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CN radical hydrogenation from solid H_2 reactions, an alternative way of HCN formation in the interstellar medium

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ABSTRACT

Context. Molecular hydrogen (H_2) 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 H_2 can act as a hydrogenation agent, reacting with CN radicals to form HCN.
Methods. In a H_2 matrix, we studied the hydrogenation of the CN radical generated from the vacuum ultraviolet photolysis (VUV-photolysis) of C_2N_2 at 3.8 K. We modified the wavelengths and the host gas in order to be sure that CN radicals can abstract H from H_2 molecules.
Results. HCN monomers, dimers, and oligomers have been characterised by Fourier transform infrared spectroscopy (FTIR). H_2CN as well as CN radicals have also been clearly observed during the photolysis performed at 3.8 K.
Conclusions. H_2 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 H_2 ice macro-particles (CHIMPs), H_2 flakes or in the first sublayers of grains where solid H_2 has accumulated.

Key words. astrochemistry – molecular processes – astrobiology – 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. H_2CO and CH_3OH 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 CH_3CHO yielding C_2H_5OH, CH_3OH, CH_4, and H_2CO (Bisschop et al. 2007). Water has also been produced by H bombardment on O, O_2, and O_3 (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; NH_3 was generated by reactions of H atoms in a N_2 matrix (Hiraoka et al. 1995). Recently, we investigated the hydrogenation of HCN (Theule et al. 2011) as well as CH_2NH producing methylamine CH_3NH_2.

In 2012, Oba et al. (2012) showed that water formation is also possible by reaction of OH radicals with H_2 via a quantum chemical tunnelling. These authors co-deposited OH obtained from a microwave discharge of water and H_2 on a cold surface. This reaction is important because it represents an example of H_2 acting as a direct hydrogenation reactant. Since H_2 is the most abundant molecule in the ISM, this experiment demonstrates the importance of direct hydrogenation by H_2. 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 H_2 interaction with water ice in ISM is increasing. The H_2 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 H_2 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 H_2 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 H_2 was proposed as flakes (Pfenniger & Puy 2003) or as H_2 dust stabilised by an electric field (Walker 2013), forming contaminated H_2 clusters (Bernstein et al. 2013). The later study proposed the presence of seeds in the ISM, where H_2 molecules can be accreted until forming cubic centimeter-sized objects called contaminated H_2 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 H_2 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 H_2 with a photoinduced radical CD_3. The reaction product was HCD_3 which demonstrates that H_2 can react with a radical forming the hydrogenated compound. Bahou et al. (2014) studied the reaction of photoinduced radicals in a H_2 matrix.

Here, we describe the hydrogenation of the astrophysically relevant radical CN produced by photolysis of cyanogen (C_2N_2). 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 H_2 matrix at 3.8 K and followed its reaction with H_2. Using this technique, we demonstrate that molecular H_2 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 H_2 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 H_2 were mixed in a vacuum line at room temperature with a small amount of C_2N_2 using standard manometric techniques. Matrices were produced by deposition of these gas mixtures through a calibrated valve on top of the cold surface. C_2N_2 was synthesised using a flash vacuum thermolysis of AgCN (Aldrich) at 10^{-2} mbar. AgCN decomposes forming CN radicals that recombine to form C_2N_2, which is trapped in liquid nitrogen. C_2N_2 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 H_2 flow lamp (Opthos Instrument), the flux was estimated to be approximately 10^{15} photons cm^{-2} s^{-1}. This flux allowed for irradiation with wavelengths higher than 120 nm through a MgF_2 window. In order to avoid direct H_2 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 wavelenghts above 160 nm. During the photolyses, spectra were recorded after different irradiation times.

3. Results and discussion

3.1. C_2N_2 deposition

C_2N_2 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.

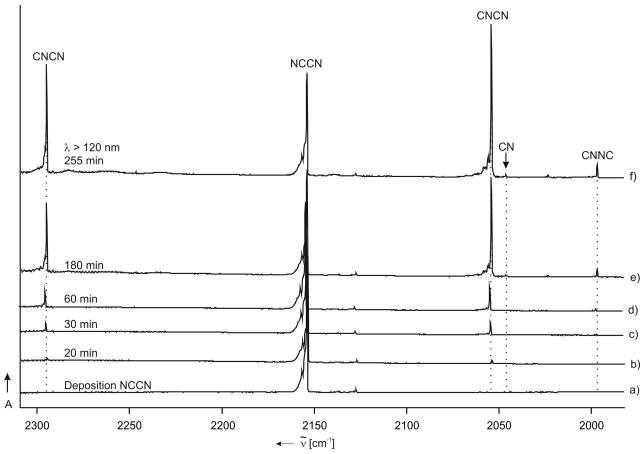


Fig. 1. IR spectrum of C_2N_2 / Ar (1/500) at 20 K with varying irradiation time using a hydrogen lamp. **a)** Deposition; **b)** 20 min; **c)** 30 min; **d)** 60 min; **e)** 180 min and **f)** 255 min of irradiation.

Figures 2a and 3a show a typical C_2N_2 matrix in H_2 deposited at 4 K in the ratio 1/500. Two main bands at 2157.3 and at 738.7 cm^{-1} are observed for C_2N_2 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 C_2N_2 synthesis from solid AgCN. According to the intensities of these bands, the water contamination impurity does not interfere with the experiments. CO_2 is also detected as a by-product of the synthesis of C_2N_2. The bands assigned to C_2N_2 are in good agreement with the literature (cf. Table 1).

In D_2 matrix, C_2N_2 displays the two same bands at 2157.6 and 741.7 cm^{-1}.

3.2. C_2N_2 VUV Irradiation in Ar matrix

C_2N_2 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 C_2N_2 has been largely studied in this range of wavelengths producing CN radicals in different electronic states (Dateo et al. 1987; Halpern & Jackson 1982; Taherian & Slanger 1984).

We irradiated C_2N_2 in Ar-matrix using a H_2 flow lamp. After a few minutes of irradiation, photolysis of the cyanogen is observed, C_2N_2 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. C_2N_2 VUV irradiation in a H_2 matrix

When the same irradiation experiments are performed in a H_2 matrix, the results are different. After 15 min of VUV

Table 1. C_2N_2 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	2157.6	2157	2156/2143	ν_{CN}
	738.7	741.7		739/724	combination bending mode

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

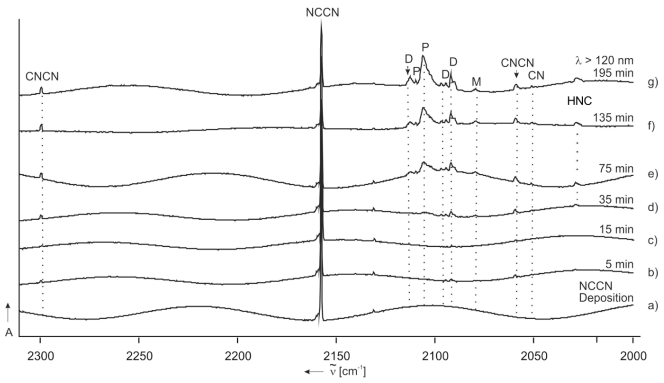


Fig. 2. IR spectra of C_2N_2 in a H_2 matrix in the range 2300−2000 cm^{-1} at different irradiation times using a hydrogen lamp and assignment of the new species. **a)** deposition; **b)** 5 min; **c)** 15 min; **d)** 35 min; **e)** 75 min; **f)** 135 min and **g)** 195 min of irradiation. D = Dimers of HCN, M = Monomer of HCN, P = Polymers of HCN.

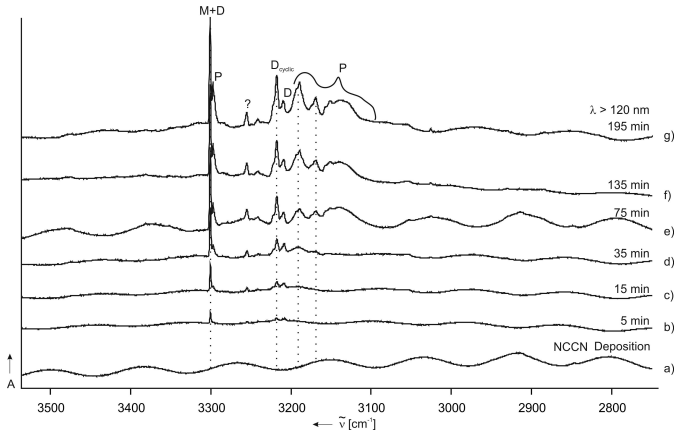


Fig. 3. IR spectra of C_2N_2 in a H_2 matrix in the range 3500−2800 cm^{-1} at different irradiation times using a hydrogen lamp and assignment of the new species. **a)** deposition; **b)** 5 min; **c)** 15 min; **d)** 35 min; **e)** 75 min; **f)** 135 min and **g)** 195 min of irradiation. D = Dimers of HCN, M = Monomer of HCN, P = Polymers of HCN.

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 H_2CN 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 C_2N_2 photodissociation subsequently reacts by abstraction of one H atom of H_2 molecules to form the hydrogenated compound. To be sure that the products are formed from the CN radicals reacting with H_2 and not by CN radical reacting with H atoms, we developed a strategy changing the wavelength of the irradiation in addition to using a D_2 matrix.

3.4. C_2N_2 VUV irradiation in a H_2 matrix using a sapphire window (λ > 147 nm) and an Ar lamp (λ > 160 nm)

The edge of the absorption band of H_2 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 H_2 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 MgF_2 window of our system with a sapphire which cuts off radiation below 147 nm. When the irradiation of the H_2 matrix containing C_2N_2 was performed using the H_2-flow lamp with a sapphire window, we observed the characteristic bands of HCN indicating that our postulated mechanism of CN radical reacting with H_2 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. C_2N_2 VUV irradiation in a D_2 matrix

We deposited C_2N_2 using the same protocol in a D_2 matrix. The two main bands of the cyanogen are observed at 2157.6 and 741.7 cm^{-1} very close to the positions in H_2 matrix (cf. Table 1). Irradiation of the D_2 matrix with the H_2 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

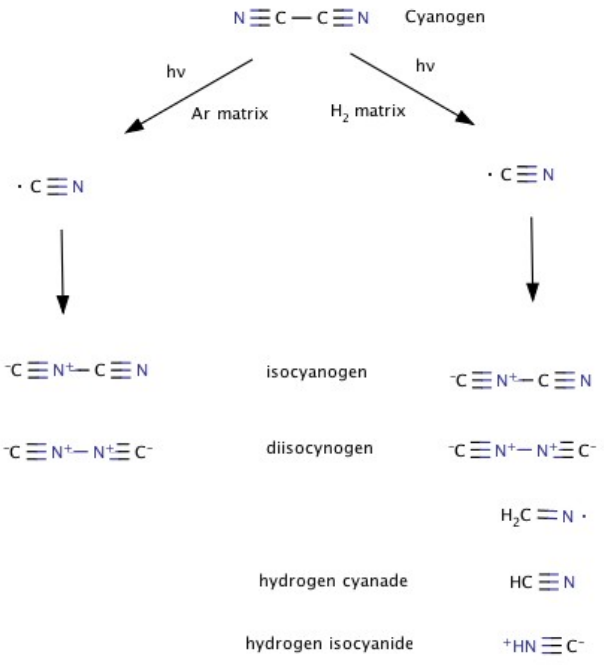


Fig. 4. C_2N_2 photolysis in an Ar matrix and in a H_2 matrix.

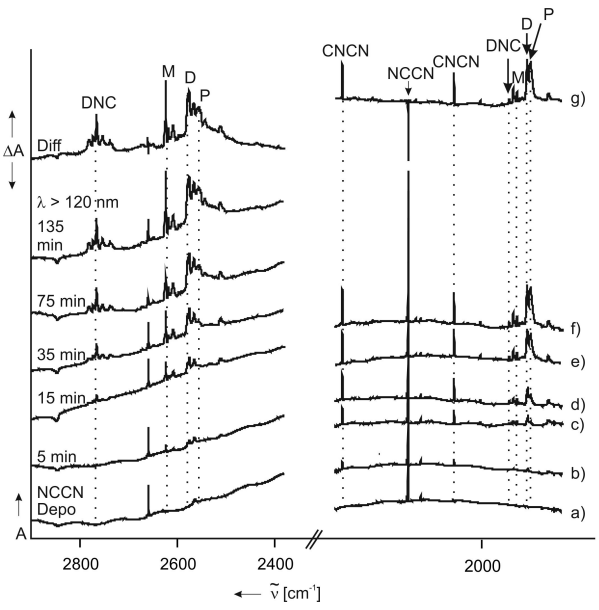


Fig. 5. IR Spectra C_2N_2 in D_2 matrix at 3.8 K with different time of VUV irradiation (λ > 120 nm). Assignments DCN-monomer (M) – dimers (D) and polymers (P), DNC and CNCN. **a)** deposition; **b)** after 5 min; **c)** 15 min; **d)** 35 min; **e)** 75 min; **f)** 135 min; and **g)** difference spectrum (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
C_2N_2/Ar	2295.3	CNCN
	2054.4	CNCN
	2050.8	CN radical
	1997.3	CNNC
C_2N_2/H_2	3622.2/3610.4	HNC
	3306.6	HCN monomer + dimer
	3297.3/3217.9	HCN polymer
	3192.9/3189.9	
	3157.6/3151.5	
	3209.1	HCN dimer
	2299.4	CNCN
	2112.4	HCN dimer
	2109.4 /2106.6	HCN polymer
	2094.3/2091.6	HCN dimer
	2079.1	HCN
	2059.1	CNCN
	2050.8	CN radical
	2028.6	HNC
	1337.5	H_2CN radical
	809.3	HCN polymer
	798.2/791.9	HCN dimer
	733.9/732.4	
	723.5	HCN
C_2N_2/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

HCN, 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 HCN 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 H_2, for instance reactions of carbenes with H_2 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 H_2 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 H_2 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 H_2.

Recently, Walker (2013) discussed the question of the solid H_2 survival in the ISM. He concluded that electrical charging processes stabilize H_2 grain surfaces even at temperatures where, usually, the volatility of H_2 is already very high (10 K). Lin et al. (2011) proposed to track H_6^+ as a probe for the presence of solid H_2. Bernstein et al. (2013) proposed the presence of contaminated CHIMPs. Molecules that are embedded in CHIMPs are in conditions very close to the H_2 matrix experiments. In these conditions, H_2 is a reagent for hydrogenation reaction. Following the classification of thermal reactions (Theule et al. 2013), H_2 is a generator of generation 0 molecules. Even at the low temperature of the ISM, it is clear that light species (H, H_2, 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, H_2 is predominant (Dixon et al. 1998) and, from a molecular point of view, H_2 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 H_2 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 H_2 forming HCN at very low temperatures. This reaction was performed in solid H_2, demonstrating that H_2 can be considered as a reactive reagent in the interstellar medium. The amount of H_2 which is embedded in ice is discussed controversially, nevertheless, Dissly et al. (1994) and Kristensen et al. (2011) estimate a molar fraction (H_2/H_2O) 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 H_2 flakes, CHIMPs, or H_2 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.

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