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Tentative identification of urea and formamide in ISO-SWS infrared spectra of interstellar ices

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Abstract. Laboratory experiments involving vacuum ultraviolet (VUV) irradiation of solid isocyanic acid (HNCO) at 10 K, followed by infrared spectroscopy (FTIR), are used to interpret the complex spectra associated with Interstellar Medium (ISM) dust grains, particularly the spectra associated with the icy phase observed toward dense molecular clouds. The comparison of the infrared spectra of the photolysis products with spectra recorded from the protostellar source NGC 7538 IRS9 shows that the “unexplained” 1700 cm^{-1} feature can be attributed to the contribution of several species H_2CO (formaldehyde), HCONH_2 (formamide) and H_2NCONH_2 (urea) mixed with H_2O as the main contributor. Urea, formaldehyde and $\text{NH}_4^+\text{OCN}^-$ (ammonium cyanate) may also contribute to a band at 1470 cm^{-1} , widely observed in many protostellar infrared sources and which remains up to now poorly explained in numerous ISO-SWS spectra. Isocyanic acid could be a precursor of formamide and urea in interstellar ices.

Key words. stars: individual: NGC 7538 IRS9 – methods: laboratory – infrared: ISM

1. Introduction

Cold dust grains (10–50 K) into dense interstellar clouds are mainly composed of H_2O , CO , CO_2 , CH_3OH , NH_3 and some trace constituents surrounding a silicate core (Greenberg 2002). These ice mixtures can be readily identified using laboratory simulations involving “classical” matrix isolation methods (d’Hendecourt & Dartois 2001). In the interstellar medium, under the UV irradiation field originating from hot stars, these ices are subject to photochemical processing and can evolve to form new and more complex products. Recent observations obtained from the Infrared Space Observatory (ISO) spectrometer SWS toward protostellar sources such as NGC 7538 IRS9 (Whittet et al. 1996) and W33A (Gibb et al. 2000) show the existence of features that remain poorly explained. Keane et al. (2001) claim that the absorption band observed in the 1700 cm^{-1} region is too broad and structured to be entirely due to H_2O ice. They suggest the presence of several complex organic species containing C=O groups. In these observations, a “XCN” band at $4.62\text{ }\mu\text{m}$ (2165 cm^{-1}), assigned to OCN^- (Soifer et al. 1979; Winnemisser & Kramer 1999; Bernstein et al. 2000; Novozamsky et al. 2001) is often detected. We assume here that the 2165 and 1700 cm^{-1} features are related and can have HNCO as precursor. HNCO is the simplest molecular specie in the interstellar medium (ISM) containing

all four most abundant elements. It has been identified in the gas phase in the ISM and in comets (Winnemisser & Kramer 1999) but never in the solid phase on interstellar grain mantles. Nevertheless HNCO can be a transient solid state species, produced and rapidly consumed by the formation of subsequent species. HNCO can be formed in the cold dust grains by vacuum ultraviolet (VUV) photolysis of CO/NH_3 mixtures (d’Hendecourt et al. 1986; Grim et al. 1989) and may play a specific role in the formation of $\text{NH}_4^+\text{OCN}^-$ from a purely acid-base reaction occurring at 10 K between HNCO and NH_3 (Novozamsky et al. 2001; Raunier et al. 2003).

We report here the VUV irradiation of HNCO monitored by means of in-situ infrared spectroscopy as a source of formaldehyde, formamide and urea, allowing the explanation of the feature observed at 1700 cm^{-1} in the spectrum of NGC 7538 IRS9 protostellar ice. We show that formamide and urea, which can be at the origin of some prebiotic molecules such as pyrimidine (Robertson & Miller 1995), are directly detected in dust grains in the ISM.

2. Experimental setup

The apparatus used in these experiments is an evacuated sample chamber (10^{-7} mbar) containing a rotating gold-plated mirror kept at 10 K, coupled to a Fourier Transform infrared spectrometer (Nicolet Magna 750) equipped with a liquid N_2 cooled detector, a germanium-coated KBr beamsplitter and a globar

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source. HNCO, synthesized from the thermal decomposition of cyanuric acid (Aldrich Chemical Co., 98%) at 650 °C, under a primary vacuum (Raunier et al. 2003) is deposited at a rate of $2 \times 10^{-2} \text{ mol min}^{-1}$ onto a gold mirror, then irradiated using a microwave discharge hydrogen flow lamp (Ophos instruments), mounted directly onto the sample chamber to simulate the interstellar radiation field. The beam of the lamp, transmitted through a MgF_2 window onto the substrate, is in the range 6 to 10 eV and its spectrum is dominated by two bands centered at 120 and 160 nm (Hagen et al. 1979; Jenniskens et al. 1993; Cottin et al. 2003). The sample chemical evolution at 10 K is monitored by measuring its IR spectrum in reflection mode between 4000 and 600 cm^{-1} at various irradiation times. For each spectrum one hundred interferograms were accumulated and the resolution was set to 1 cm^{-1} .

To verify the nature of the products formed during the HNCO photolysis, we successively deposited on the substrate the following species.

$\text{NH}_4^+\text{OCN}^-$ was produced by thermal reaction between ammonia (Air Liquide N36, $\text{H}_2\text{O} < 200 \text{ ppmv}$) and HNCO. HNCO and NH_3 (in a ratio 1/10) were deposited at a rate of $2 \times 10^{-2} \text{ mol min}^{-1}$ from two separate inlets onto the mirror held at 10 K, at a constant pressure of 10^{-7} mbar . The concentration was estimated by standard manometric techniques. Pure $\text{NH}_4^+\text{OCN}^-$ is obtained after sublimation of excess NH_3 and residual HNCO at 120 and 145 K respectively.

Formamide (HCONH_2 , Prolabo) was deposited at 10 K after purification by vacuum distillation.

Formaldehyde (H_2CO) was prepared from paraformaldehyde (Aldrich) at 65 °C in a stainless steel U-tube then carried in argon to the mirror cooled at 50 K to get a solid. Because of its low vapour pressure at ambient temperature, urea (H_2NCONH_2 , Aldrich 99%) at 10^{-7} mbar is heated at 50 °C then carried in argon to the mirror cooled to 50 K.

3. Results and discussion

Figure 1a shows the unirradiated HNCO infrared spectrum at 10 K in the $3600\text{--}1000 \text{ cm}^{-1}$ range. Three HNCO fundamental vibrational modes are observed and the frequencies are displayed in Table 1 with their assignments (Lowenthal et al. 2002; Raunier et al. 2003). The HNCO spectrum is characterized by an intense vibrational band at 2252 cm^{-1} and a broad feature split in two bands at $3365\text{--}3200 \text{ cm}^{-1}$, which are respectively related to ν as NCO and νNH stretching modes. Figures 1b and 1c show the IR spectra of the sample after 3.5 and 8.5 h of VUV photolysis; the positions and identifications of the IR features of each new product are listed in Table 1.

In the $2600\text{--}2100 \text{ cm}^{-1}$ region, we observe that both CO and CO_2 absorption bands at 2138 and 2343 cm^{-1} increase continuously during irradiation. Besides these two bands, we observe the growth of a symmetrical band at 2165 cm^{-1} , with a width (*FWHM*) of 25 cm^{-1} , in good agreement with the expected frequency for OCN^- (Hudson et al. 2001).

Another broad band, located near 2800 cm^{-1} , can be ascribed to NH_4^+ , based on the spectral data of this species (Raunier et al. 2003). These observations show the presence

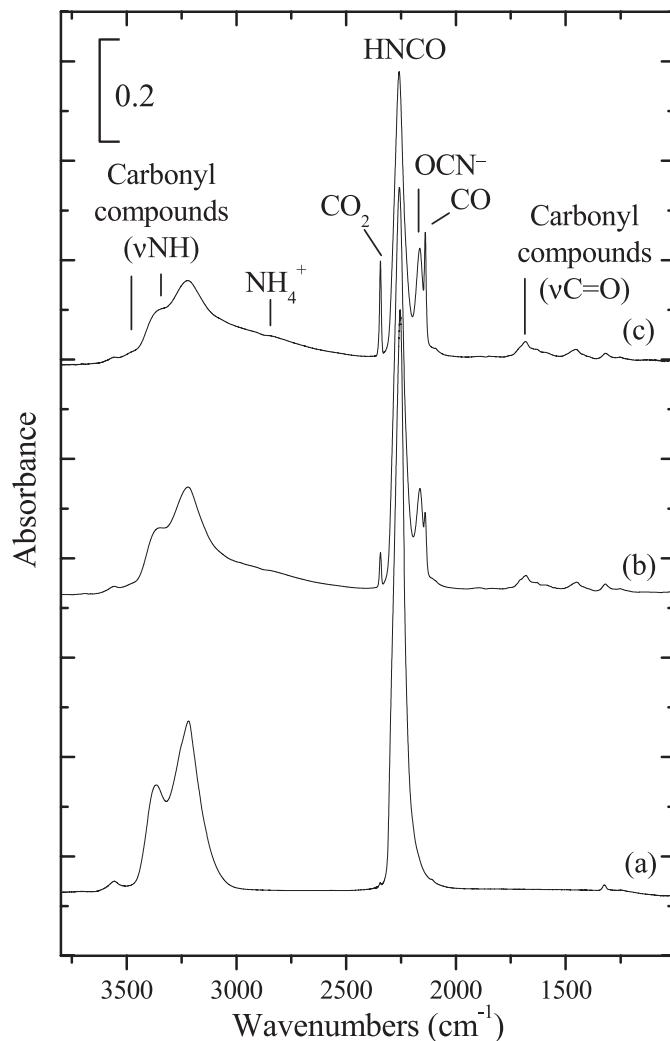


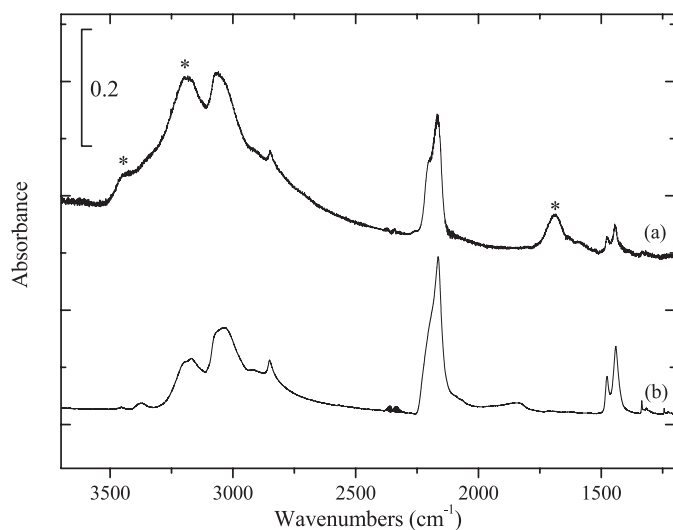
Fig. 1. VUV irradiation of solid HNCO at 10 K a) 0 h, b) 3.5 h, c) 8.5 h.

of NH_4^+ and its counterion OCN^- . Clear evidence of the presence of $\text{NH}_4^+\text{OCN}^-$ in the mixture is obtained when the sample is warmed above 150 K to sublime the residual HNCO. Under these conditions, we can observe the vibrational bands related to this species by comparison with the $\text{NH}_4^+\text{OCN}^-$ spectrum obtained from the thermal reaction at 10 K between ammonia and HNCO (Fig. 2). However, during irradiation, no trace of NH_3 , necessary to produce $\text{NH}_4^+\text{OCN}^-$, is detected. This result is not surprising because NH_3 reacts spontaneously with HNCO at 10 K and leads to $\text{NH}_4^+\text{OCN}^-$ (Raunier et al. 2003). In addition, NH_3 is strongly sensitive to irradiation in the VUV region and can be easily photodissociated into NH and H (Jacox & Milligan 1964).

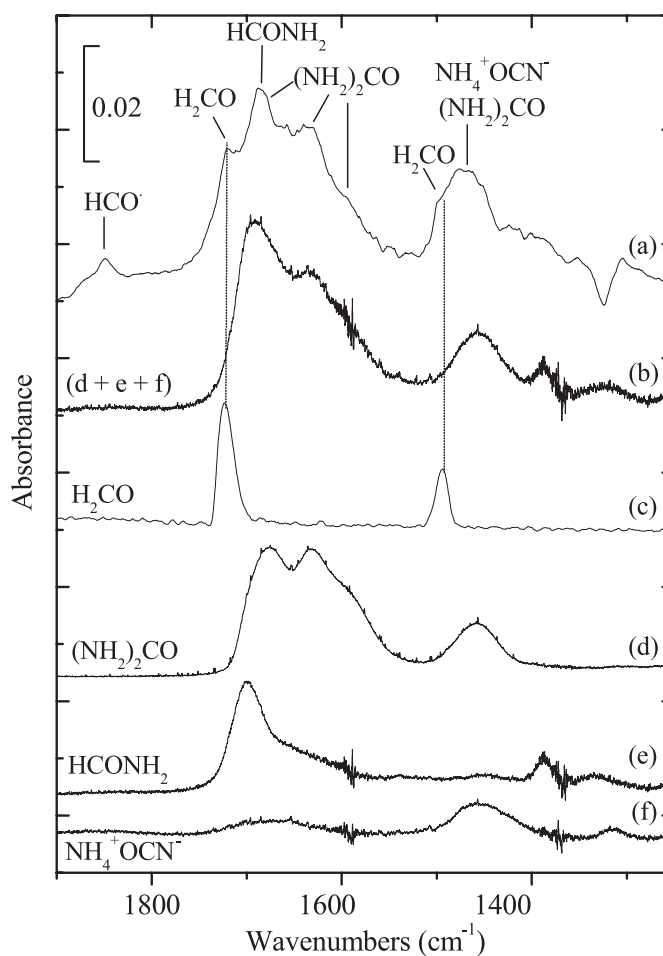
In the $1900\text{--}1100 \text{ cm}^{-1}$ range, a broad and structured band grows at 1700 cm^{-1} indicating the formation of several carbonyl compounds. On the spectrum relative to the primary photoproducts recorded between 3.5 and 8.5 h of irradiation (Fig. 3a), we identify formaldehyde (H_2CO), formamide (HCONH_2) and urea (H_2NCONH_2) as deduced from comparison with spectra of the pure sample recorded at 10 K. Formaldehyde is characterized by bands at 1722

Table 1. Fundamental infrared band positions (cm^{-1}) with their assignments of the species produced during the VUV irradiation of solid HNCO.

Vibration	HNCO	CO	CO ₂	OCN ⁻	NH ₄ ⁺	H ₂ CO	HCONH ₂	H ₂ NCONH ₂
N–H stretch	3365–3220				2800		3316	3450
N=C=O _{asym.} stretch	2252			2165				
N–H _{sym.} bend								1675
N–H _{asym.} bend								1630
C=O stretch		2138	2343			1722	1700	1590
C–H _{sym.} bend						1494		
C–N _{asym.} stretch								1460
N–H _{sym.} bend					1470		1386	
N=C=O _{sym.} stretch	1322–1252							

**Fig. 2.** Comparison of the spectra of **a)** the sample at 200 K obtained from 8.5 h HNCO irradiation at 10 K (The * show the presence in the residue of carbonyl compounds, formamide and urea) with **b)** NH₄⁺OCN⁻ at 200 K obtained from a co-deposition of HNCO/NH₃. This spectrum is different to that recorded at 10 K.

and 1494 cm^{-1} , whereas formamide and urea are characterized by the band sets, $1700\text{--}1386 \text{ cm}^{-1}$ and $1675\text{--}1630\text{--}1590\text{--}1460 \text{ cm}^{-1}$. The last irradiation time (8.5 h) corresponds to a 50% disappearance of HNCO allowing one to obtain a maximum of absorption for the vibrational bands relative to the carbonyl compound products. A simple addition of the spectra corresponding to cyanate ammonium, formamide, urea (Fig. 3b) and formaldehyde (Fig. 3c) gives an excellent match with the spectrum of the irradiated sample (Fig. 3a). This confirms the formation of these carbonyl compounds during the photolysis process. It is more difficult to obtain a good fit in the νNH region because the HNCO band remains present. However, we note that new and weak features near 3300 cm^{-1} appear around 3450 and 3300 cm^{-1} (Fig. 1c) which are very close to the expected frequencies for solid urea (Rousseau et al. 1998) and formamide (Bukowska 1979). Our results also show a good agreement for the broad band located near 1470 cm^{-1} between the spectrum of the primary photoproduct irradiated (Fig. 3a) and the spectrum resulting from the addition of formaldehyde, urea and ammonium cyanate spectra (Fig. 3b).

**Fig. 3.** Comparison between the spectra at 10 K of **a)** VUV primary photoproducts irradiated and **b)** sum of spectra corresponding to **c)** pure solid formaldehyde, **d)** pure solid urea, **e)** pure solid formamide and **f)** pure solid ammonium cyanate. The spectrum **a)** results from the irradiation of primary photoproducts induced from the VUV solid HNCO at 10 K and is relative to the difference spectrum recorded between the 3.5 h (Fig. 1b) and 8.5 h (Fig. 1c) irradiation times.

The spectrum of the primary irradiated photoproducts (Fig. 3a) can also be used to characterize the species existing in the interstellar ice. Molecular ice towards the young stellar object NGC 7538 IRS9 contain H₂O and NH₃, where NH₃/H₂O ratio is about 10%. It follows the formation of ammonia hydrate (NH₃.H₂O) which has an absorption band in

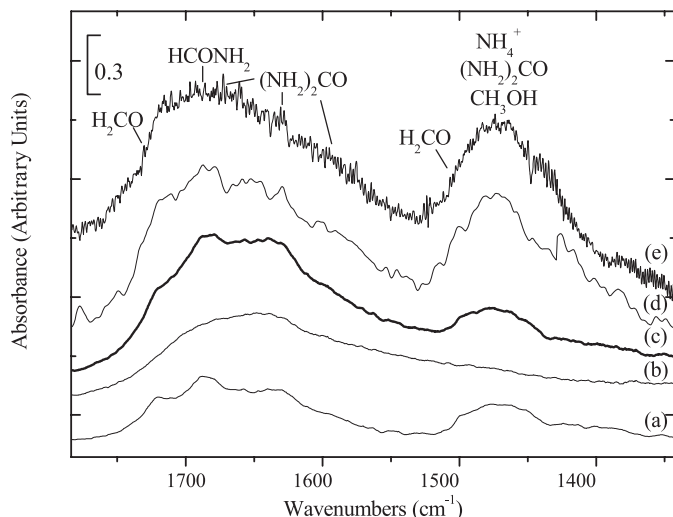


Fig. 4. Comparison between the e) SWS 06, d) SWS 01, ISO-SWS spectra of the protostellar object NGC 7538 IRS9 (Whittet et al. 1996) with the c) sum at 10 K corresponding to the addition of the spectra of b) solid $\text{NH}_3/\text{H}_2\text{O}$ (10/100) and a) VUV primary photoproducts of HNCO irradiated (the same as Fig. 2a). The b) spectrum of ammonia hydrate ($\text{NH}_3 \cdot \text{H}_2\text{O}$) is multiplied by a factor of 20 to get saturation of the νOH feature near 3200 cm^{-1} as observed in the ISO spectrum recorded toward the protostellar object NGC 7538 IRS9. The a) spectrum is multiplied by a factor of 90 in order to get features comparable in intensity to those of the ISO spectrum recorded toward the protostellar object NGC 7538 IRS9. ISO Short Wavelength Spectrometer (ISO-SWS) spectra of NGC 7538 IRS9 have been extracted from the ISO database (<http://iso-www.estec.esa.nl>). The SWS01 (low resolution 500) and SWS06 (high resolution 2000) were recorded on February 23th, 1996 and correspond to a total integration time of 1816 and 6894 s (SWS01 and 06 respectively).

the $1600\text{--}1700\text{ cm}^{-1}$ range (Dartois & d'Hendecourt 2001). Thus, to be compared with the NGC 7538 IRS9 spectrum in this range, our previous spectrum (Fig. 4a, the same as Fig. 3a) has been added to that corresponding to the $\text{NH}_3/\text{H}_2\text{O}$ in a ratio 10/100 (Fig. 4b) to give Fig. 4c. The contributions relative to the $\text{C}=\text{O}$ stretch and NH bend absorptions of these molecules are both in good agreement with the NGC 7538 IRS9 1700 cm^{-1} feature. It is clear that the 1470 cm^{-1} feature recorded in astrophysical ice is not only the result of NH_4^+ absorption but also of other species (Schutte & Khanna 2003). Thus, formaldehyde and urea must also contribute to the 1470 cm^{-1} band. The intensity difference observed between the spectra of the irradiated sample and of NGC 7538 IRS9 could be explained from the methanol CH bend absorption present in the dust grains and not taken into account in our experiments. The methanol may contribute between 30 and 50% of this absorption (Dartois et al. 1999).

The formation of these carbonyl compounds can be simply explained from the literature. In the VUV region, two HNCO dissociation channels are allowed, leading respectively to $\text{H} + \text{NCO}$ (reaction 1) and $\text{HN} + \text{CO}$ (reaction 2) (Zhang et al. 1995; Brownsword et al. 1997). Reaction 1 is a source of H atoms which can play a role in the production of new species. Thus NH_3 , necessary to form $\text{NH}_4^+\text{OCN}^-$, should be the result of a reaction between H atoms and successively NH (induced from

reaction 2) and NH_2 radicals (Lundell et al. 1998). The HCO radical formation observed during the VUV irradiation process (band at 1850 cm^{-1}) (Fig. 2a) (Allamandola et al. 1988) suggests that formaldehyde is produced according to the successive hydrogenation reactions $\text{CO} + \text{H} \rightarrow \text{HCO}$ and $\text{HCO} + \text{H} \rightarrow \text{H}_2\text{CO}$. Formamide formation can be explained by the following reactions $\text{H} + \text{HNCO} \rightarrow \text{NH}_2\text{CO}$ and $\text{H} + \text{NH}_2\text{CO} \rightarrow \text{HCONH}_2$ involving the NH_2CO radical as a transient species. This radical has been detected in matrix isolation experiments (Pettersson et al. 1999). Finally, we assume that urea formation can result from a recombination between NH_2CO and NH_2 radicals formed in the prior reactions. Formamide and urea formation require the intervention of at least three and four molecules of HNCO in the mechanism.

4. Conclusions

Contribution of formamide and urea can be directly detected at low temperatures in the cold dust grains in NGC 7538 IRS9 especially from their strongest bands located at 1700 , 1675 , 1630 and 1590 cm^{-1} . These values can be used to find traces of these molecules inside other astrophysical ices. The detection of urea in our work corroborates the results obtained earlier by Agarwal et al. (1985) who identified urea by GC-MS analysis of the products obtained from the photolysis at 10 K of CO/NH_3 mixtures.

The non-detection of HNCO in interstellar grains may be due to its high reactivity with NH_3 at temperatures as low as 10 K to form $\text{NH}_4^+\text{OCN}^-$ and its dissociation under VUV irradiation to form the products mentioned.

The results of these experiments have important implications for both interstellar and cometary chemistry. The organic molecules detected here, mainly formamide and urea, are biologically interesting and may help establish the importance of extraterrestrial sources of organic material for the Earth prior to the onset of life. Urea plays a large part in the prebiotic synthesis of pyrimidines (Robertson & Miller 1995) which have been detected, for example, in the Murchison meteorite (Stock & Schwartz 1981).

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