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# Formation of methyl ketenimine ( $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ ) and ethylcyanide ( $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$ ) isomers through successive hydrogenations of acrylonitrile ( $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ ) under interstellar conditions: The role of $\text{CH}_3\text{C}^\circ\text{H}-\text{C}\equiv\text{N}$ radical in the activation of the cyano group chemistry

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**Abstract:** Possible formation routes of interstellar amino acids have been proposed where the first step consists in the transformation of organic nitriles ( $\text{RCH}_2-\text{C}\equiv\text{N}$ ) into ketenimines ( $\text{RCH}=\text{C}=\text{NH}$ ). Such a transformation shows high energy barriers and needs energetic processing to occur. We show in the present study that the CN bond could be activated through H-addition reactions to form ketenimines when starting from organic  $\alpha,\beta$ -unsaturated nitriles ( $\text{C}\equiv\text{N}$ ). Consequently both methyl ketenimine  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$  and ethylcyanide  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$  might have their origin from  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N} + 2\text{H}$  reaction occurring on the interstellar icy grains. During the hydrogenation of  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$  ice under interstellar conditions,  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$  has been formed with an abundance 10 times higher than that of  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ . Our measurements lead us to conclude that such a distribution would be directly linked to the  $\pi$ -electrons delocalization  $\text{H}_3\text{C}-\text{C}^\circ\text{H}-\text{C}\equiv\text{N} \leftrightarrow \text{H}_3\text{C}-\text{CH}=\text{C}=\text{N}^\circ$  occurring during the reduction of the CC double bond of acrylonitrile.

## Keywords:

astrochemistry – methods: laboratory – techniques: spectroscopic – ISM: molecules

## I. Introduction

The nitrogen-containing compounds account for about one third of the species detected in the interstellar medium (ISM). Organic carbonitriles ( $\text{RC}\equiv\text{N}$ ) including vibrationally excited species, isotopologues and isomeric forms have been widely detected in different regions of the ISM. In Sagittarius B2(N) massive star-forming region, large complex molecules with an alkyl substituent and a carbonitrile group have been observed, such as isobutyronitrile (i- $\text{C}_3\text{H}_7\text{CN}$ ) (Belloche et al. 2016a), the first molecule detected in the ISM with a branched carbon backbone, or n- $\text{C}_3\text{H}_7\text{CN}$  (Belloche et al. 2009) which was the third alkyl cyanide to be identified in this medium after  $\text{CH}_3\text{CN}$  (Solomon et al. 1971) and  $\text{C}_2\text{H}_5\text{CN}$  (Johnson et al. 1977). All  $^{13}\text{C}$  and  $^{15}\text{N}$  substituted isotopologues of acetonitrile and ethylcyanide have been detected toward Orion or Sagittarius including bis-labeled compounds (Demyk et al. 2007; Margulès et al. 2009; Margulès et al. 2016). In the case of deuterated isotopologues of ethylcyanide, Margulès et al. (2009) have investigated the rotational spectra of the two monodeuterated ethylcyanide  $\text{CH}_2\text{DCH}_2\text{CN}$  and  $\text{CH}_3\text{CHDCN}$  in order to assist the possible detection of both compounds. Nevertheless neither  $\text{CH}_3\text{CHDCN}$  nor  $\text{CH}_2\text{DCH}_2\text{CN}$  have been properly detected while  $\text{CDH}_2\text{CN}$  has been unambiguously observed by Belloche et al. (2016b).

For the unsaturated derivatives, several 1-alkynylcyanides have been observed and they constitute to date the most represented family in the ISM, namely:  $\text{HC}\equiv\text{C}-\text{CN}$  (Turner et al. 1971),  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CN}$  (Avery et al. 1976),  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CN}$  (Kroto et al. 1978),  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CN}$  (Brotten et al. 1978),  $\text{MeC}\equiv\text{C}-\text{CN}$  (Brotten et al. 1984) and  $\text{Me}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CN}$  (Snyder et al. 2006). The acrylonitrile  $\text{H}_2\text{C}=\text{CHCN}$  (Gardner and Winnewisser 1975) has been detected in the molecular cloud SgrB2 and is to date the only 1-alkenylcarbonitrile detected in the ISM. In TMC-1, with a column density of the order of  $10^{12}$  molecules  $\text{cm}^{-2}$  and a rotational temperature of 4 K,  $\text{H}_2\text{C}=\text{C}=\text{CHCN}$  has been found to be more abundant than  $\text{CH}_3\text{CCCN}$  by a factor of  $\sim 4.5$  (Lovas et al. 2006a).

On the other hand, imines seem to be relatively uncommon in the ISM, with only a few exceptions detected in Sgr B2: methanimine ( $\text{H}_2\text{C}=\text{NH}$ ) (Godfrey et al. 1973), E- and Z-ethanimine ( $\text{CH}_3\text{CH}=\text{NH}$ ) (Loomis et al. 2013), the E-cyanomethanimine ( $\text{HN}=\text{CHCN}$ ) (Zaleski et al. 2013) and the Z-derivative (Rivilla et al. 2018). Ketenimine (1-propen-1-imine,  $\text{H}_2\text{C}=\text{C}=\text{NH}$ ) was tentatively observed in Sgr B2 by Lovas et al. (2006b) who proposed a direct formation from its isomer ( $\text{CH}_3\text{CN}$ ) by tautomerization driven by shocks in star-forming region. In the case of the ethanimine detection in Sgr B2(N), a column density on the

order of  $10^{13}$  molecules  $\text{cm}^{-2}$  and a rotational temperature of 6 K were measured. Accordingly, Loomis et al. (2013) proposed several reaction pathways to form the interstellar  $\text{CH}_3\text{CHNH}$  which may involve sequential hydrogen atom addition on  $\text{CH}_3\text{CN}$  in interstellar ices. In this context laboratory investigation have been focused in energetic processing leading to isomerization of  $\text{CH}_3\text{CN}$  into  $\text{CH}_3\text{NC}$  and  $\text{CH}_2\text{CNH}$ . The formation of  $\text{CH}_2\text{CNH}$  having a relatively less bonded  $\text{C}=\text{N}$  group would lead to a rich chemistry through either energetic (UV) or non energetic processing (H-addition reaction) and could be considered as one of the first steps towards the chemical complexity of the ISM. The strong bonded CN group in CN-containing species such as  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NC}$  seems to be chemically inactive to induce complex chemistry in the coldest regions of the ISM under non-energetic conditions. In this context many groups have investigated the chemical reactivity on interstellar ice analogues containing species with a CN group. Kimber et al. (2018) have recently shown that, in the case of  $\text{C}_2\text{H}_3\text{CN} + \text{O}$  solid state reaction, the oxygen atom attack occurred totally on the  $\text{C}=\text{C}$  double bond while the CN group remained unchanged. The high stability of the CN group has also been observed in reactions involving acid species such as HCN (Noble et al. 2003), HNC (Moore & Hudson 2003) and  $\text{HC}_3\text{N}$  (Couturier-Tamburelli et al. 2012) which interacting in solid phase with ammonia involved chemical transformation through thermal induced acid–base reactions to form  $\text{H}_4\text{N}^{(+)}\text{-CN}^{(-)}$  and  $\text{H}_3\text{N}^{(+)}\text{-CH}=\text{C}^{(-)}\text{-CN}$  zwitterion, respectively. Naturally, in order to activate the CN group in CN-containing species such as  $\text{CH}_3\text{CN}$  many investigations have been focused into  $\text{CH}_3\text{CN} \rightleftharpoons \text{CH}_2\text{CNH}$  photo-induced conversion. Figure 1 shows the energy position levels of the three  $\text{CH}_3\text{CN}$  isomers.

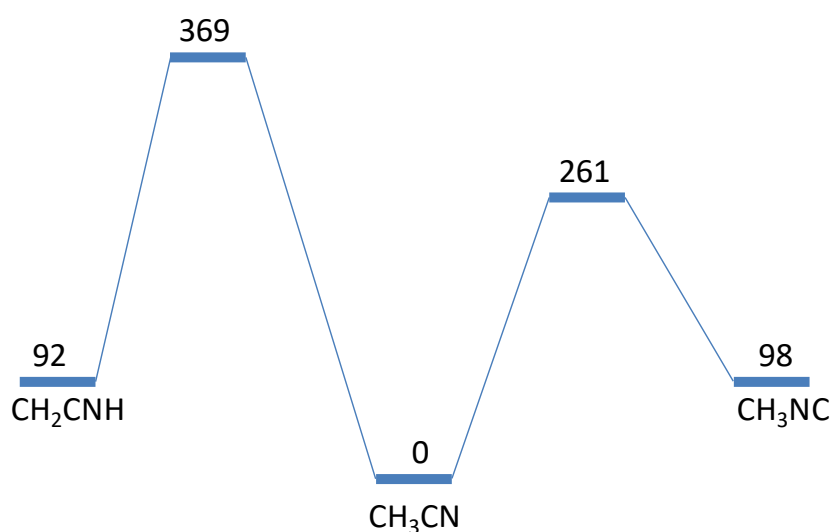


Figure 1: Relative energies (kJ/mol) of  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NC}$  and  $\text{CH}_2\text{CNH}$  separated by energy barriers (according to Cho (2013)).

Cho et al. (2013) investigated the formation of ketenimine  $\text{CH}_2\text{CNH}$  through laser irradiation of  $\text{CH}_3\text{CN}$  trapped in argon matrix. Hudson and Moore (2004) investigated UV photolysis and  $\text{p}^+$  bombardment of several saturated and unsaturated nitriles such as  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CH}_2\text{CN}$  and  $\text{CH}_2\text{CHCN}$ . They showed that in the case of saturated nitriles,  $\text{CH}_3\text{CN}$  isomerizes into  $\text{CH}_3\text{NC}$  and  $\text{CH}_2\text{CNH}$ , in addition to the formation of  $\text{HCN}$  and  $\text{CH}_4$ , while  $\text{CH}_3\text{CH}_2\text{CN}$  isomerizes into  $\text{CH}_3\text{CH}_2\text{NC}$  and  $\text{CH}_3\text{CHCNH}$  and dehydrogenates leading to the formation of unsaturated nitriles ( $\text{CH}_2=\text{CHCN}$ ,  $\text{CHCCN}$ ). In all these experiments carried out under energetic conditions, we notice that the CN bond is not dissociated but partially converted into less bonded group  $\text{C}=\text{N}$ . In the present work, we have investigated the hydrogenation of saturated and unsaturated nitriles,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CH}_2\text{CN}$ ,  $\text{CH}_2\text{CHCN}$  under ISM conditions, in order to monitor the activation of the CN group induced by H-addition reactions which are known as non-energetic processing and to dominate the chemistry of dense molecular clouds.

## II. Experimental and theoretical section

Acrylonitrile also known as prop-2-enenitrile ( $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ ) and ethylcyanide ( $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$ ) are commercially available from Sigma-Aldrich with a purity of 99 %. Hydrogen (99.9995 %) and Deuterium (99.999 %) gases were purchased from Messer. Pure interstellar ice analogues made of acrylonitrile or ethylcyanide were prepared under ultrahigh vacuum of  $10^{-10}$  mbar by condensation of the corresponding vapor gas on a Rh-plated copper mirror maintained at 10 K using a closed-cycle helium cryogenerator (Sumitomo cryogenics F-70). Before condensation, the pure organic compounds are kept in cooling baths made of liquid nitrogen and acetone, in order to control the fractions of saturated vapor pressures injected into the experimental chamber and to evaluate the amounts of deposited material forming the organic ices at 10 K. A microwave discharge, purchased from SPECS company, is used as H-atomic source in order to study the hydrogenation of our organic ices under ISM conditions. It has been modified by adding to its output a curved Teflon tube. With such a structure the UV light from the plasma discharge into  $\text{H}_2$  gas is completely blocked in order to avoid possible photo-irradiation processing during the H-bombardment of our samples. The sample holder consists of six mirrors optically polished. All these mirrors are mounted on a hexagonal face copper block which provides thermal transmission and stabilization in the cold environment. This hexagonal copper block can be rotated up by  $0^\circ$  to  $360^\circ$  which allows to a given cryogenic mirror to orient in different directions, as shown in figure 2: front of the

reactant injection ports, front of Fourier transform infrared (FTIR) spectrometer, or towards the microwave discharge.

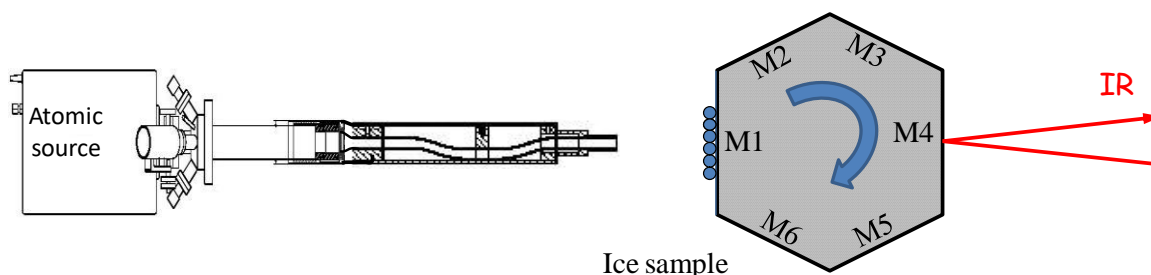


Figure 2: Ice bombardment experiment.

Just after the sample depositions, the ices are bombarded during 45 min by atomic hydrogen generated with a flux of  $10^{17}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$  from a microwave discharge into molecular hydrogen gas. We have measured the yield dissociation of  $\text{H}_2$  molecules around 15 %, using a Quadrupole Mass Spectrometer (QMS - Hidden Analytical). The atom flux of  $10^{17}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$  has been estimated with an uncertainty of 40 % (Krim et al. 2018). Although water is the main component of the interstellar ices we have preferred to investigate the H-bombardment on pure organic ices in order to increase the probability of interactions between the H-atoms and organic molecules. Before and after H/ $\text{H}_2$  bombardment, the solid samples are probed by recording infrared spectra between 5000 and 500  $\text{cm}^{-1}$ , with a resolution of 0.5  $\text{cm}^{-1}$ , using a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer, in the transmission–reflection mode with an incidence angle of  $8^\circ$ . Similar experiments have also been carried out using D/ $\text{D}_2$  bombardment in order to characterize the isotopic composition of the reaction products formed during the hydrogenation processing. Additional H-addition reaction experiments have also been performed by varying the H-atom fluxes. All the hydrogenation experiments carried out in the present study have been performed with very high H-atom fluxes in comparison with those estimated (Accolla et al. 2011) for dense molecular clouds ( $\sim 10^4$  atoms  $\text{cm}^{-2} \text{s}^{-1}$ ). However, such experimental conditions are very important in order to reach high reaction yields in a few hours of laboratory experiments. This would help to have an unambiguous description at the molecular scale in how COMs would interact with hydrogen atoms in solid state on the surface of interstellar grains.

Quantum chemical theory was used to characterize structures and energies of minima and the transition states for acrylonitrile ( $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ ) + H reactions, where the H may in principle add to any of the four atoms in the C1–C2–C3–N backbone. Optimizations of the reactant,

products, and transition states were performed with unrestricted second-order perturbation theory (Møller & Plesset 1934) (UMP2) as implemented in Gaussian09 (Frisch et al. 2009) (following initial B3LYP density function theory optimizations for the four H addition adducts). Spin-projected MP2 energies (PMP2) were used to refine the relative energetics. We also performed some calculations at the RCCSD(T) level (Purvis & Bartlett 1982, Raghavachari et al. 1989, Knowles et al. 1993; Watts et al. 1993) with Molpro 2010.1 (Werner et al. 2008), including single point calculations at the UMP2 geometries and limited optimizations. Molpro was also utilized to perform some internally contracted multireference configuration interaction calculations at the MRCI+Q level (Knowles & Werner 1988, Werner and Knowles 1988). The structure of acrylonitrile was reoptimized at the RCCSD(T) level, and partial optimizations were performed for the critical transition states at the same level of theory by scanning the dominant part of the reaction coordinate (the CH distance for the H atom being added for addition steps and the relevant angle for shifting the H from the C1 adduct to the C2 adduct). Relative energetics at the PMP2 and RCCSD(T) levels of theory were corrected with UMP zero-point energies. All of the calculations enumerated here were performed with aug-cc-pVTZ basis sets (Dunning 1989; Kendall et al. 1992). In the discussion below, PMP2//UMP2 and RCCSD(T)//UMP2 indicate single-point calculations at the PMP2 or RCCSD(T) levels, respectively, at the UMP2 geometry.

### III. Results

Before studying the solid state  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + \text{H}$  reaction, we have first investigated hydrogenations of saturated cyanides species such as  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CH}_2\text{CN}$  in order to confirm or contradict that  $\text{C}\equiv\text{N}$  group would be efficiently converted into imine or amine ( $\text{RCH}=\text{NH}$  and  $\text{RCH}_2-\text{NH}_2$ ) under interstellar conditions. Accordingly, Theulé et al. (2011) investigated the hydrogenation of solid hydrogen cyanide HCN and methanimine  $\text{CH}_2\text{NH}$  at low temperature. Using only mass spectrometry to discriminate all the reaction products releasing into the gas phase during the sublimation of solid hydrogen cyanide beforehand hydrogenated at 10K, they have shown that HCN can be hydrogenated to the fully saturated species methylamine  $\text{CH}_3\text{NH}_2$ . However, they did not observe  $\text{CH}_2\text{NH}$  which is a stable hydrogenation-intermediate species for the HCN + H reaction. The non-detection of  $\text{CH}_2\text{NH}$  during the HCN hydrogenation remains actually puzzling, especially when the same experimental study showed that the H-atom bombardment of solid  $\text{CH}_2\text{NH}$  leads to the formation of methylamine  $\text{CH}_3\text{NH}_2$  and the  $\text{CH}_2\text{NH} + \text{H}$  reaction seems far from being instantaneous or 100 % efficient. In the present study, we have investigated the hydrogenation

of saturated nitriles larger than HCN such as  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CH}_2\text{CN}$ . We found that  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CH}_2\text{CN}$  ices behave similarly under H attacks. Consequently, we present thereafter only the experimental results related to the hydrogenation of  $\text{CH}_3\text{CH}_2\text{CN}$  which is also one of the potential reaction products for the second system we will present afterward, concerning the hydrogenation of an unsaturated nitrile,  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + \text{H}$ .

Figures 3a and 3b show the IR spectra of ethyl cyanide  $\text{CH}_3\text{CH}_2\text{CN}$  ice before and after H-bombardments, respectively. The assignments of all vibrational modes (Duncan and Janz 1955) are directly reported in figure 3. The IR signal characteristic of CN group is located at  $2247.1 \text{ cm}^{-1}$  for  $\text{CH}_3\text{CH}_2\text{CN}$ . Figure 3c shows the difference spectrum before and after H bombardments as an example of the results one may obtain, under our experimental conditions, by bombarding  $\text{CH}_3\text{CH}_2\text{CN}$  ice formed at 10 K by H-atoms during 45 min. By comparing figures 3a and 3b, one can notice that the IR spectra of  $\text{CH}_3\text{CH}_2\text{CN}$  before and after H-bombardments are quite similar. We detect no new signal which would be attributed to a given reaction product of  $\text{CH}_3\text{CH}_2\text{CN} + \text{H}$  reaction. In such experiments, the difference spectrum before and after sample H-bombardment may reveal new information concerning the reaction, where the negative signals would be due to  $\text{CH}_3\text{CH}_2\text{CN}$  consumed during the reaction while the positive signals would inform on the nature of the resulting reaction products formed. In our case, we do observe no new signal which can be attributed to a reaction product. There is no a real decrease in ethyl cyanide absorbance bands after hydrogenation processing. Consequently,  $\text{CH}_3\text{CH}_2\text{CN}$  molecules are chemically inactive when interacting with H atoms under IMS conditions. The only new positive signal observed in the difference spectrum of figure 3c is due to  $\text{CO}_2$  ( $2343 \text{ cm}^{-1}$ ), a species usually detected as traces in our bombardment experiments.



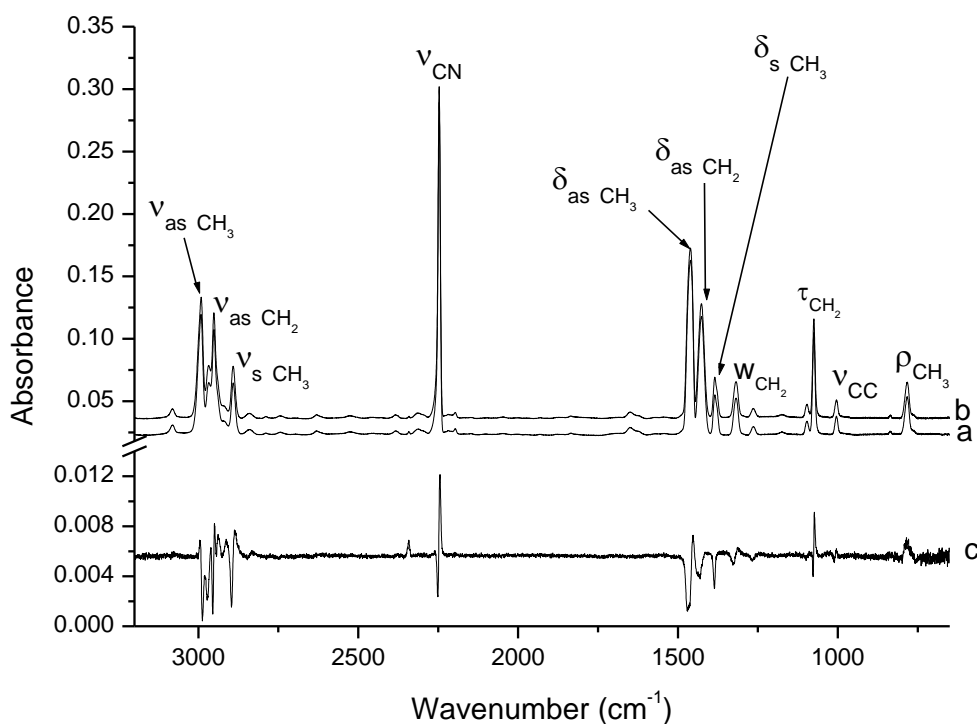


Figure 3: a) IR spectrum of ethyl cyanide ( $\text{CH}_3\text{CH}_2\text{-C}\equiv\text{N}$ ) ice formed at 10K. b) Hydrogenation of solid ethyl cyanide at 10K. c) Difference spectrum before and after H-bombardments of ethyl cyanide ice formed at 10 K. v: stretch,  $\delta$ : bend, w: wag,  $\tau$ :twist,  $\rho$ : rock

Similar results, not shown here, have been obtained under the same experimental conditions during the H bombardments of  $\text{CH}_3\text{CN}$  ice, proving that the CN group in saturated cyanides compounds such as  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CH}_2\text{CN}$  seems to be stable under H bombardments and cannot be a source of compounds with  $=\text{NH}$  or  $-\text{NH}_2$  functional groups in ISM through H-addition processing. Based on these first results one can anticipate that  $\text{CH}_2=\text{CH-C}\equiv\text{N} + \text{H}$  reaction would lead to the formation of  $\text{CH}_3\text{CH}_2\text{CN}$  through the selective hydrogenation of the C=C bond. In order to confirm or invalidate such a supposition figures 4a and 4b show the spectra of  $\text{CH}_2=\text{CH-C}\equiv\text{N}$  ice before and after H-bombardments, respectively. Figure 4c shows the difference spectrum before and after H-bombardments of  $\text{CH}_2=\text{CH-C}\equiv\text{N}$  ice, while figure 4d illustrates the IR spectrum of  $\text{CH}_3\text{CH}_2\text{CN}$  as a reference spectrum for the reaction product we are supposed to obtain during the hydrogenation of acrylonitrile ice.

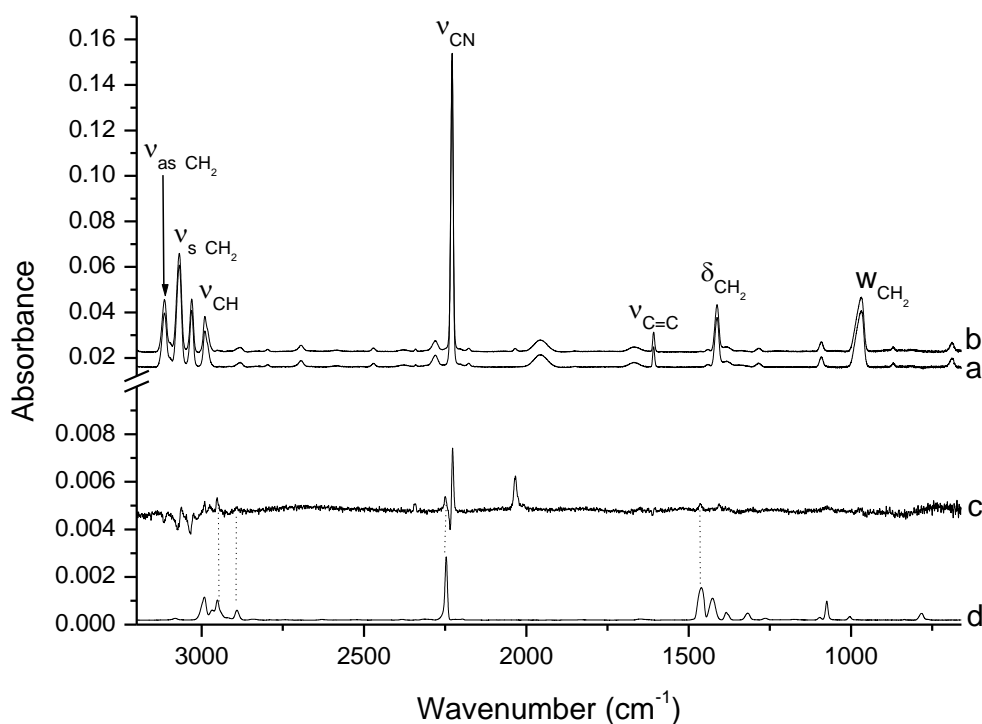


Figure 4: a) IR spectrum of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice formed at 10K. b) IR spectrum of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice after H-bombardments. c) Difference spectrum before and after H-bombardments of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice. d) Deposition of pure  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  on a mirror maintained at 10 K. v: stretch,  $\delta$ : bend, w: wag.

The assignments of all vibrational modes of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  (Halverson et al. 1948) are directly reported in figure 4. As shown in figures 4a and 4b, the characteristic IR signal of the CN group in unsaturated  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  is located at  $2228.6\text{ cm}^{-1}$  while that, in the saturated  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$ , is observed at  $2247.1\text{ cm}^{-1}$ . The IR analysis of the  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  spectra before and after H-bombardments shows that new signals appear clearly at  $2952.3$ ,  $2895.8$ ,  $2247.4$ ,  $2034.4$  and  $1464.5\text{ cm}^{-1}$ . These new signals are more clearly visible in the difference spectrum of figure 4c. Most of the new signals observed in the difference spectrum of figure 4c fit the main IR signatures of  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  molecules which absorb under our experimental conditions at  $2951.7$ ,  $2891.1$ ,  $2247.1$  and  $1461.8\text{ cm}^{-1}$  as shown in the reference spectrum of  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  ice of figure 4d. One can then conclude that  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  may be converted into  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  through  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + 2\text{ H}$  reaction. Although, there is a good agreement between the spectral positions of the new absorption bands observed in the difference spectrum of figure 4c and those of solid  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$ , we notice that the most intense signal observed in the difference spectrum is not that corresponding to one of  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  vibrational modes. Another new signal is observed in the difference spectrum

at  $2034.4 \text{ cm}^{-1}$  and may be due to ketenimine formation, a species with a  $\text{C}=\text{C}=\text{NH}$  functional group. Although complete IR spectra of ketenimine are not available in the literature, many investigation using UV photolysis of CN-bearing species have already shown that the characteristic IR absorption band of several ketenimines (Jacox 1979; Hudson & Moore 2004) are located in the Mid-IR between  $2029$  and  $2038 \text{ cm}^{-1}$ . In this context, Hudson & Moore reported the characteristic IR spectral positions of  $\text{CH}_2=\text{C}=\text{NH}$  (the isomer of  $\text{CH}_3\text{CN}$ ) and  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$  (the isomer of  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$ ) at  $2033$  and  $2032 \text{ cm}^{-1}$ , respectively. As the difference spectrum of figure 4c is mainly dominated by a signal at  $2034.4 \text{ cm}^{-1}$ , we suggest that in addition to  $\text{CH}_3\text{CH}_2\text{CN}$  formation, another reaction product, the methyl ketenimine ( $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ ) can be formed through  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + 2\text{H}$  reaction. The amounts of reactant consumed ( $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ ) and products formed ( $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  and  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ ) can be evaluated from the difference spectrum before and after H-bombardments of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice (figure 4c). The column densities  $n$  ( $\text{molecules cm}^{-2}$ ) of the reactant and products can be deduced from integrated intensities of the corresponding characteristic absorption bands (Mencos et al. 2017). Table 1 presents the IR positions and strengths of CN bands for  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ ,  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  and  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ . As it has been widely discussed in Hudson and Moore (2004) work, the band strengths of ketenimine  $\text{A}(\text{C}=\text{NH})$  and organic nitriles  $\text{A}(\text{C}\equiv\text{N})$  have been estimated around  $7.2 \cdot 10^{-17}$  and  $2.2 \cdot 10^{-18}$   $\text{molecules cm}^{-1}$ , respectively. Calculations of integrated intensities of the CN absorption band show that under our experimental conditions,  $8.8 \cdot 10^{15}$   $\text{molecules cm}^{-2}$  of  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$  are consumed to produce only  $3.1 \cdot 10^{15}$  and  $0.3 \cdot 10^{15}$   $\text{molecules cm}^{-2}$  of  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  and  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ , respectively. This suggests that more than 60 % of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  is not reduced through  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + \text{H}$  solid state reaction but desorbs during the hydrogenation processing. Although those estimations cannot give the exact amount of the products formed during the hydrogenation of  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$ , they help to quantify the  $[\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}]/[\text{CH}_3\text{CH}=\text{C}=\text{NH}]$  ratio in order to compare it to ratios potentially given from astronomical observations of dense molecular clouds. We estimate that  $[\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}]/[\text{CH}_3\text{CH}=\text{C}=\text{NH}] = 10$  with an error of  $\pm 30$  %. Consequently the  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + 2\text{H}$  reaction produce 91 % of  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  and 9 % of  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ .

Table 1: Column densities of reactants consumed ( $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ ) and products formed ( $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  and  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ ) during  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + 2\text{H}$  reaction

	$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	$\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$	$\text{CH}_3\text{CH}=\text{C}=\text{NH}$
Amounts of	reactant consumed	Products formed	
Mode	$-\text{C}\equiv\text{N}$	$-\text{C}\equiv\text{N}$	$\text{C}=\text{N}$
Spectral position ( $\text{cm}^{-1}$ )	2228.6	2247.1	2034.4
Integrated IR intensity ( $\text{cm}^{-1}$ )	0.017	0.006	0.020
A ( $\text{cm molecule}^{-1}$ )	$2.2 \cdot 10^{-18}$	$2.2 \cdot 10^{-18}$	$7.2 \cdot 10^{-17}$
n ( $\text{molecules cm}^{-2}$ )	$8.8 \cdot 10^{15}$	$3.1 \cdot 10^{15}$	$0.3 \cdot 10^{15}$

The attribution of the  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$  structure to the product formed under our experimental conditions is based only on the fact that we have detected a signal characterizing the  $\text{C}=\text{C}=\text{NH}$  vibrational mode at  $2034.4 \text{ cm}^{-1}$ . However, in order to confirm the formation of ketenimine through  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + 2\text{H}$  reaction, we have carried out the same experiments using H/D isotopic substitution to study the  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + 2\text{D}$  reaction. Figures 5a and 5b show the IR spectra of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice before and after D-bombardments, respectively, while Figures 5c and 5d show the IR spectra of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice before and after H-bombardments, respectively. We notice that the  $2034.4 \text{ cm}^{-1}$  band attributed to ketenimine and observed during the bombardment of the acrylonitrile ice with H-atoms is red shifted by  $19.4 \text{ cm}^{-1}$  (spectral band position measured at  $2015.0 \text{ cm}^{-1}$ ), which proves that the reaction product we have detected during the H- and D-bombardments contains  $\text{C}=\text{C}=\text{NH}$  and  $\text{C}=\text{C}=\text{ND}$  functional groups, respectively. This is in good agreement with the H/D isotopic substitution in ketenimines as Jacox (1979) has already reported that  $\text{H}_2\text{C}=\text{C}=\text{NH}$  and  $\text{D}_2\text{C}=\text{C}=\text{ND}$  isotopomers have their spectral position ranged between  $1998$  and  $2040 \text{ cm}^{-1}$ .

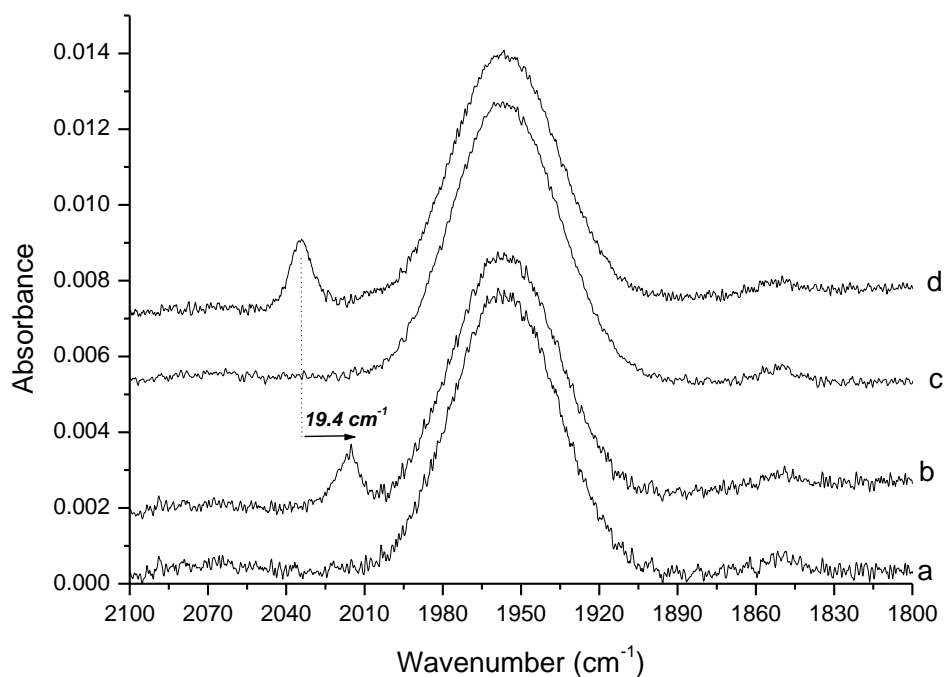


Figure 5: a) IR spectrum of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice formed at 10K. b) IR spectrum of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice after D-bombardments. c) IR spectrum of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice formed at 10K. d) IR spectrum of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice after H-bombardments.

Additionally, we have investigated the influence of the atomic hydrogen flux on the IR intensity of the band we attributed to ketenimine. As mentioned in the experimental section, there are six cryogenic mirrors arranged hexagonally on the sample holder. With such a configuration, we can then monitor the flux of H atoms bombarding different ices with the same thickness. Three similar  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$  ices have been deposited at 10 K on three mirrors M1, M2 and M4 as shown in figure 6. During the same H-bombardment experiment, all the mirrors are directly or indirectly bombarded by H atoms. The sample on mirror M1 has been put front of the microwave discharge to be straight bombarded while the two samples deposited on mirrors M2 and M4 are indirectly exposed to H atoms, with H-fluxes lower in comparison with that received by Mirror M1.

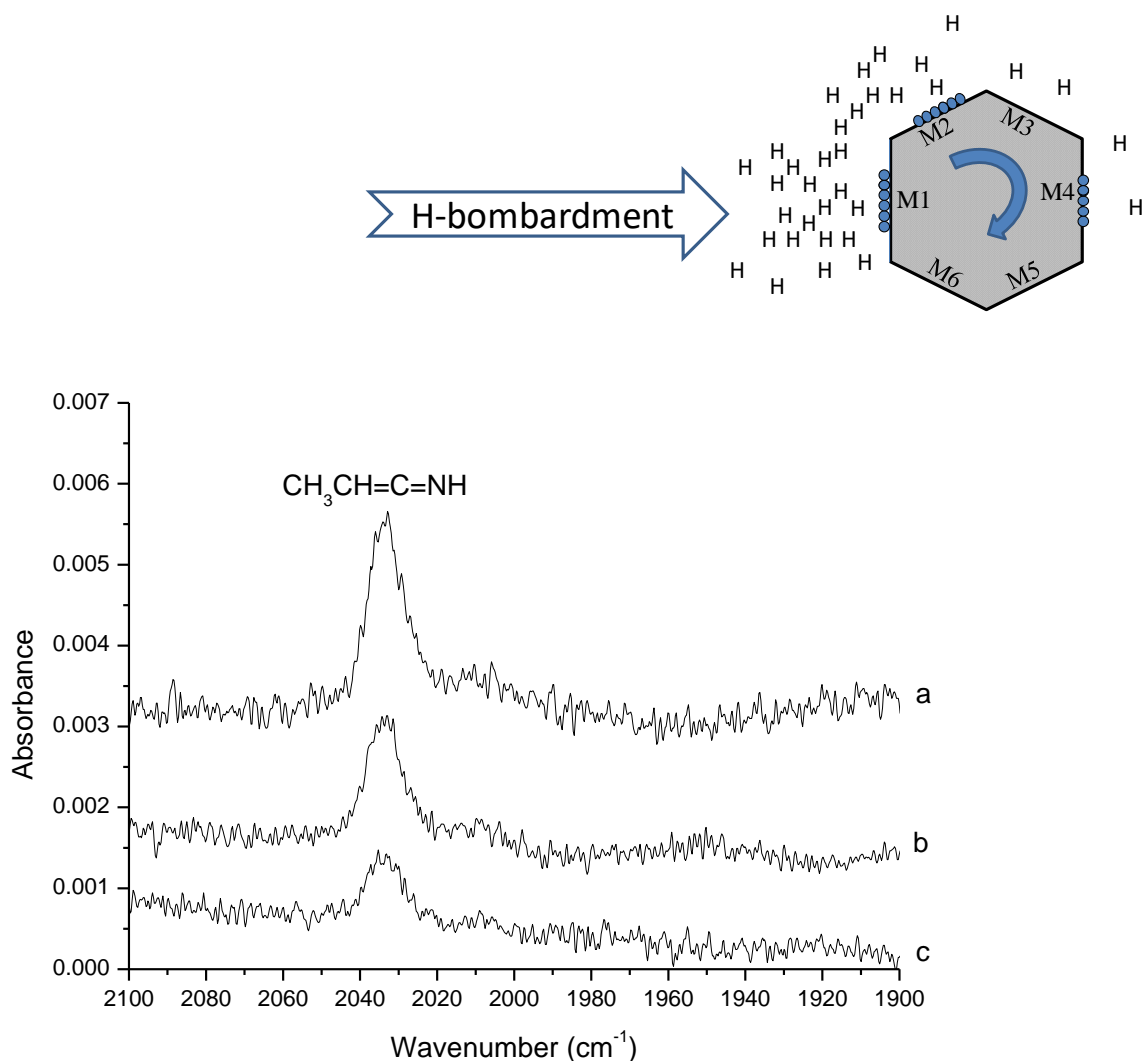


Figure 6: Simultaneous H-bombardment of three ices with same thickness. Difference spectrum before and after H-bombardments of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice on : a) Mirror M1 (the mirror front of the microwave discharge). b) Mirror M2 (lateral mirror with respect to the microwave discharge). c) Mirror M4 (opposite mirror with respect to the microwave discharge). Under these experimental conditions, M2 and M4 receive less H-atoms than M1.

Figure 6 shows the difference spectrum before and after direct and indirect H-bombardments of the three similar  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ices. We notice that after H-bombardments, the band at  $2034.4\text{ cm}^{-1}$  is observed for the three samples with different IR intensities. The band with the highest intensity (figure 6a) is obtained with the sample on M1 which has been directly exposed to H atoms during the H bombardments, while that with the lowest intensity (figure 6c) is obtained with the sample on M4, located in the opposite side with respect to the atomic source. An intermediary IR intensity has been obtained with the sample on the lateral mirror M2.

## IV. Discussion

H-atoms interacting with complex organic molecules COMs may be the source of reduction of several unsaturated species detected in the ISM. However they can also be a source of fragmentation and isomerization. Many studies have been focused on the competition between H-addition, H-abstraction and H-transfer on COMs. We have recently shown that the reduction of  $\text{H}_2\text{CO}$  to  $\text{CH}_3\text{OH}$  seems to be an exception (Jonusas et al. 2017). We showed in the case of unsaturated substituted aldehydes ( $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$  or  $\text{CH}\equiv\text{C}-\text{CH}=\text{O}$ ) that while double and triple CC bonds are easily hydrogenated, aldehyde -CO functional group cannot be reduced into alcohol function. In this sense, (Zaverkin et al. 2018) investigated by means of quantum chemical methods the hydrogen addition and abstraction reactions of substituted aldehydes (propanal, propenal, propynal). They showed, in the case of molecules larger than CO and  $\text{H}_2\text{CO}$ , that in addition to the existing competition between H-addition and H-abstraction processes, hydrogen diffusion from one side of the molecule to another may influence the chemistry of many large COMs when interacting with H atoms. In the present work, we have investigated the interactions of H atoms with saturated and unsaturated COMs having a cyano group  $-\text{C}\equiv\text{N}$ , acrylonitrile and ethyl cyanide:



These two reactions are similar to the reactions involving propenal and propanal we investigated recently (M. Jonusas et al. 2017):



We showed in the previous study that for reactions 3 and 4, propenal is reduced into propanal and that CO group cannot be reduced. There is no molecular fragmentation, nor H-abstraction nor H-transfer. Based on these conclusions, one would think that under H-attacks, acrylonitrile and ethyl cyanide would behave similarly as, propenal and propanal, respectively. As the CN bond is stronger than CO bond, there would be no reduction of CN group at cryogenic temperatures under non energetic conditions. The only expected result would be the reduction of acrylonitrile into ethyl cyanide. Interacting with H-atoms, ethyl cyanide behaves as propanal. The two species are stable under H-bombardments. However the  $\text{H} + \text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  reaction shows a chemistry much more complex than  $\text{H} + \text{CH}_2=\text{CH}-\text{CH}=\text{O}$ . We show experimentally, that the  $\text{H} + \text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  reaction leads

partially to  $\text{CH}_3\text{CH}_2\text{CN}$  through the hydrogenation of the CC double bond and also to the formation of methyl ketenimine  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$ , an isomer of  $\text{CH}_3\text{CH}_2\text{CN}$ .

The formation of  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$  has been reported by Hudson and Moore (2004) using UV-photolysis and  $p^+$  bombardment of  $\text{CH}_3\text{CH}_2\text{CN}$ . The observation of methyl ketenimine using high energy sources and  $\text{CH}_3\text{CH}_2\text{CN}$  as precursor is not really surprising. As it is shown in figure 1, the nitrile  $\text{CH}_3\text{CN}$  needs at least an energy of 369 kJ/mol to overcome the potential barrier and be converted into ketenimine  $\text{CH}_2\text{CNH}$ . However, in our case, ketenimine  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$  is formed in parallel with  $\text{CH}_3\text{CH}_2\text{CN}$  through non-energetic H-addition processing on  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  ice. In order to better understand how  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  reacts with H atoms under non-energetic conditions to form the  $\text{CH}_3\text{CH}_2\text{CN}$  and  $\text{CH}_3\text{CHCNH}$  isomers, the potential surfaces of  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N} + \text{H}$  reaction were analyzed at different levels of theory as summarized in the methods section. The results of these calculations are presented in figure 7 and table 2.

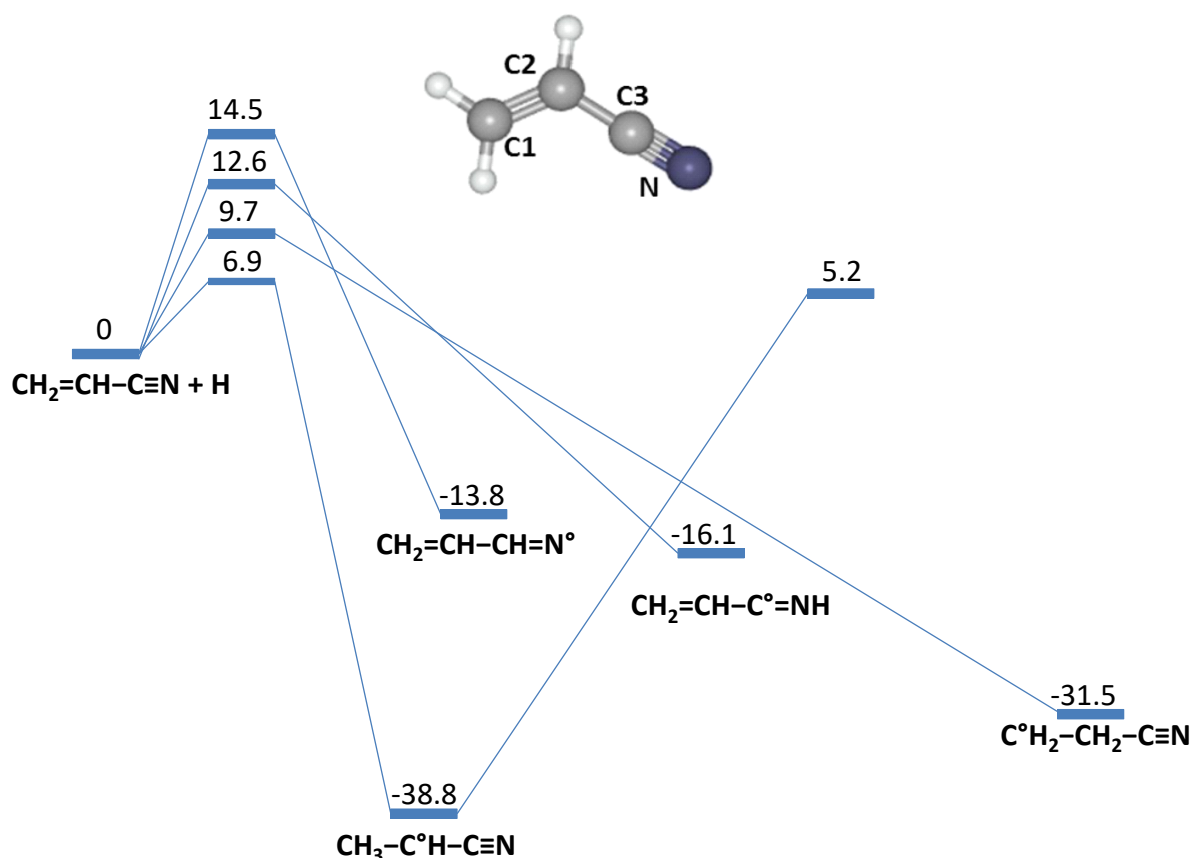
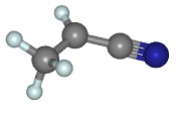
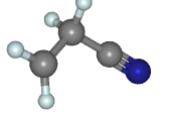
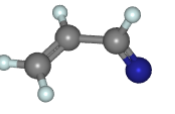
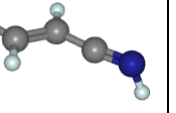


Figure 7: Relative energies (kcal/mol) at the RCCSD(T)//UMP2/aug-cc-pVTZ level for reaction products and transition states for  $\text{H} + \text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  reaction, corresponding to the H attachment to one of the three carbons or to nitrogen.



Table 2: Energetics for H-addition reaction pathways on H<sub>2</sub>C=CH-C≡N

		Add H to			
		C1 (CH <sub>3</sub> CHCN)	C2 (CH <sub>2</sub> CH <sub>2</sub> CN)	C3 (CH <sub>2</sub> CHCHN)	N (CH <sub>2</sub> CHCNH)
	Method*				
Product Bond Energy	B3LYP	-45.3	-32.8	-24.2	-26.7
	UMP2	-28.4	-27.9	+1.5	-6.2
	PMP2//UMP2	-35.5	-29.5	-5.2	-13.4
	RCCSD(T)//UMP2	-38.8	-31.5	-13.8	-16.1
Relative to C1	B3LYP	+0.0	+12.5	+21.1	+18.6
	RCCSD(T)//UMP2	+0.0	+7.3	+25.0	+22.7
Barrier Height	B3LYP	no barrier	-	+5.7	-
	UMP2	+18.3	+20.1	+30.2	+27.2
	PMP2//UMP2	+7.7	+10.4	+18.4	+15.4
	RCCSD(T)//UMP2	+6.9	+9.7	<b>+14.5</b>	<b>+12.6</b>
	RCCSD(T)	<b>+5.3</b>	<b>+8.2</b>	-	-

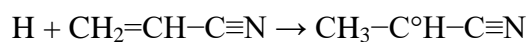
\* aug-cc-pVTZ basis sets, all energies in kcal/mol with ZPE corrections, with UMP ZPE corrections used for PMP2 and RCCSD(T); PMP2=projected MP2 (reduces spin contamination); //UMP2 indicates single point calculation at UMP2 geometry.

In such a progressing, tunneling would control the H-addition reaction at cryogenic temperatures. However the efficiency of a given reaction would depend strongly on the energy barrier and stability of the reaction product. One of the most studied hydrogenation reaction is H + H<sub>2</sub>CO which shows energy barriers of the order of 4 kcal/mol (2000 K) and 11 kcal/mol (5540 K) to form H<sub>3</sub>CO and H<sub>2</sub>COH, respectively. In this context Alvarez-Barcia et al. (2018) calculated the rate constants  $k_{\text{CH}_3\text{O}}$  and  $k_{\text{CH}_2\text{OH}}$  of H + H<sub>2</sub>CO → CH<sub>3</sub>O and H + H<sub>2</sub>CO → CH<sub>2</sub>OH reactions, respectively, in the 65-140 K temperature range. They gave a  $k_{\text{CH}_3\text{O}}/k_{\text{CH}_2\text{OH}}$  ratio around 10<sup>3</sup> and 10<sup>5</sup> at 140 and 65 K, respectively, showing that there is a very large difference between the two rate constants when the temperature decreases (in comparison with what it would be expected from the barrier heights). Consequently, tunneling would govern the two H-addition reactions. However, the reaction with the lowest energy barrier would be the most probable. Similarly, in the H + CH<sub>2</sub>=CH-C≡N reaction, the H attack on carbon C1 possesses the lowest energy barrier, comparable to that of H + H<sub>2</sub>CO →

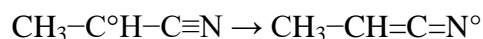
CH<sub>3</sub>O reaction. The calculated activation energy at the RCCSD(T)//UMP2 level is 6.9 kcal/mol, which is lowered by 1.6 kcal/mol to 5.3 kcal/mol when partially optimized at the RCCSD(T) level. The C1 adduct is also the most stable species formed through the H + CH<sub>2</sub>=CH-C≡N reaction. The H-addition on C<sub>2</sub> has 9.7 kcal/mol has an energy barrier, similar to that of H + H<sub>2</sub>CO → CH<sub>2</sub>OH reaction. Accordingly, the reaction pathways involving C1 and C2 would be as efficient as H + H<sub>2</sub>CO → CH<sub>3</sub>O and H + H<sub>2</sub>CO → CH<sub>2</sub>OH, respectively. Though, as the H attacks on C3 and N show very high activation energies (12.6 and 14.5 kcal/mol) and also less stable adducts, they are less probable and certainly unfeasible under non-energetic conditions. This would suggest that the first reaction step during the H-bombardment of CH<sub>2</sub>=CH-C≡N ice under non-energetic conditions would be mainly the formation of CH<sub>3</sub>-C°H-C≡N, which would easily react with a second H atom to form CH<sub>3</sub>-CH<sub>2</sub>-C≡N, one of the species we have detected experimentally.

The formation of methyl ketenimine CH<sub>3</sub>CH=C=NH, the second reaction product we obtain under our experimental conditions with the H + CH<sub>2</sub>=CH-C≡N solid state reaction, should not occur through direct isomerization of CH<sub>3</sub>CH<sub>2</sub>-C≡N, once it is formed. The calculations found that while H could transfer between the C1 and C2 adducts (over a barrier of 4.8 kcal/mol at the partially optimized RCCSD(T) level), no transition states were found for transferring H between C2 and C3 or between C3 and N. On the other hand we did not detect CH<sub>3</sub>CH=C=NH during the H-bombardments of CH<sub>3</sub>CH<sub>2</sub>-C≡N ice as the CH<sub>3</sub>CH<sub>2</sub>-C≡N → CH<sub>3</sub>CH=C=NH isomerization needs high energy to occur. Consequently, CH<sub>3</sub>CH=C=NH would form in competition with the CH<sub>3</sub>CH<sub>2</sub>-C≡N formation during the hydrogenation of CH<sub>2</sub>=CH-C≡N ice. As the first H-addition occurs on carbon C1, the CH<sub>3</sub>-C°H-C≡N radical is formed primarily. We suggest the following reaction pathways to explain the ketenimine formation under non energetic conditions:

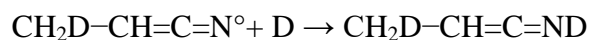
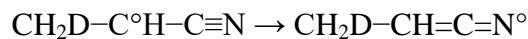
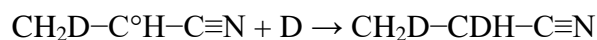
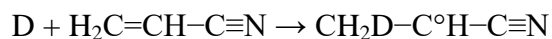
***First reaction pathway: Formation of CH<sub>3</sub>CH<sub>2</sub>-C≡N***



***Second reaction pathway: Formation of CH<sub>3</sub>CH=C=NH***



*The case of  $D + CH_2=CH-C\equiv N$  reaction: formation of  $CH_2D-CDH-C\equiv N$  and  $CH_2D-CH=C=ND$*



The first reaction pathway leading to the formation of  $CH_3CH_2-C\equiv N$  through  $CH_2=CH-C\equiv N + 2H$  reaction is obvious, as we have shown that such a processing has the lowest energy barrier and leads to the formation of  $CH_3-CH-C\equiv N$  reaction intermediate, which recombines with a second H atom to form  $CH_3CH_2-C\equiv N$ . However the second reaction pathway to form ketenimine  $CH_3CH=C=NH$  is possible only if H can also add to the N in the  $CH_3CHCN$  intermediate. We show below how this is not only possible but likely.

It is simplistic to think that the C1 adduct  $CH_3CHCN$  has all of its radical character localized on C2 (as it is in the methyl radical). In fact, its electronic structure reflects a resonance between two localized forms,  $CH_3-C^\circ H-C\equiv N$  and  $CH_3-CH=C=N^\circ$ . The calculations bear this out: the Mulliken spin populations on C2, C3, and the N atom are 1.13, -0.61, and 0.63, respectively, at the UMP2/aug-cc-pVTZ level (there is also -0.18 on the methyl carbon C1 and minor amounts on the H atoms). While this yields a net doublet, it also means that a second H can form a favorable overlap elsewhere on the backbone than at C2. Some electronic redistribution is required so it may not be as favorable for H to attach to C3 or N as it is at C2. This can account for the lower stability of the ketenimine product and the observed ~9:1 ratio of the two products shown in table 1.

We explored these two pathways in the related but simpler system  $H_2CCN + H$ . Replacing the methyl group of  $CH_3CHCN$  with H should not greatly affect the energetics of H addition. Like  $CH_3CHCN$ , the  $H_2CCN$  radical shows resonance behavior between two forms, as indicated by radical character on all three heavy atoms. For  $H_2C1-C2-N$ , the Mulliken spin populations at the UMP2/aug-cc-pVTZ level on C1, C2, and N are 1.09, -0.64, and 0.65, respectively, which are quite similar to the spin densities on the analogous atoms in  $CH_3-CH-CN$  above (there are also minor amounts of spin density on the two H atoms). We might therefore expect to form both  $CH_3CN$  (methyl cyanide) and  $H_2CCNH$  (ketenimine) by adding H to C1 and N of  $H_2CCN$ , respectively. To test the likelihood of forming both products, we ran additional calculations. These calculations required a multireference treatment since closed-shell singlet molecules are being formed from open-shell doublet reactants. At the

MRCI+Q/aug-cc-pVTZ level, we found that neither addition involves a reaction barrier. The issue thus becomes trying to understand why there is a preference for the cyanide product over the ketenimine product. With no barriers for either addition, the favorability of one product over the other must be due to the specific character of the full reaction surface. In the addition of H to CH<sub>3</sub>CHCN, ethyl cyanide is more stable than the ketenimine product, and the same is true when adding H to H<sub>2</sub>CCN: methyl cyanide is more stable than ketenimine. The first channel has a "wider" entrance on the potential energy surface; it is deeper and extends further out from C1. This is likely what favors cyanide formation over ketenimine formation in these reaction systems.

To gain further insight into the ratio of the two products, we note that the study of delocalized radicals containing nitrogen atoms has been theoretically investigated in the case of the simplest of the cyanoalkyl radicals, CH<sub>2</sub>CN. Delbecq (1983) has shown using valence-bond analysis that cyanomethyl radical CH<sub>2</sub>CN has two different limit structures, C<sup>o</sup>H<sub>2</sub>CN and CH<sub>2</sub>=C=N<sup>o</sup> with relative weights of 83 % and 14 %, respectively. The H<sub>2</sub>CN π-delocalized structure was found with a low weight of the order of 3 %. Similarly, under our experimental conditions, the formation of CH<sub>3</sub>-C<sup>o</sup>H-C≡N through CH<sub>2</sub>=CH-C≡N + H reaction, would lead as shown in figure 8, to the formation of a second localized form with ketenimine character CH<sub>3</sub>-CH=C=N<sup>o</sup> which explains the possibility of reaction at the nitrogen end to form CH<sub>3</sub>CH=C=NH.

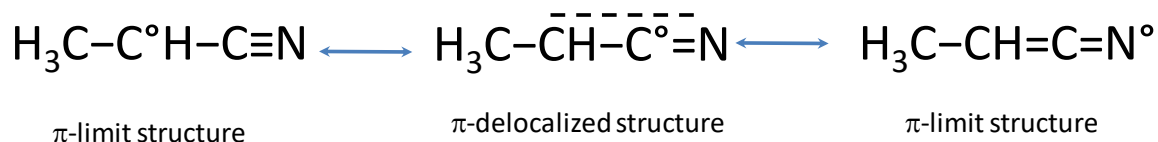


Figure 8: Two different limit structures and one π-delocalized structure of CH<sub>3</sub>CHCN radical formed during the CH<sub>2</sub>=CH-C≡N + H reaction.

Based on the calculations carried out by Delbecq on CH<sub>2</sub>CN radical which showed that C<sup>o</sup>H<sub>2</sub>CN is found to be more abundant than CH<sub>2</sub>=C=N<sup>o</sup>, we can estimate the amount of the two different limit structures of CH<sub>3</sub>CHCN radical we form under our experimental conditions during the hydrogenation of CH<sub>2</sub>=CH-C≡N. From table 1, we notice that CH<sub>2</sub>=CH-C≡N + 2H reaction produces 91 % of CH<sub>3</sub>CH<sub>2</sub>-C≡N and 9 % of CH<sub>3</sub>CH=C=NH. We can deduce that CH<sub>3</sub>CHCN radical has two different limit structures, CH<sub>3</sub>-C<sup>o</sup>H-C≡N and CH<sub>3</sub>-CH=C=N<sup>o</sup> with relative weights of 91 % and 9 %, respectively. Consequently, in the case of CH<sub>2</sub>=CH-C≡N + 2D reaction, we form selectively, two isotopic species CH<sub>2</sub>D-CDH-C≡N and CH<sub>2</sub>D-CH=C=ND.

Likely formation routes of interstellar amino acids have been discussed by Loomis et al. (2013) and Lovas et al. (2006b) where the first step consists in the transformation of the CN group of nitriles into ketenimines. Such transformations show high barriers and need energetic processing to occur. We show that the CN bond could be activated to form ketenimines from organic unsaturated nitriles ( $C\equiv N$ ) through H-addition reactions. We notice that during the hydrogenation of  $CH_2=CH-C\equiv N$  under interstellar conditions that  $CH_3CH_2-C\equiv N$  has been formed with an abundance 10 times higher than that of  $CH_3CH=C=NH$ . Such a distribution is directly linked to  $\pi$ -electrons delocalization  $H_3C-C^\circ H-C\equiv N \leftrightarrow H_3C-CH=C=N^\circ$  of  $H_3CCHCN$  radical formed during the  $CH_2=CH-C\equiv N + H$  reaction. As many species with CN and CNH groups such as  $H_2C=CHCN$ ,  $H_2C=NH$ ,  $CH_3CH=NH$  and  $CH_3CH_2-C\equiv N$  have been detected in molecular cloud SgrB2 with very low rotational temperatures, we expect that  $CH_3CH=C=NH$  would also be detectable in these cold region of the ISM. This suggests it would form in solid phase on the interstellar grains either through successive hydrogenation of unsaturated organic precursor  $H_2C=CHCN$  or through radical recombination and it would afterwards undergo non-thermal desorption into the gas phase. However as we show that the H-addition reaction on solid  $H_2C=CHCN$  leads to  $CH_3CH_2-C\equiv N$  and  $CH_3CH=C=NH$  with an abundance ratio  $[C_2H_5CN]/[C_2H_5CNH]$  equal to 10, the knowledge of the interstellar abundances of  $C_2H_5CN$  and  $C_2H_5CNH$  would allow to access to their synthesis routes in the ISM. In this sense, Johnson et al. (1977) reported the detection of  $CH_3CH_2-C\equiv N$  with the column density around  $10^{14}$  molecules  $cm^{-2}$  and accordingly if methyl ketenimine would not react during its desorption it would be detected at least with a column density of the order of  $10^{13}$  molecules  $cm^{-2}$ . As mentioned in the introduction part, in order to assist the possible detection of  $CH_3CH_2CN$  isotopologues, Margulès et al. (2009) have studied the rotational spectra of two deuterated ethylcyanide  $CH_2DCH_2CN$  and  $CH_3CHDCN$ . However,  $CH_3CHDCN$  and  $CH_2DCH_2CN$  have still not been formally detected. Based on our experiments, in addition of  $CH_3CH=C=NH$  for which the detection is dependent on the recording of its rotational spectra, we show that specific isotopic species should be considered in the future observations such as  $CH_3CH=C=ND$  and  $CH_2DCH=C=NH$  which may derive from  $CH_2=CH-C\equiv N + H + D$  solid state reaction.

## V. Conclusion

The interstellar detection of complex organic imines ( $RC=N-H$  with  $R = H, Me$ ) and ketenimine  $H_2C=C=NH$  has open proceedings between communities both from laboratory simulations and astronomical observations in how and where interstellar prebiotic species in

general and more specifically amino acids would form. As the association of imines with species having COOH group, abundant in the ISM in compounds such as formic or acetic acids, may be the source of amino acids family, many groups have been focused in how ketenimines are formed under interstellar conditions. Some groups proposed that reaction pathways to form interstellar  $\text{H}_2\text{CCNH}$  and  $\text{CH}_3\text{CHCNH}$  would involve sequential hydrogen atom addition on  $\text{CH}_3\text{CN}$  in interstellar ices while other groups suggested that ketenimines would possibly form directly by tautomerization of nitriles ( $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CH}_2\text{CN}$ ) driven by shocks in star-forming region. We show in the present study that saturated nitriles ( $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CH}_2\text{CN}$ ) are stable when interacting with hydrogen atoms while previous studies have already shown that  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CH}_2\text{CN}$  isomerize into  $\text{CH}_2\text{CNH}$  and  $\text{CH}_3\text{CHCNH}$ , respectively, under energetic processing. Consequently, from saturated nitriles ( $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CH}_2\text{CN}$ ) interstellar ketenimines may be formed only through energetic processing in interstellar regions near to an energy source, such as hot cores or diffuse interstellar clouds. However, based on the present laboratory experiment, there is evidence for substituted ketenimine formation from unsaturated nitriles ( $\text{C}\equiv\text{N}$ ) inside of dark interstellar clouds where non energetic processing such as H-addition reactions are predominant. In this sense, we show that the unsaturated nitrile  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  is converted into  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  and  $\text{CH}_3\text{CH}=\text{C}=\text{NH}$  through successive hydrogenation with relative weights of 91 % and 9 %, respectively.

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