^{-18} cm molecule^{-1}, respectively, calculations of integrated intensities of the CN absorption bands show that the heating of the sample from 10 to 40 K leads to an increase of CH$_3$NC and CH$_2$CNH from 2.3×10^{15} to 4.6×10^{15} and from 2.2×10^{14} to 6.8×10^{14} molecule cm^{-2}, respectively. Taking absorption band area measurement uncertainties into account, we measure an [CH$_3$NC]/[CH$_2$CNH] abundance

ratio of 10.4 ± 1.2 just after the CH_3CN + N/N_2 sample deposition at 10 K. While the heating of the sample from 10 to 40 K leads to an [CH_3NC]/[CH_2CNH] ratio of 6.8 ± 0.8, showing that even though we form more of CH_3NC than CH_2CNH through CH_3CN + N solid state reaction, CH_2CNH formation becomes more favorable than that of CH_3NC during the sample heating.
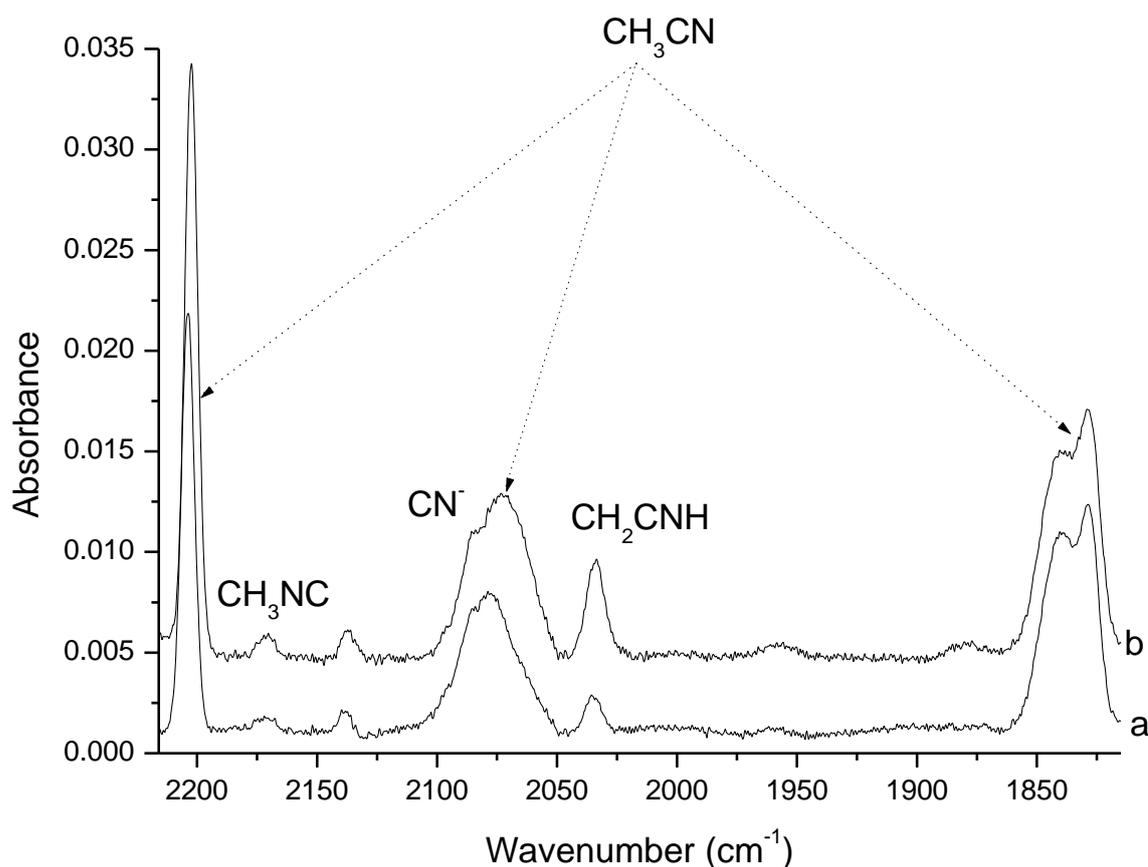
Figure 4: a) CH_3CN + N/N_2 co-deposition at 10 K. b) CH_3CN + N/N_2 co-deposition at 10 K and sample heating to 40 K.

From these two experimental results related to sample depositions at 10 and 20 K followed by sample heating to 40 K, we show that the CH_3CN + N reaction is temperature dependent. The reaction is complete with a CH_3CN + N/N_2 co-deposition carried out at 20 K as the N-atoms are used up during the sample formation. At 10 K, the reaction is not complete and keeps occurring in solid phase during the heating of the sample between 10 and 40 K to stimulate the $N(^4S)$-$N(^4S)$ recombination and to form $N_2(A)$ reactive metastable which induces the chemical transformation of CH_3CN. However nitrogen molecules desorb[26] at 26 K and as the

CH$_3$CN + N seems to depend in the formation of N$_2$(A) reaction intermediate which also desorbs at 26 K, we have investigated a CH$_3$CN + N/N$_2$ co-injection at temperature higher than 26 K to avoid condensation of N$_2$ during the sample deposition. Spectra 5a, 5b and 5c show a comparative study of CH$_3$CN + N/N$_2$ co-injections at 10, 20 and 40 K, respectively. We notice that the CH$_3$NC, CH$_2$CNH, and CN$^-$ reaction products derived from CH$_3$CN + N solid state reaction are formed at 10 and 20 K but not at 40 K.

Consequently, even though a temperature of 40 K is high enough to increase the mobility of nitrogen atoms in the sample and to enhance the N(^{4}S)-N(^{4}S) recombination, it does not lead to the chemical transformation of CH$_3$CN when the reactants are co-deposited at 40 K. This proves that in order to be efficient in solid phase, the CH$_3$CN + N reaction needs the N$_2$(A) reaction intermediate with a surface residence time long enough to allow the N$_2$(A) ↔ CH$_3$CN energy transfer. While at 40 K, the residence time of N atoms on the surface is too short to even allow the N(^{4}S)-N(^{4}S) recombination. By varying the reaction temperature between 10 and 40 K, we give thus an upper limit for the solid state reactivity of atomic nitrogen which would be efficient only in a specific temperature range combining long residence time and high mobility of N-atoms to induce N(^{4}S)-N(^{4}S) recombination and then N$_2$(A) reaction intermediate formation.
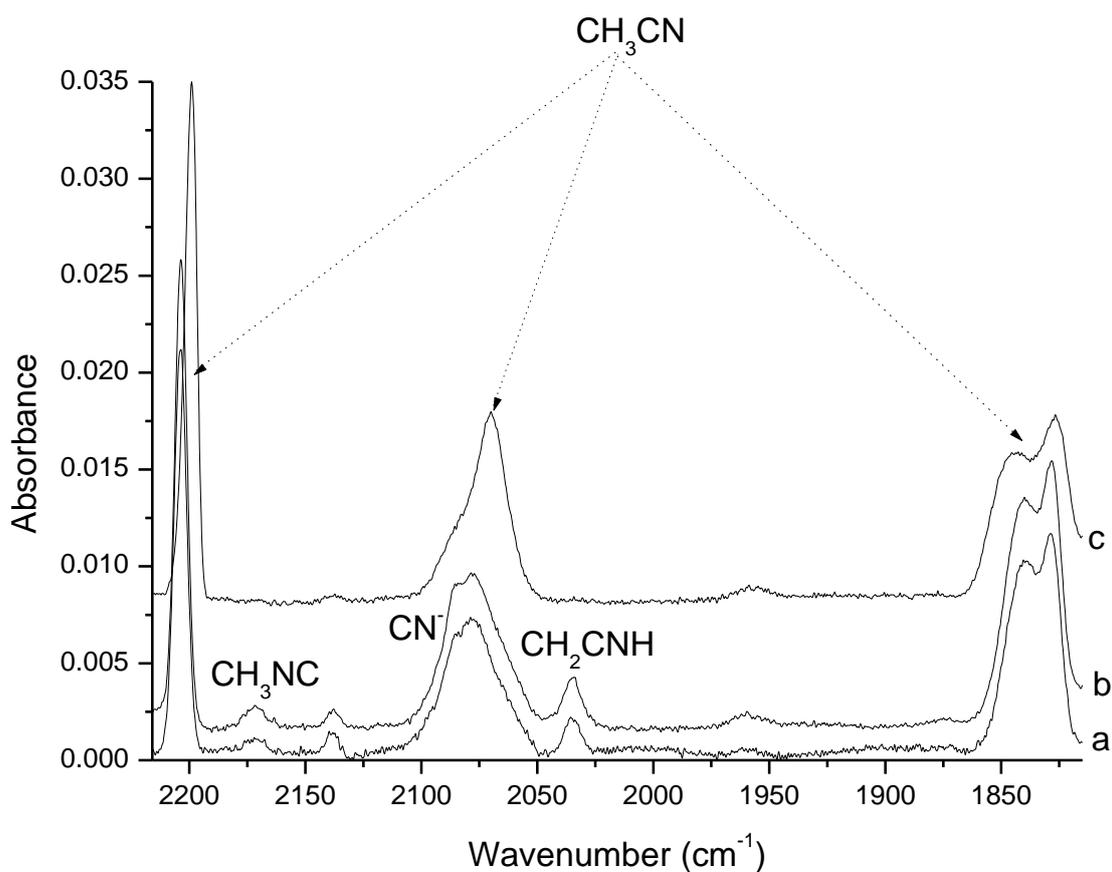
Figure 5: CH₃CN + N/N₂ co-deposition at a)10 K, b) 20 K, c) 40K

As mentioned above, we have the possibility with our experimental setup to investigate icy samples formed though indirect deposition through simultaneous condensation of CH_3CN + N/N_2 mixture gas suspended in the vacuum chamber. Spectra 6a and 6b show the results of indirect deposition at 20 K of CH_3CN + N_2 and CH_3CN + N/N_2, respectively. Although we observe the same IR signals as for a direct co-injection experiment but with very low intensity, there is a clear distinction between the signals due to the reactants and those due to the reaction products.

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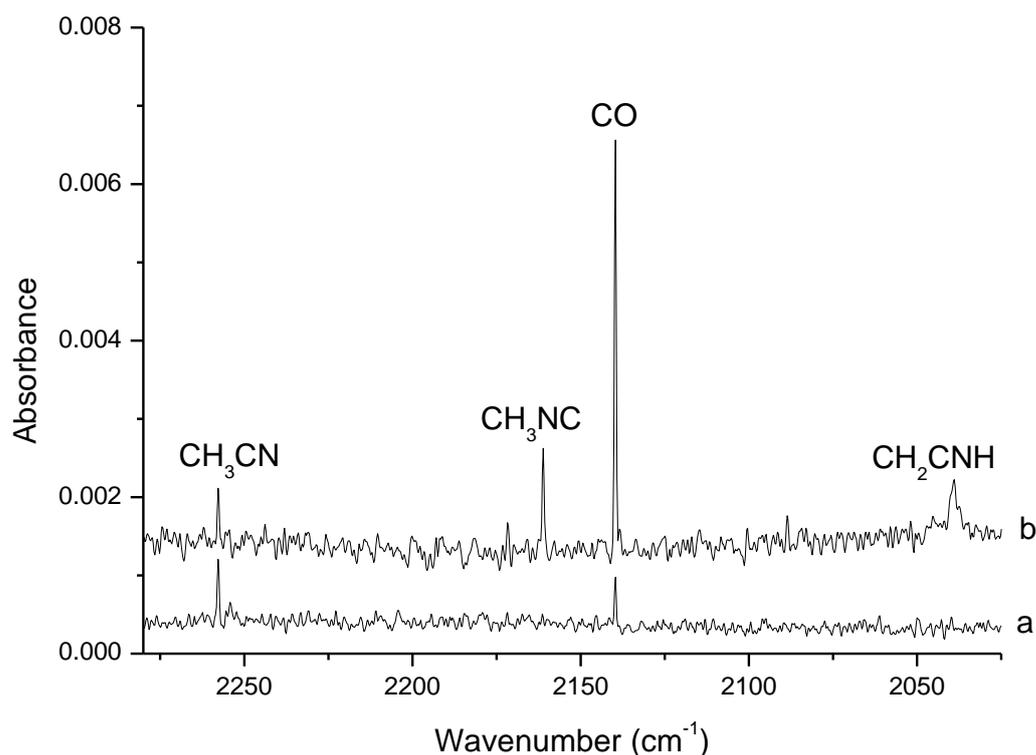
Figure 6: Simultaneous condensation at 20 K of mixture gas suspended in the vacuum chamber of a) $CH_3CN + N_2$ b) $CH_3CN + N/N_2$. CO molecule is detected as an impurity.

We have calculated the integrated absorption areas of the CN absorption bands of CH_3CN, CH_3NC and CH_2CNH, for direct (spectrum 1b) and indirect co-depositions (spectrum 6b). We found a set of (9.70, 0.013 and 0.025 cm^{-1}) and (0.001, 0.002 and 0.003 cm^{-1}) for the integrated absorption areas of (CH_3CN, CH_3NC, CH_2CNH), respectively, with relative uncertainties ranged between 0.5 and 20%. Knowing the band strengths[25] of the CN absorption bands of CH_3CN, CH_3NC and CH_2CNH at 2255, 2167 and 2038 cm^{-1} (2.2×10^{-18} cm molecule^{-1} for CH_3CN, CH_3NC and 7.2×10^{-17} cm molecule^{-1} for CH_2CNH) allows to have a concentration distribution between the three species for the two deposition methods. For the direct $CH_3CN + N/N_2$ co-deposition, we form a solid sample made of 4.4×10^{18} molecule cm^{-2} of CH_3CN mixed to 5.9×10^{15} and 3.5 10^{14} molecule cm^{-2} of CH_3NC and CH_2CNH, respectively. It is mainly a CH_3CN ice containing 0.13% of CH_3NC and 0.008% of CH_2CNH. While for the indirect co-deposition, even if the CH_3CN is the primary reactant, the main species in the resulting solid sample is the reaction product CH_3NC, the less stable isomer of CH_3CN. In fact we measure 4.5×10^{14} molecule cm^{-2} of CH_3CN versus 9.0×10^{14} and 4.2×10^{13} molecule cm^{-2} of CH_3NC and CH_2CNH, respectively. It is a mixed ice made of 64.6% of

CH$_3$NC, 32.3% of CH$_3$CN and 3.1% of CH$_2$CNH. These two co-deposition methods give concentration ratios [CH$_3$CN]/[CH$_3$NC]/[CH$_2$CNH] equal to 4400/5.9/0.4 and 4.5/9.0/0.4 for the direct and indirect co-depositions, respectively. Table 1 sums up the column densities of the three isomers involved in CH$_3$CN + N reaction, for samples formed through direct and indirect CH$_3$CN + N/N$_2$ co-deposition at 20 K.

Table 1: Column densities of CH$_3$CN, CH$_3$NC and CH$_2$CNH in interstellar ice analogues formed through direct and indirect CH$_3$CN + N/N$_2$ co-depositions at 20 K.

Molecule	Column Density / molec cm^{-2}	
	Direct deposition	Indirect deposition
CH$_3$CN	4.4×10^{18}	4.5×10^{14}
CH$_3$NC	5.9×10^{15}	9.0×10^{14}
H$_2$CCNH	3.5×10^{14}	4.2×10^{13}

Taking measurement uncertainties into account, we have measured [CH$_3$NC]/[CH$_2$CNH] abundance ratios of 16.9 ± 2.0 and 21.4 ± 4.3 for the direct and indirect CH$_3$CN + N/N$_2$ co-deposition carried out at 20 K, respectively. As mentioned above this ratio has been estimated around 10.4 ± 1.2 for the direct co-deposition performed at 10 K. The [CH$_3$NC]/[CH$_2$CNH] ratio seems to depend not only in the temperature of the reactants co-deposition but also in the method of the formation of the solid sample, more precisely in how CH$_3$CN, N and N$_2$ reach the mirror surface of the sampler to form the CH$_3$CN containing ice.

We notice also that for a direct sample deposition, [CH$_3$NC]/[CH$_2$CNH] abundance ratio increases with increasing the temperature of CH$_3$CN + N/N$_2$ co-deposition while it shows a behavior completely different during the heating of the sample from 10 to 40 K. At 10 K just after the sample deposition CH$_3$NC and CH$_2$CNH have been formed with an [CH$_3$NC]/[CH$_2$CNH] abundance of 10.4 ± 1.2 which decreases to 6.8 ± 0.8 with increasing the sample temperature. Consequently, the evolution of [CH$_3$NC]/[CH$_2$CNH] abundance ratios versus temperature would inform in the mechanisms involved into CH$_3$NC and CH$_2$CNH formation from CH$_3$CN + N solid state reaction. By increasing the temperature of the reaction, high [CH$_3$NC]/[CH$_2$CNH] ratios would be obtained for CH$_3$CN + N reaction occurring at the interface solid-gas while low ratios are found for reactions taking place

exclusively in solid phase. In fact, during the sample deposition, the $CH_3CN + N$ reaction combines processes from solid phase, surface and interface solid-gas. While during the heating from 10 to 40 K, of the sample formed at 10 K the $CH_3CN + N$ reaction occurs only in solid phase, leading to a decrease of $[CH_3NC]/[CH_2CNH]$ abundance ratio from 10.4 ± 1.2 to 6.8 ± 0.8, showing that at high temperatures the most stable isomer is favored against the less stable one while at low temperatures the reverse occurs. Such a behavior is similar to that of the $[HNC]/[HCN]$ abundance ratio[27] which also shows a decrease with increasing temperature in star forming regions. In fact, the less stable isomer HNC is found[28] about 60.3 kJ/mol above HCN while CH_3NC is only 6 kJ/mol above[8] CH_2CNH. However in both cases, the mounts of the higher energy isomer seem to decrease with rising the temperature. Similarly in the case of HNCO metastable isomers, HOCN and HCNO which have been detected in several sources of prestellar cores and low-mass protostellar[29] objects the amount of HCNO isomer which is higher[30] in energy by 192 kJ/mol than HOCN seems to be depleted in molecular clouds when the temperature increases. In order to explain the behavior of $[HCNO]/[HOCN]$ abundance ratio of the two metastable isomers of HNCO versus temperature and why the less stable isomer HCNO is under-abundant with respect to HOCN in the warm sources but not in the cold ones, Schuurman et al. suggest that it would be due either the mechanism that converts HCNO into HOCN, in comparison[27] with the conversion of HNC into HCN in warm sources, or the solid state chemistry on interstellar grains which may play a key role in the relative abundances of $[HCNO]/[HOCN]$. The detection towards Sagittarius B2(N) hot cores of CH_3CN, CH_3NC and CH_2CNH with $[CH_3CN]/[CH_3NC]$ and $[CH_3CN]/[CH_2CNH]$ ratios approximately equal to 30 and 100, respectively, would suggest that the $[CH_3NC]/[CH_2CNH]$ abundance ratio should be around 7 which is the same order of magnitude as the one we obtain experimentally for $CH_3CN + N$ reaction when the temperature increases from 10 to 40 K. While in previous studies involving energetic processing of solid CH_3CN, Hudson[25] et al. showed that UV photolysis and proton irradiation of CH_3CN ices lead to the formation of CH_3NC and CH_2CNH with $[CH_3NC]/[CH_2CNH]$ abundance ratios equal to 1.7 and 0.3, respectively. The $[CH_3NC]/[CH_2CNH]$ ratios derived from UV photolysis and proton irradiation of CH_3CN ices are much lower than those reported from astronomical observations or those obtained through $CH_3CN + N$ solid state reactions. The present study suggests that CH_3NC and CH_2CNH would form in cold molecular regions of star forming regions where CH_3CN and nitrogen atoms may be trapped in the icy interstellar grains. CH_3NC and CH_2CNH would form in solid phase through $CH_3CN + N$ solid state reaction at temperatures lower than 40 K before desorbing in the gas phase. The analysis

[CH$_3$NC]/[CH$_2$CNH] ratios and their behaviors versus temperature would then permit to access to synthesis routes of CH$_3$NC and CH$_2$CNH form CH$_3$CN as precursor in the ISM.

4. CONCLUSIONS

We show by varying the reaction temperature between 10 and 40 K that CH$_3$CN + N is efficient in solid phase in a very specific temperature range, leading to the formation of CH$_3$NC and CH$_2$CNH with [CH$_3$NC]/[H$_2$C=C=NH] abundance ratios which depend in the temperature of the reaction and also in the environments where the reactants are trapped. To be efficient, the temperature domain of the CH$_3$CN + N reaction must combine long surface residence time and high mobility of N atoms to allow the N(^{4}S)-N(^{4}S) recombination and the formation of the long lived metastable species N$_2$(A) which induces through energy transfer process the CH$_3$CN isomerization. Additionally, in order to change the environment where the three isomers involve, we have investigated two different methods of synthesis of our interstellar ice analogues containing CH$_3$CN and N as precursors. The first method is a traditional one, adopted by many groups studying molecule + atom/radical solid phase reactions, which consists on the co-deposition of the reactants on a surface of a cryogenic mirror located front of the reactants injection ports. The second method we have applied is to form the solid samples through an instantaneous condensation of the mixture gas suspended in the vacuum chamber on a cryogenic mirror. These two experimental methods are used simultaneously to give two different interstellar ice analogues under the same experimental conditions, however, we have managed with the latter method to get solid samples containing more reaction products than reactants which impacts the [CH$_3$CN]/[H$_2$C=C=NH]/[CH$_3$NC] abundance ratios. We have observed a decrease of [CH$_3$NC]/[CH$_2$CNH] abundance ratio by increasing the temperature of CH$_3$CN + N reaction, showing that at high temperatures the most stable isomer is favored against less stable one. Such a behavior is similar to those of the [HNC]/[HCN] and [HCNO]/[HOCN] abundance ratios which also shows a decrease with increasing temperature in molecular clouds.

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