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► **To cite this version:**

Fabien Borget, Sandra Müller, Dirk Grote, Patrice Theulé, Vassilissa Vinogradoff, et al.. CN radical hydrogenation from solid H₂ reactions, an alternative way of HCN formation in the interstellar medium. *Astronomy and Astrophysics - A&A*, 2017, 598, pp.A22. 10.1051/0004-6361/201526383 . hal-01452094

HAL Id: hal-01452094

<https://amu.hal.science/hal-01452094>

Submitted on 1 Feb 2017

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CN radical hydrogenation from solid H₂ reactions, an alternative way of HCN formation in the interstellar medium

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Received 22 April 2015 / Accepted 12 October 2016

ABSTRACT

Context. Molecular hydrogen (H₂) is the most abundant molecule of the interstellar medium (ISM) in gas phase and it has been assumed to exist in solid state or as coating on grains.

Aims. Our goal is to show that solid H₂ can act as a hydrogenation agent, reacting with CN radicals to form HCN.

Methods. In a H₂ matrix, we studied the hydrogenation of the CN radical generated from the vacuum ultraviolet photolysis (VUV-photolysis) of C₂N₂ at 3.8 K. We modified the wavelengths and the host gas in order to be sure that CN radicals can abstract H from H₂ molecules.

Results. HCN monomers, dimers, and oligomers have been characterised by Fourier transform infrared spectroscopy (FTIR). H₂CN as well as CN radicals have also been clearly observed during the photolysis performed at 3.8 K.

Conclusions. H₂ is a hydrogenation reagent towards CN radicals producing HCN. This type of reaction should be taken into account for the reactivity at low temperature in contaminated H₂ ice macro-particles (CHIMPs), H₂ flakes or in the first sublayers of grains where solid H₂ has accumulated.

Key words. astrochemistry – molecular processes – astrobology – ISM: molecules

1. Introduction

Chemical reactions occurring on the grains, and in the ice covering the grains, of the interstellar medium (ISM) are considered as fundamental in understanding the diversity and the complexity of the approximately 180 molecules that have been detected so far in dense clouds (Hama & Watanabe 2013; van Dishoeck et al. 2013). In all the different types of reactions happening on the grains, hydrogenation is probably one of the most important. H₂CO and CH₃OH formation through the hydrogenation of CO has been studied by Hiraoka et al. (1994), Watanabe et al. (2003) and Fuchs et al. (2009). Alcohols and aldehydes were formed by H atom bombardment of CH₃CHO yielding C₂H₅OH, CH₃OH, CH₄, and H₂CO (Bisschop et al. 2007). Water has also been produced by H bombardment on O, O₂, and O₃ (Ioppolo et al. 2008; Matar et al. 2008; Miyauchi et al. 2008; Mokrane et al. 2009; Romanzin et al. 2011). Some nitrogen-bearing molecules could also be formed by hydrogenation; NH₃ was generated by reactions of H atoms in a N₂ matrix (Hiraoka et al. 1995). Recently, we investigated the hydrogenation of HCN (Theule et al. 2011) as well as CH₂NH producing methylamine CH₃NH₂.

In 2012, Oba et al. (2012) showed that water formation is also possible by reaction of OH radicals with H₂ via a quantum chemical tunnelling. These authors co-deposited OH obtained

from a microwave discharge of water and H₂ on a cold surface. This reaction is important because it represents an example of H₂ acting as a direct hydrogenation reactant. Since H₂ is the most abundant molecule in the ISM, this experiment demonstrates the importance of direct hydrogenation by H₂. Moreover, from previous work (Buch et al. 1993; Hixson et al. 1992; Dissly et al. 1994; Sandford & Allamandola 1993; Sandford et al. 1993), evidence of H₂ interaction with water ice in ISM is increasing. The H₂ adsorption energy on amorphous water ice (Amiaud et al. 2006; Fillion et al. 2009; Kristensen et al. 2011; Pirronello et al. 1997) was studied and it was shown that H₂ can remain in water ice pores up to a temperature of 35 K (Sandford et al. 1993; Dulieu et al. 2005).

Astronomers have been interested in solid H₂ in the ISM (Lin et al. 2011) since the late 1960s (Reddish & Wickramasinghe 1968; Wickramasinghe & Reddish 1968). In addition to the few layers adsorbed on water ice mentioned earlier, the presence of solid H₂ was proposed as flakes (Pfenninger & Puy 2003) or as H₂ dust stabilised by an electric field (Walker 2013), forming contaminated H₂ clusters (Bernstein et al. 2013). The later study proposed the presence of seeds in the ISM, where H₂ molecules can be accreted until forming cubic centimeter-sized objects called contaminated H₂ ice macro-particles (CHIMPs). In these particles various molecules are embedded, and at temperatures between 3 and 15 K, reactive molecules are kinetically stabilised. Conditions similar to that in the CHIMPs can be simulated in the laboratory by cryogenic matrix isolation experiments where solid H₂ is

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used as a matrix (Norman & Porter 1954; Whittle et al. 1954; Kötting & Sander 1999; Zuev & Sheridan 2001; Hoshina et al. 2004; Henkel et al. 2014).

Momose et al. (1998) studied the reaction of H₂ with a photoinduced radical CD₃. The reaction product was HCD₃ which demonstrates that H₂ can react with a radical forming the hydrogenated compound. Bahou et al. (2014) studied the reaction of photoinduced radicals in a H₂ matrix.

Here, we describe the hydrogenation of the astrophysically relevant radical CN produced by photolysis of cyanogen (C₂N₂). This radical is the second species detected in the ISM in 1940 (McKellar 1940), confirmed in 1941 (Adams 1941) and also detected in SgrB2 in 1970 (Jefferts et al. 1970). To investigate reactions of CN in hydrogen-rich environments, we generated the CN radical in a H₂ matrix at 3.8 K and followed its reaction with H₂. Using this technique, we demonstrate that molecular H₂ can be a hydrogenation reactant at cryogenic temperatures, and propose a HCN synthesis that can be realised under conditions of the ISM.

2. Experimental

Experiments were performed in H₂ cryogenic matrices during which a KBr window was cooled to 3.8 K using a Sumitomo CKW-21 cryogenerator in a cryostat maintained at 10⁻⁷ mbar. A Lakeshore 232 temperature controller was used to regulate the temperature between 3 K and room temperature. FTIR spectra were recorded at a resolution of 0.5 cm⁻¹ with a MCT detector on a Bruker IFS 66 spectrometer.

For low temperature experiments in Ar matrix at 10 K or 20 K, the sample was deposited on a surface of polished gold on copper, connected directly to the cold head (ARS Cryo, DE-204-SB). This set-up can reach minimal temperatures of approximately 8 K. The FTIR spectra were recorded on a Bruker VERTEX 70 spectrometer with a 0.5 cm⁻¹ resolution using a MCT detector.

Ar or H₂ were mixed in a vacuum line at room temperature with a small amount of C₂N₂ using standard manometric techniques. Matrices were produced by deposition of these gas mixtures through a calibrated valve on top of the cold surface. C₂N₂ was synthesised using a flash vacuum thermolysis of AgCN (Aldrich) at 10⁻² mbar. AgCN decomposes forming CN radicals that recombine to form C₂N₂, which is trapped in liquid nitrogen. C₂N₂ was stored at low temperature and further purified by several freeze-thaw cycles and removal of the first fraction.

Vacuum UV (VUV) light ($\lambda > 120$ nm) was produced with a discharge H₂ flow lamp (Ophos Instrument), the flux was estimated to be approximately 10¹⁵ photons cm⁻² s⁻¹. This flux allowed for irradiation with wavelengths higher than 120 nm through a MgF₂ window. In order to avoid direct H₂ photolysis, we used a sapphire window to cut off at 150 nm in several experiments. Argon was also used in the discharge lamp, which produces light with wavelengths above 160 nm. During the photolyses, spectra were recorded after different irradiation times.

3. Results and discussion

3.1. C₂N₂ deposition

C₂N₂ was deposited in Ar matrix with a matrix ratio of 1/500 (Fig. 1a). A main IR band is observed at 2156 cm⁻¹, which is characteristic of the ν_{CN} mode.

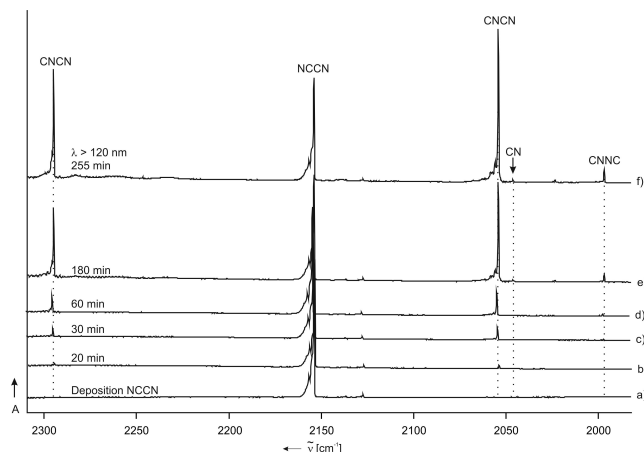


Fig. 1. IR spectrum of C₂N₂ / Ar (1/500) at 20 K with varying irradiation time using a hydrogen lamp. **a)** Deposition; **b)** 20 min; **c)** 30 min; **d)** 60 min; **e)** 180 min and **f)** 255 min of irradiation.

Figures 2a and 3a show a typical C₂N₂ matrix in H₂ deposited at 4 K in the ratio 1/500. Two main bands at 2157.3 and at 738.7 cm⁻¹ are observed for C₂N₂ in the hydrogen matrix and are characteristic of the ν_{CN} vibration and a combination of bending modes (cf. Table 1). We also observe traces of water, which is a contamination introduced during the C₂N₂ synthesis from solid AgCN. According to the intensities of these bands, the water contamination impurity does not interfere with the experiments. CO₂ is also detected as a by-product of the synthesis of C₂N₂. The bands assigned to C₂N₂ are in good agreement with the literature (cf. Table 1).

In D₂ matrix, C₂N₂ displays the two same bands at 2157.6 and 741.7 cm⁻¹.

3.2. C₂N₂ VUV Irradiation in Ar matrix

C₂N₂ has a large absorption band in the VUV between 114 and 136 nm and a sharper and less intense series of bands between 152 and 168 nm (Nuth & Glicker 1982). The photodissociation of C₂N₂ has been largely studied in this range of wavelengths producing CN radicals in different electronic states (Dateo et al. 1987; Halpern & Jackson 1982; Taherian & Slinger 1984).

We irradiated C₂N₂ in Ar-matrix using a H₂ flow lamp. After a few minutes of irradiation, photolysis of the cyanogen is observed, C₂N₂ bands decrease and new bands grow at 2295.3 and 2054.4 cm⁻¹ (Fig. 1). These two bands have already been characterised and are assigned to isocyanogen (CNCN) (Suter et al. 2007). This isomerisation is common for nitrile compounds (Hudson & Moore 2004; Milligan & Jacox 1967; Toumi et al. 2014) under UV light. When the irradiation is prolonged to over 90 min, a new band begins to grow at 1997.3 cm⁻¹, which is assigned to diisocyanogen (CNNC) (Stroh et al. 1989; Stroh & Winnewisser 1989; Maier et al. 1992) finalising the photoisomerisation of cyanogen. No other bands are observed in these experiments in Ar, indicating that no other major process is involved. Nevertheless, a very small band at 2050.8 cm⁻¹ can be assigned to the CN radical (Jacox & Thompson 2007), provided information on the mechanism of the isonitrile isomerisation through a dissociation-recombination process.

3.3. C₂N₂ VUV irradiation in a H₂ matrix

When the same irradiation experiments are performed in a H₂ matrix, the results are different. After 15 min of VUV

Table 1. C₂N₂ IR bands in different matrices deposited at low temperature.

Ar matrix 10 K (cm ⁻¹)	H ₂ matrix 3.8 K (cm ⁻¹)	D ₂ matrix 3.8 K (cm ⁻¹)	Ar matrix (cm ⁻¹) (1)	Gas phase (cm ⁻¹) (2)	Assignment
2156	2157.3 738.7	2157.6 741.7	2157	2156/2143 739/724	ν_{CN} combination bending mode

References. (1) Maier et al. (1992); (2) Bailey & Carson (1939).

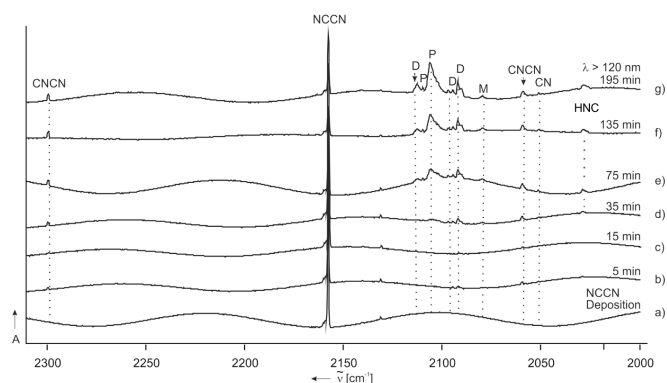


Fig. 2. IR spectra of C₂N₂ in a H₂ matrix in the range 2300–2000 cm⁻¹ at different irradiation times using a hydrogen lamp and assignment of the new species. **a)** deposition; **b)** 5 min; **c)** 15 min; **d)** 35 min; **e)** 75 min; **f)** 135 min and **g)** 195 min of irradiation. D = Dimers of HCN, M = Monomer of HCN, P = Polymers of HCN.

irradiation, isocyanogen (CNCN) is detected with bands at 2299.4 and 2059.1 cm⁻¹, which are just slightly shifted compared to those observed in Ar, allowing a clear assignment. The most striking observation is that those bands are very weak in comparison to other bands growing in this region (Figs. 2 and 3).

In the 2300–2000 cm⁻¹ zone (Fig. 2), new bands are formed during the irradiation. Among them, a band at 2079.1 cm⁻¹ can clearly be assigned to the HCN molecule (Milligan & Jacox 1967). This assignment is confirmed in other regions of the spectrum where characteristic bands of HCN are observed especially at 3306.4 cm⁻¹ (Fig. 3) and 723.5 cm⁻¹. At longer irradiation times, the HCN dimer is formed with a band at 791.9 cm⁻¹ (King & Nixon 2003) and oligomers with a band at 809.3 cm⁻¹ (cf. Table 2, for detailed assignments). Bands at 3622.2 and 2028.6 cm⁻¹ are characteristic of the HCN photoisomerisation producing the isonitrile HNC.

After 75 min of irradiation, the CN radical (Jacox & Thompson 2007) is detected with its characteristic band at 2050.8 cm⁻¹. One additional peak is also detected at 1337.5 cm⁻¹, which is tentatively assigned to the radical H₂CN that was already observed in an Ar matrix (Milligan & Jacox 1967).

The first interpretation of these results is that the CN radical formed by the C₂N₂ photodissociation subsequently reacts by abstraction of one H atom of H₂ molecules to form the hydrogenated compound. To be sure that the products are formed from the CN radicals reacting with H₂ and not by CN radical reacting with H atoms, we developed a strategy changing the wavelength of the irradiation in addition to using a D₂ matrix.

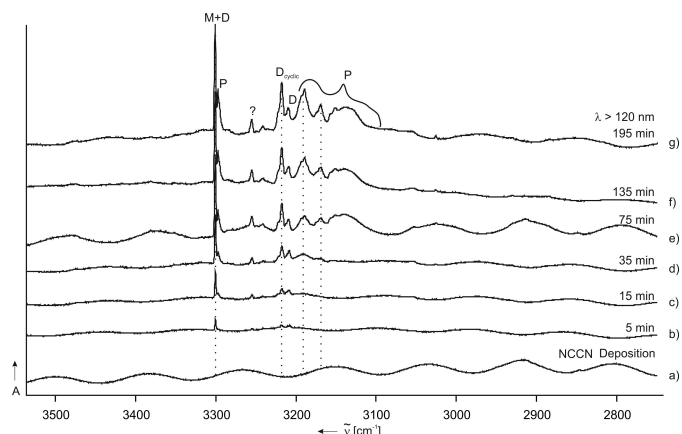


Fig. 3. IR spectra of C₂N₂ in a H₂ matrix in the range 3500–2800 cm⁻¹ at different irradiation times using a hydrogen lamp and assignment of the new species. **a)** deposition; **b)** 5 min; **c)** 15 min; **d)** 35 min; **e)** 75 min; **f)** 135 min and **g)** 195 min of irradiation. D = Dimers of HCN, M = Monomer of HCN, P = Polymers of HCN.

3.4. C₂N₂ VUV irradiation in a H₂ matrix using a sapphire window (λ > 147 nm) and an Ar lamp (λ > 160 nm)

The edge of the absorption band of H₂ overlaps with the 121 nm radiation (Bunch et al. 1958) and therefore we have to take into account that an excited state or photodissociation of H₂ could be involved in the previous formation of HCN.

To verify that the observed reactivity is exclusively due to the cleavage of cyanogen, we changed the MgF₂ window of our system with a sapphire which cuts off radiation below 147 nm. When the irradiation of the H₂ matrix containing C₂N₂ was performed using the H₂-flow lamp with a sapphire window, we observed the characteristic bands of HCN indicating that our postulated mechanism of CN radical reacting with H₂ is reliable.

To confirm this observation, we also used an Ar plasma for the irradiation that produces vacuum UV light with a wavelength longer than 160 nm. Again the formation of HCN is observed, thus confirming our proposed mechanism (Fig. 4).

3.5. C₂N₂ VUV irradiation in a D₂ matrix

We deposited C₂N₂ using the same protocol in a D₂ matrix. The two main bands of the cyanogen are observed at 2157.6 and 741.7 cm⁻¹ very close to the positions in H₂ matrix (cf. Table 1). Irradiation of the D₂ matrix with the H₂ lamp produced isocyanogen with bands at 2058.6 and 2299.7 cm⁻¹ (Fig. 5). DCN is also observed (Walsh et al. 1978) after 5 min of irradiation with bands at 2624.3, 2576.2, 2566.7 and 1931.9 cm⁻¹. Note that in this spectral range, we also observe a band at 2668 cm⁻¹ due

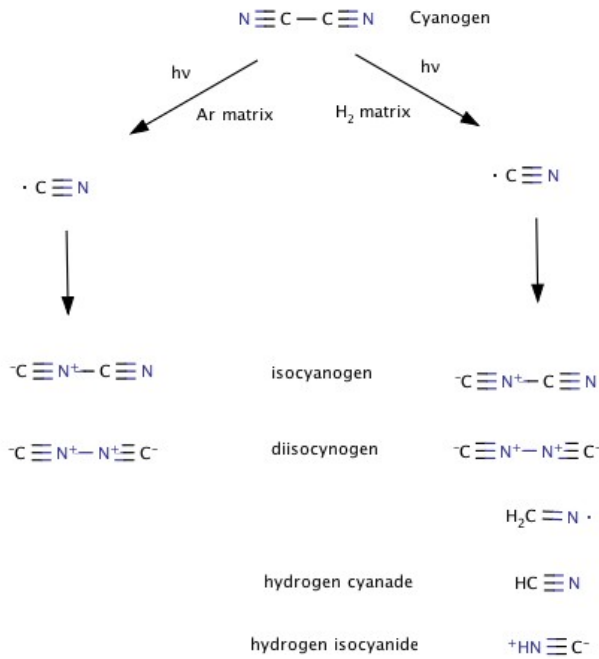


Fig. 4. C_2N_2 photolysis in an Ar matrix and in a H_2 matrix.

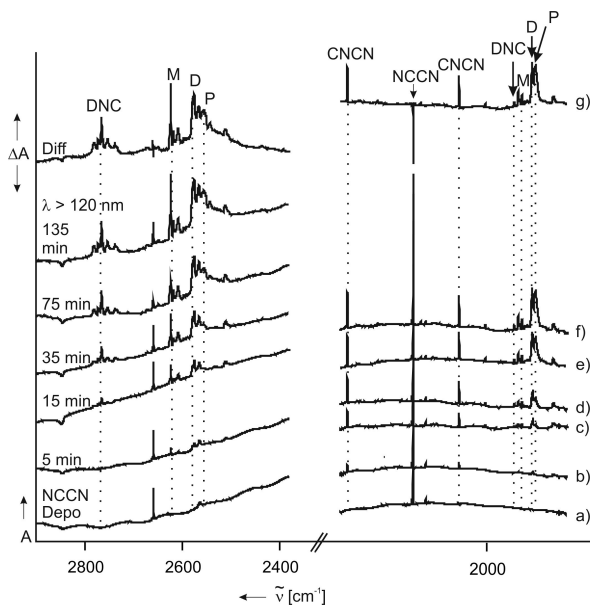


Fig. 5. IR Spectra C_2N_2 in D_2 matrix at 3.8 K with different time of VUV irradiation ($\lambda > 120$ nm). Assignments DCN-monomer (M) – dimers (D) and polymers (P), DNC and CNCN. **a)** deposition; **b)** after 5 min; **c)** 15 min; **d)** 35 min; **e)** 75 min; **f)** 135 min; and **g)** difference spectrum (135 min – deposition). The band at 2668 cm^{-1} is a C_2N_2 combination mode.

to the $\nu_2 + \nu_5$ combination mode of C_2N_2 (Andrews et al. 1984). After longer irradiation times, the dimers, trimers and oligomers of DCN are also detected. After 15 min of VUV irradiation new peaks are detected at 2766.4 and 1938.6 cm^{-1} corresponding to the formation of the photoisomer DNC (Walsh et al. 1978).

Table 2. Positions and assignments of infrared bands growing during the VUV-irradiation of C_2N_2 in different matrices.

Matrix	Wavenumbers (cm^{-1})	Assignment
$\text{C}_2\text{N}_2/\text{Ar}$	2295.3	CNCN
	2054.4	CNCN
	2050.8	CN radical
	1997.3	CNNC
$\text{C}_2\text{N}_2/\text{H}_2$	3622.2/3610.4	HNC
	3306.6	HNC monomer + dimer
	3297.3/3217.9	HNC polymer
	3192.9/3189.9	
	3157.6/3151.5	
	3209.1	HNC dimer
	2299.4	CNCN
	2112.4	HNC dimer
	2109.4 /2106.6	HNC polymer
	2094.3/2091.6	HNC dimer
	2079.1	HNC
	2059.1	CNCN
	2050.8	CN radical
	2028.6	HNC
	1337.5	H_2CN radical
	809.3	HNC polymer
	798.2/791.9	HNC dimer
733.9/732.4		
723.5	HNC	
$\text{C}_2\text{N}_2/\text{D}_2$	2766.4	DNC
	2624.3	DCN
	2579.8/2576.2	DCN dimer
	2566.7/2556.2	DCN polymer
	2299.7	CNCN
	2058.6	CNCN
	1938.6	DNC
	1931.9	DCN
	1902.3/1900.0	DCN dimer
	1893.9	DCN polymer
	1178.2	DCN
	587.1	DCN polymer
579.0	DCN	

4. Astrophysical implications

HNC, detected in 1971 in the ISM (Snyder & Buhl 1971), is the simplest existing neutral and stable molecule that contains a nitrile group. This molecule could be involved in different chemical processes towards increasing molecular complexity, such as the formation of amino-acid precursors (Danger et al. 2011, 2012). Surprisingly however, there is a lack of experimental evidence of HNC formation in the ISM. Few pathways have been described in chemical models of the ISM (Hily-Blant et al. 2010).

Gas phase experiments supported by theoretical calculations have shown that the H abstraction from H_2 by CN radicals has an activation barrier between 12 and 17 kJ/mol (Sims & Smith 1988; Sun et al. 1990; Zhu et al. 1998). The values are almost the same for D_2 . Those activation barriers are higher in energy than the thermal energy available at 3.8 K, the temperature of our matrices. Momose et al. (1998) and Hoshina et al. (2004) studied methyl radical with H_2 and concluded that methane is formed via a tunnel effect. This phenomenon was described for several other

reactions in H₂, for instance reactions of carbenes with H₂ as described by Zuev and Sheridan (Zuev & Sheridan 2001) or more recently by Henkel et al. (2014). Moreover, Oba et al. (2012) concluded that a tunnel effect is responsible for the H abstraction of H₂ by OH radicals resulting in the formation of water molecules in astrophysical conditions. The importance of the tunnel effect in chemistry is discussed in more than one review (Ley et al. 2012; Schreiner et al. 2011) as well as for its implication in the surface reactions happening in an astrochemical context (Hama & Watanabe 2013; Trixler 2013; Reboussin et al. 2014). Our study demonstrates that H₂ can be a source of hydrogenation of CN radicals, but since we are using VUV to generate CN radicals, kinetic studies to confirm tunneling reaction are not possible. Moreover, as we are under UV flux, we cannot rule out that an excited state of the formed radical is implied for the reaction with H₂.

Recently, Walker (2013) discussed the question of the solid H₂ survival in the ISM. He concluded that electrical charging processes stabilize H₂ grain surfaces even at temperatures where, usually, the volatility of H₂ is already very high (10 K). Lin et al. (2011) proposed to track H₆⁺ as a probe for the presence of solid H₂. Bernstein et al. (2013) proposed the presence of contaminated CHIMPs. Molecules that are embedded in CHIMPs are in conditions very close to the H₂ matrix experiments. In these conditions, H₂ is a reagent for hydrogenation reaction. Following the classification of thermal reactions (Theule et al. 2013), H₂ is a generator of generation 0 molecules. Even at the low temperature of the ISM, it is clear that light species (H, H₂, C, N, O, etc.) have enough mobility on the grain surfaces to react easily to start an efficient bimolecular chemistry. In the denser part of the ISM, H₂ is predominant (Dixon et al. 1998) and, from a molecular point of view, H₂ is the most abundant compound of the dark clouds (Pagani et al. 2011). Our study shows that radicals are good candidates to react directly with H₂ and form hydrogenated compounds, which can be considered as the first step of processes forming more complex molecules.

5. Conclusion

We observed that CN radicals are hydrogenated via H abstraction of H₂ forming HCN at very low temperatures. This reaction was performed in solid H₂, demonstrating that H₂ can be considered as a reactive reagent in the interstellar medium. The amount of H₂ which is embedded in ice is discussed controversially, nevertheless, Dissly et al. (1994) and Kristensen et al. (2011) estimate a molar fraction (H₂/H₂O) of approximately 0.05 and 0.3, respectively. These ratios would make the hydrogenation process of radicals, as proposed in this study, highly efficient as soon as reactive intermediates, such as radicals, are present.

We propose an original way of HCN formation that could occur in various objects of the ISM such as H₂ flakes, CHIMPs, or H₂ layers on grains. The prerequisite of this reaction is the existence of an intermediate, which is a radical in our study. The radical chemistry in ISM simulations should be studied more systematically in order to acquire quantitative data, such as the reaction barriers, that will allow a better understanding of this chemistry. Our results also make it clear that it is important to characterise other radicals and radical-like intermediates such as nitrenes and carbenes under ISM conditions.

Acknowledgements. This work funded was by a Hubert Curien Program from Campus France and DAAD agencies for the travelling cost between France and Germany. The authors thank Dr Jean-Claude Guillemin from ENSC-Rennes for indicating the synthesis of the C₂N₂. This work has been funded by the French National Program "Physique et Chimie du Milieu Interstellaire" (PCMI) and by

the CNES (Centre National d'Études Spatiales) agency. This work was supported by the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft (DFG).

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