

Laboratory identification of the $4.62\mu\text{m}$ solid state absorption band in the ISO-SWS spectrum of RAFGL 7009S^{*}

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Received 5 January 1998 / Accepted 22 August 1998

Abstract. We focus on the problem of the assignment of the “XCN” solid state feature observed in the spectra of numerous protostellar objects. This feature, located at $4.62\mu\text{m}$ has been tentatively identified with the molecular ion OCN^- . New laboratory experiments have been performed in order to confirm this identification. OCN^- is produced by UV photolysis of mixtures of $\text{CO}:\text{NH}_3$ (1:1) deposited on a cold substrate. Simultaneously, the counterion NH_4^+ is also produced to balance the charge in the matrix. The use of electron donor and acceptor dopants incorporated in the mixtures allows us to reduce or enhance the production of the OCN^- and NH_4^+ features, thus establishing their ionic character. The production of HNCO when an electron acceptor is used, and the formation of the OCN^- band during thermal annealing, constitute convincing arguments in favour of the formation of OCN^- and NH_4^+ by acid-base reactions where the acid HNCO transfers a proton to the base NH_3 . We consider the astrophysical implications for the interpretation of the ISO-SWS spectrum of the protostellar source RAFGL 7009S. In this source, the $4.62\mu\text{m}$ band is deep and large, although the derived abundance of this ion, relative to H_2O ice, is on the order of 4%. Identification of OCN^- is considered in several other sources. The contribution of NH_4^+ to the unidentified $6.85\mu\text{m}$ feature is discussed.

Key words: ISM: individual objects: RAFGL 7009S – ISM: molecules – ISM: abundances – molecular processes – dust, extinction

1. Introduction

Ground based observations towards dense clouds have for a long time revealed the presence of grain mantles composed of molecules such as H_2O , CO , CH_3OH ... (Willner et al. 1982,

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^{*} Based on observations with ISO, an ESA project with instruments funded by ESA Member States (especially the PI countries: France, Germany, the Netherlands and the United Kingdom) and with the participation of ISAS and NASA.

Grim et al. 1991). Extensive laboratory work has been undertaken over a long period in order to understand the solid state chemical reactions that occur on the interstellar grains. These reactions are induced by interactions between the molecules in the ices and the UV radiation field and/or cosmic rays which deposit energy in the ices. The deposited energy drives reactions with activation energies and can break molecular bonds to form radicals which react with other species to form new molecules.

Laboratory experiments have shown that the UV photolysis of interstellar ice analogs is very efficient at producing new species. For example, d'Hendecourt et al. (1986b) showed that molecules such as CO_2 , H_2CO and others are easily produced by the photolysis of ices, and much laboratory work has confirmed this (e.g. Allamandola et al. 1988). Laboratory spectroscopy of astrophysical ice analogs have thus permitted the identification of numerous molecules in interstellar spectra (Whittet 1993). As an example, CO_2 was detected by d'Hendecourt & Jourdain de Muizon (1989) in the spectra of three protostellar objects obtained with the IRAS-LRS instrument. This detection was made using the laboratory spectra of photolysed ice mixtures that closely matched the IRAS-LRS spectra.

For the first time, thanks to its large spectral range ($2.5\text{--}45\mu\text{m}$ for the Short Wavelength Spectrometer, de Graauw et al. 1996), the ISO satellite (Kessler et al. 1996) has unambiguously confirmed that molecules such as H_2O , CO , CO_2 are widely present in protostellar environments (Whittet et al. 1996). Methanol is observed in most protostars (Grim et al. 1991, Allamandola et al. 1992). Solid CH_4 has been identified by d'Hendecourt et al. (1996) in the spectrum of the protostellar object RAFGL 7009S with an abundance of 4% relative to H_2O . Compared to the detection of CH_4 by Boogert et al. (1996), in the protostars W33A and NGC7538:IRS9 (with abundances of 0.4–1.9% of the H_2O abundance) the abundance found in RAFGL 7009S is large. All these ISO observations thus confirm the previous detection of methane made by Lacy et al. (1991). In addition to these identified spectral features, most protostellar sources show two strong absorption features in their spectra that are not yet unambiguously identified: the 4.62 (the so-called XCN band) and the $6.85\mu\text{m}$ bands.

The 4.62 μm feature was first observed by Soifer et al. (1979) in the spectrum of the protostar W33A. Lacy et al. (1984) observed this band in four other protostars. The position and width of this feature led them to assign it to a solid molecular species containing a triple CN bond. They found that this band was most easily produced by UV photolysis of laboratory mixtures containing CO and NH_3 . Tegler et al. (1993) detected the XCN band in the protostellar object L1551 IRS5 and tried to fit the band with laboratory spectra of photolysed mixtures containing H_2O , CH_3OH , CO, NH_3 . Numerous carriers have been proposed for this band, such as nitriles ($\text{R}-\text{C}\equiv\text{N}$) or isonitriles ($\text{R}-\text{N}\equiv\text{C}$) (Larson et al. 1985, d'Hendecourt et al. 1986b). Grim & Greenberg (1987) discussed the spectroscopic validity of the assignment of the XCN band to nitriles and isonitriles and proposed the negative ion OCN^- as an alternative assignment. Schutte & Greenberg (1997) studied the shift of the XCN band position induced by the use of the isotope ^{18}O . They also detected in their experiments three other weak bands of OCN^- at 1296, 1206 and 630cm^{-1} and concluded that OCN^- is a good candidate for the XCN band. Recently Bernstein et al. (1997) studied the infrared properties of numerous nitrile and isonitrile compounds in argon and H_2O ice. They argue for an assignment of the XCN band to a nitrile or isonitrile species that forms a strong complex with H_2O .

Another strong unidentified feature, the 6.85 μm feature, is usually observed in infrared sources where the XCN band is present (Tielens et al. 1984; Tielens & Allamandola 1987). The possible carriers proposed for this band were hydrated silicates, carbonates, methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$) bending vibrations in hydrocarbons or in alcohol (Grim et al. 1989a and references therein). Grim et al. (1989b) assigned this feature to the positive ion NH_4^+ and proposed that OCN^- and NH_4^+ are produced simultaneously by acid-base reactions. During these reactions, the base NH_3 and the acid HNCO react through proton transfer, leading to the formation of the two ions.

We have performed laboratory experiments in order to show the ionic nature of the carrier of the 4.62 μm band and to confirm its identification with OCN^- . Sect. 2 of this paper describes the set-up and the laboratory experiments performed. In Sect. 3 we present the results concerning the ionic character of the carriers of the two bands, the identification of OCN^- and NH_4^+ in the laboratory ices, the correlation of the two bands under photolysis and annealing, and the mechanism of formation of these ions. Finally, the astrophysical implications for the composition of ices and the contribution of NH_4^+ to the 6.85 μm interstellar band are discussed with an application to the protostellar object RAFGL 7009S (Sect. 4).

2. Laboratory experiments

2.1. Set-up

Laboratory experiments aimed at simulating the chemical evolution of interstellar ices are numerous and have been described by various authors (e.g. Allamandola 1987). These experiments use the classical method of "Matrix Isolation Spectroscopy" where

various gases are deposited on a cold substrate. This method allows unstable species such as ions or radicals to be studied because the low temperature of the matrix (10-15K) does not allow further evolution of these species (Jacox 1989).

In our laboratory, mixtures are prepared in the gas phase at ambient temperature in a stainless steel vacuum chamber evacuated to a pressure of 10^{-6}mb . The partial pressures of the gases are monitored with an absolute pressure gauge (1-50mb). Gases are then deposited in a cryogenic cell cooled to liquid helium temperature (4.2K). At this temperature the ambient pressure is around 10^{-7}mb . The CsI window on which the gases are deposited is maintained at a temperature of 12K. The infrared spectra are recorded with a Bruker FTS-IFS 66v spectrometer at a resolution of 2cm^{-1} , well-adapted for solid state features and also for comparison with astronomical observations, especially those obtained with the ISO-SWS instrument. The samples were photolysed using a UV lamp to simulate the interstellar radiation field and drive the photochemical processing. The lamp used is a microwave discharge hydrogen flow lamp which produces photons of energy ranging from 6 to 10eV with two peaks at around 1200 and 1600Å.

2.2. Experiments

To establish the ionic character of both the 4.62 and 6.85 μm bands in the laboratory, we have used electron acceptors and donors. Electron acceptors slow down the production of negative ions while favouring the formation of positive ones. We have used carbon tetrachloride (CCl_4) and sulfur hexafluoride (SF_6) as electron acceptors. CCl_4 is a non reactive molecule, commonly used as a solvent in chemistry. Its infrared spectrum presents no feature at the wavelengths of interest, 4.62 and 6.85 μm (2165 and 1460cm^{-1} respectively). Its role as an electron acceptor in cryogenic matrices has been studied by Salama & Allamandola (1991). They concluded that CCl_4 attracts electrons by forming a three electron bond between a Cl atom, dissociated from the CCl_4 molecule during the photolysis, and a Cl atom from the CCl_3^+ group, i.e. $\text{CCl}_3^+ \cdot \cdot \cdot \text{Cl}$. SF_6 was used as a second electron acceptor to differentiate features due to the acceptors from features due to other species in the matrix. The electron donor used was 2-methyltetrahydrofuran (C_5OH_3). This molecule contains a furan cycle which can loose an electron thus acting as an electron donor. When added to a mixture it dramatically decreases the production of positive ions while increasing that of negative ions. Furthermore, its infrared spectrum shows no feature at 1460 or 2165cm^{-1} .

In the mixture $\text{CO}:\text{NH}_3$ (1:1), the CO band is located at 2137cm^{-1} and has a FWHM of 10cm^{-1} . For pure amorphous CO it is known that the position of the band is 2138cm^{-1} and that the FWHM is 5cm^{-1} (Sandford et al. 1988). The broadness of the CO band in the $\text{CO}:\text{NH}_3$ mixture indicates that the mixture is polar, due to the presence of the highly polar molecule NH_3 . The studied mixtures contain CO, NH_3 and SF_6 or the electron donor in abundance ratios of 10:10:1 and 10:10:2 for the mixture containing CCl_4 . The spectra of these non-photolysed mixtures, compared with the $\text{CO}:\text{NH}_3$ (1:1) one, show a maximum shift

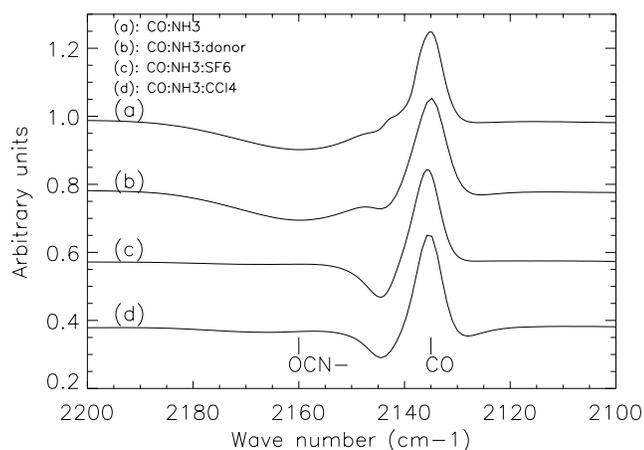


Fig. 1a–d. Ratio of the transmittance spectra of the photolysed to the non-photolysed mixture for CO:NH₃ (1:1), CO:NH₃:e⁻ donor (10:10:1), CO:NH₃:SF₆ (10:10:1) and CO:NH₃:CCl₄ (10:10:2). All the spectra are normalised to the CO band. During photolysis the CO at 2135cm⁻¹ is consumed while the OCN⁻ at 2160cm⁻¹ is produced, except in **c** and **d** where the electron acceptors inhibit the production of OCN⁻. Note that the band at 2145cm⁻¹ in the curves is due to the deformation of the CO band during the photolysis and not to a photochemically produced molecule.

of 2cm⁻¹ for the CO band at 2137cm⁻¹ and of 1 and 2cm⁻¹ for the NH₃ bands at 1627 and 1061cm⁻¹ respectively. The FWHM of the CO band is about 9–10cm⁻¹ for all mixtures. Thus the presence of these electron donors and acceptors does not further perturb the spectrum of the initial CO:NH₃ mixture. After photolysis the position of the two studied bands in the different mixtures varies from 2160 to 2165cm⁻¹ for the XCN band and from 1460 to 1500cm⁻¹ for the “1460 cm⁻¹” band. During annealing the shift of the XCN band does not exceed 5cm⁻¹, whereas the “1460cm⁻¹” band can be shifted up to 50cm⁻¹. This will be discussed in more detail later.

3. Results

3.1. Ionic nature of the carriers of the two bands

As mentioned above, the ionic nature of both features is studied by using electron acceptors and donors. Mixtures CO:NH₃ (1:1), CO:NH₃:SF₆ (10:10:1), CO:NH₃:CCl₄ (10:10:2) and CO:NH₃:2-methyltetrahydrofuran (10:10:1) were irradiated with increasing photolysis times. A spectrum was taken at each step of the photolysis in order to study the evolution of the chemical reactions that take place during the photolysis. This also facilitates the identification of the molecules produced during the photolysis because it permits a correlation of the different bands that appear. Figs. 1 and 2 present the ratio of the photolysed to the non-photolysed spectra for these mixtures. These curves show what has been produced (downward peaks) and consumed (upward peaks) during the photolysis. They are normalized to the diminishing quantity of CO, which expresses the efficiency of the photolysis. Such a normalisation thus permits us to compare the results of about the same UV photon exposure

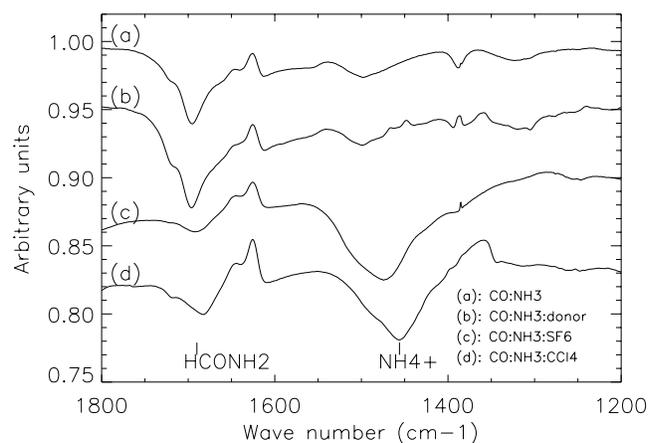


Fig. 2a–d. Ratio of the transmittance spectra of the photolysed to the non-photolysed mixture for CO:NH₃ (1:1), CO:NH₃:e⁻ donor (10:10:1), CO:NH₃:SF₆ (10:10:1) and CO:NH₃:CCl₄ (10:10:2). The normalisation is the same as in Fig. 1. The bands at 1460 (1500cm⁻¹ in **(a)** and **(b)**) and 1696cm⁻¹ show respectively the production of NH₄⁺ and HCONH₂ during photolysis.

for the four experiments. The optical depth of the two lines at 2165 and 1460cm⁻¹ are much affected by the use of the electron acceptors and donors. When an electron acceptor is used (Figs. 1c and 1d), the production of the XCN feature is much less efficient than when a donor is used (Fig. 1b). This indicates that the carrier of this band is a negative ion because its production is favoured when the mixture is electron-rich, i.e. when an electron donor is present. Conversely, the use of an electron acceptor increases the production of the 1460cm⁻¹ band (Figs. 2c and 2d) while this band is inhibited when an electron donor is present (Fig. 2b), indicating that this feature is due to a positive ion.

3.2. Identification to OCN⁻ and NH₄⁺

When the production of the XCN band is inhibited a band appears at 2255cm⁻¹. This band, characteristic of the ν_2 vibration of NCO in HNCO (Bondybey & English 1982), is absent in the spectrum of mixtures without an electron acceptor. Fig. 3 shows the photolysed spectra of the mixture CO:NH₃:CCl₄ (10:10:2) at different temperatures. As the temperature increases, the 2255cm⁻¹ band diminishes while that due to XCN increases. Grim et al. (1989a) assigned the band at 2255cm⁻¹ to HNCO. This molecule is produced from CO and the decomposition products of NH₃ under photolysis. The presence of this band when the production of XCN is limited, and the transfer from HNCO to the XCN band as the temperature increases, strongly support the identification of the XCN band with OCN⁻, assuming that OCN⁻ is produced via an acid-base reaction where HNCO is the acid. This is in agreement with previous laboratory experiments that showed that the XCN band is not produced in oxygen-free mixtures (Grim & Greenberg 1987). Furthermore it confirms, using a different method, the identification made by Schutte & Greenberg (1997) based on isotope shift and on the

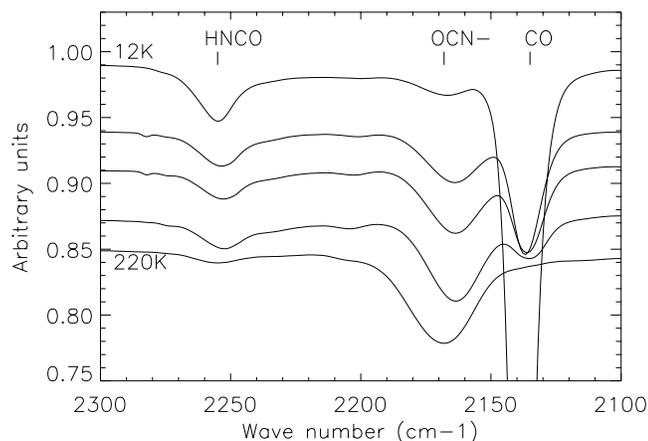


Fig. 3. Transmittance spectra of the photolysed mixture CO:NH₃:CCl₄ (10:10:2) at different temperatures. The temperature increases linearly from 12K (upper spectrum) to about 220K (lowest spectrum). As the temperature increases the HNCO band at 2255cm⁻¹ weakens and the OCN⁻ band at 2165cm⁻¹ strengthens as the CO evaporates (2138cm⁻¹).

detection of three other weak OCN⁻ bands that correlate with the XCN band.

Similarly, we note that the band at 1696cm⁻¹ (Fig. 2) is much deeper when the production of the 1460cm⁻¹ band is weak. Other features seen at 1389, 1328 and 2874cm⁻¹ show the same behaviour as the band at 1696cm⁻¹. Comparison with the laboratory spectrum of pure solid formamide at 10K permits us to assign these bands to the formamide molecule, HCONH₂. This identification is in agreement with that of Grim et al. (1989a). The behaviour of these two bands can be understood if the carrier of the 1460cm⁻¹ feature is NH₄⁺. When an electron acceptor is used, the production of NH₄⁺ is enhanced and much more ammonia present in the mixture is converted into the ammonium ion NH₄⁺. On the contrary, when its formation is inhibited, the NH₃ is available to produce other nitrogen-containing molecules such as HCONH₂. Furthermore, thermal annealing of the laboratory mixtures shows that the 1460cm⁻¹ band in CO:NH₃:CCl₄ mixture is distorted and red-shifted to 1410cm⁻¹ (Fig. 4). Comparison of this spectrum with spectra of solid NH₄Br and NH₄SCN shows that the shape and the position of this band are close to those of the NH₄⁺ cation vibration in these two salts (Fig. 5), thus confirming the assignment of the 1460cm⁻¹ band to NH₄⁺ in our laboratory data.

3.3. Correlation of the bands

In all the studied mixtures, the OCN⁻ and NH₄⁺ bands are well-correlated. In the CO:NH₃ mixture the evolution of the OCN⁻ and NH₄⁺ features is identical: both bands appear and grow simultaneously during photolysis. Note that when a dopant is used there is no correlation under photolysis since one or the other band is favoured. During annealing, a correlation of the two bands is observed in all mixtures and their behaviour is

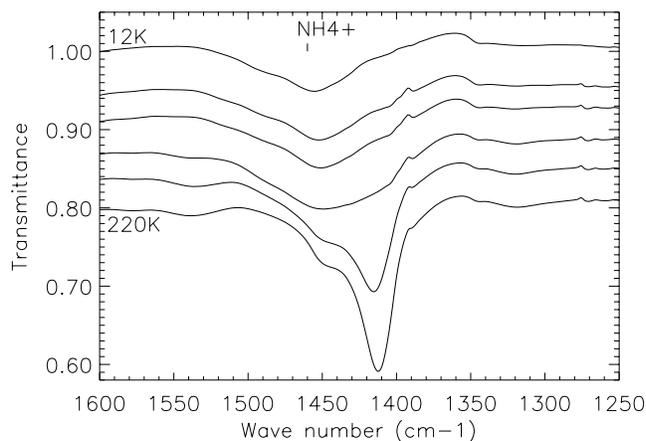


Fig. 4. Transmittance spectra of the photolysed mixture CO:NH₃:CCl₄ (10:10:2) at different temperatures. The temperature increases linearly from 12K (upper spectrum) to about 220K (lowest spectrum). As the temperature increases the NH₄⁺ band is shifted from 1460 to 1410cm⁻¹ and the band shape alters.

identical. The optical depth of both bands increases and the position of the bands shifts.

The simultaneous appearance of the two features supports the assumption that these ions are formed by the same mechanism. Furthermore, the transfer of the HNCO to the OCN⁻ band observed during the annealing of mixtures containing an electron acceptor (Fig. 3) suggests that the mechanism is an acid-base reaction with HNCO as the acid and NH₃ as the base. The acid HNCO transfers a proton to the base NH₃ thus producing NH₄⁺ ··· OCN⁻.

The observed increase of the efficiency of the proton transfer under annealing is in agreement with the theory of acid-base reactions. Zundel & Fritsch (1986) show that the most important parameter in the shift of the equilibrium to proton transfer from the acid to the base is the interaction of hydrogen bonds with the environment. When the temperature is increased, the interactions in the ice become stronger and thus the proton transfer increases the production of OCN⁻ and NH₄⁺ with a corresponding increase of the two associated bands.

3.4. Integrated cross section

3.4.1. OCN⁻

We have calculated the integrated cross section per molecule \mathcal{A}_x for OCN⁻ by using the following relation:

$$N_x = \frac{\int_{\nu_1}^{\nu_2} \tau_\nu d\nu}{\mathcal{A}_x}$$

in which N_x is the number of absorber x per cm² and $\int_{\nu_1}^{\nu_2} \tau_\nu d\nu$ is the integrated optical depth of an absorption line of the species x (the area of the band, hereafter denoted S). In the CO:NH₃ mixture, following the evolution of the molecules containing oxygen, the CO consumed during the photolysis is converted into CO₂, OCN⁻, HCONH₂. Furthermore in the initial mixture, the oxygen is only present in the CO molecules thus two CO

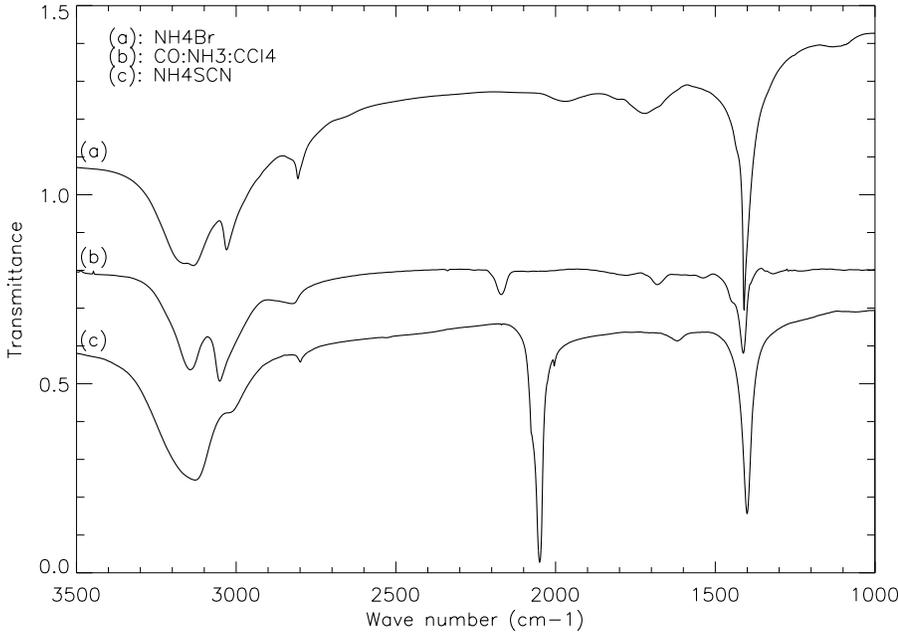


Fig. 5a–c. Comparison of the spectrum of photolysed mixture containing CCl_4 at $T \sim 220\text{K}$ (middle trace) with spectra of two salts NH_4Br (upper trace) and NH_4SCN (lower trace) at room temperature in CsI pellets. Bands around 3000 and 1400cm^{-1} are assigned to the NH_4 cation vibrations modes in the salts. The band at 2050cm^{-1} in **c** is due to the SCN vibration of NH_4SCN , the one at 2160cm^{-1} in **b** to the OCN vibration.

molecules are required to produce one molecule of CO_2 . We thus have the relation:

$$\frac{S_{\text{CO}}}{A_{\text{CO}}} = 2 * \frac{S_{\text{CO}_2}}{A_{\text{CO}_2}} + \frac{S_{\text{OCN}^-}}{A_{\text{OCN}^-}} + \frac{S_{\text{HCONH}_2}}{A_{\text{HCONH}_2}} \quad (1)$$

where $S_x = \int_{\nu_1}^{\nu_2} \tau_\nu d\nu$ is the area of the band. The integrated cross sections of CO_2 and CO are known ($A_{\text{CO}} = 1.1 \times 10^{-17} \text{cm/molecule}$ and $A_{\text{CO}_2 \text{ stretch}} = 7.6 \times 10^{-17} \text{cm/molecule}$, Gerakines et al. 1995) but the value for HCONH_2 is unknown. We have used an experiment of UV photolysis of HCONH_2 to express A_{HCONH_2} in terms of the integrated cross sections of CO , CO_2 and OCN^- . Following again the oxygen, the HCONH_2 consumed during UV photolysis is converted in CO , CO_2 , OCN^- . This can be expressed by the following relation:

$$\frac{S_{\text{HCONH}_2}}{A_{\text{HCONH}_2}} = 2 * \frac{S_{\text{CO}_2}}{A_{\text{CO}_2}} + \frac{S_{\text{OCN}^-}}{A_{\text{OCN}^-}} + \frac{S_{\text{CO}}}{A_{\text{CO}}} \quad (2)$$

Combination of (1) and (2) allows to calculate the integrated cross section of OCN^- . The area of each band was calculated using gaussian fit of the band. We have chosen the stretching mode of CO_2 at 2345cm^{-1} and a band which is not too perturbed at 1322cm^{-1} for HCONH_2 . We find:

$$A_{\text{OCN}^-} \geq 4.28 \times 10^{-17} + \theta(\text{CO:NH}_3) \text{ cm/molecule.}$$

Where $\theta(\text{CO:NH}_3)$ stands for other molecules not taken into account in the estimate (such as HNCO) but which are of much less importance in the evaluation (we believe this uncertainty to be less than a few percent). This implies that we only get a lower limit on the value of A_{OCN^-} . This value of A_{OCN^-} is in good agreement with the value of $2\text{--}4 \times 10^{-17} \text{cm/molecule}$ calculated by d’Hendecourt & Allamandola (1986a).

3.4.2. NH_4^+

It is interesting to derive the integrated band strength of NH_4^+ because the position of its strongest feature at 1460cm^{-1} suggests that this molecule participates to the interstellar $6.85\mu\text{m}$ band. Grim et al. (1989a) made several experiments in order to derive, with different methods, the value of the integrated cross section of NH_4^+ . They found that $A_{\text{NH}_4^+}$ is in the range of 4×10^{-17} to $4 \times 10^{-16} \text{cm/molecule}$, with $2 \times 10^{-16} \text{cm/molecule}$ the most reasonable value.

The value of $A_{\text{NH}_4^+}$ can be calculated using the fact that in the CO:NH_3 mixture, NH_4^+ and OCN^- are produced in the same amount since the mechanism of formation is an equilibrium mechanism (it conserves electrical neutrality in the matrix) and since no other ions have been identified in the photolysed mixture. Using this assumption we have the relation:

$$A_{\text{NH}_4^+} = \frac{S_{\text{NH}_4^+}}{S_{\text{OCN}^-}} A_{\text{OCN}^-}$$

There is a large uncertainty on the value of the area of the NH_4^+ band because the band is large and the continuum in this region is not well-defined. This uncertainty is far superior to the one induced by the uncertainty on A_{OCN^-} . Taking into account these uncertainties we found $A_{\text{NH}_4^+} = 1.3\text{--}3 \times 10^{-17} \text{cm/molecules}$. This value is only a lower limit and implies $A_{\text{NH}_4^+} \geq 1.3 \times 10^{-17} \text{cm/molecule}$. This value is small compared to the value of Grim et al. (1989a). It is even not comprised in their experimental range. Contrary to OCN^- , the value of $A_{\text{NH}_4^+}$ is poorly constrained and does not allow to derive accurate quantitative information.

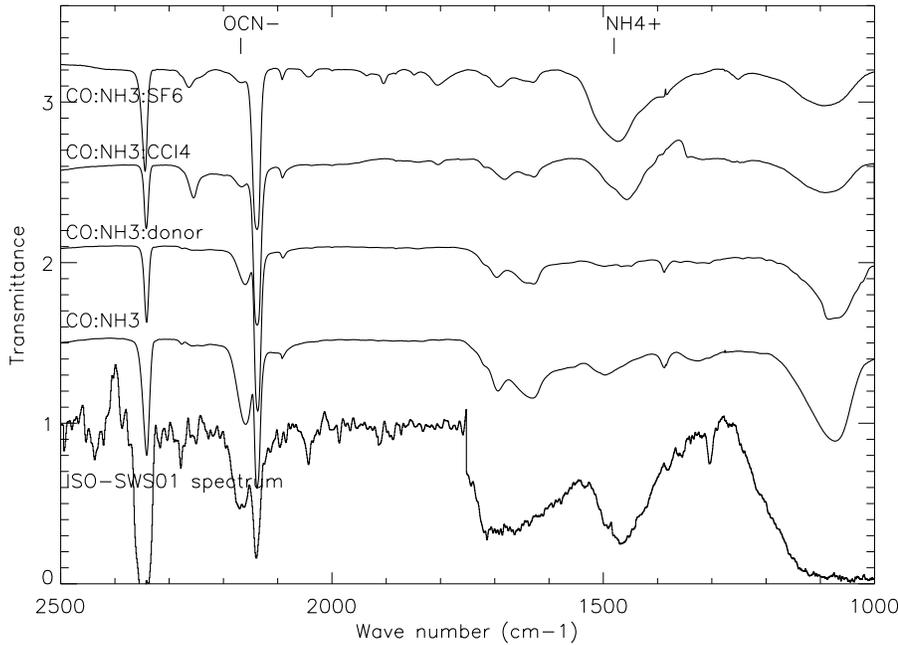


Fig. 6. Comparison of the ISO-SWS01 spectrum of the protostellar object RAFGL 7009S with spectra of the photolysed laboratory mixtures CO:NH₃ (1:1), CO:NH₃:e⁻ donor (10:10:1), CO:NH₃:SF₆ (10:10:1) and CO:NH₃:CCl₄ (10:10:2). Position of the OCN⁻ and NH₄⁺ bands in the laboratory mixtures have been indicated. See text for assignment of the other bands.

Table 1. Identification of OCN⁻ in protostars.

Sources	τ_{OCN^-} obs.	$\Delta\nu_{OCN^-}$ cm ⁻¹	$\tau_{6.8}$ obs.	$\Delta\nu_{6.8}$ cm ⁻¹	N_{H_2O} /cm ⁻²	N_{OCN^-} /cm ⁻²	OCN ⁻ % /H ₂ O	$\tau_{NH_4^+}$ this work	$\tau_{NH_4^+}$ Grim et al. 1989a
RAFGL 7009S ^a	.65	32	1.1	86	$1.2 \cdot 10^{19}$	$4.75 \cdot 10^{17}$	4	.07	1.1
W33A	1.4^b	24.7^b	1.49^c	100^d	$0.9-4.2 \cdot 10^{19i}$	$7.85 \cdot 10^{17}$	2-8	.11	1.66
NGC7538:IRS9	$.2^e$	20^c	$.33^f$	80^*	$8 \cdot 10^{18g}$	$9.35 \cdot 10^{16}$	1	.017	.26
RNO91	$.19^h$	20^h	-	70^f	$2.2 \cdot 10^{18h}$	$8.87 \cdot 10^{16}$	4	.015	.22
L1551:IRS1	$.16^e$	20^e	-	80^*	$3.5 \cdot 10^{18e}$	$7.47 \cdot 10^{16}$	2	.012	.18
GL961 ^b	.06	23.5	-	80^*	$4 \cdot 10^{18}$	$3.29 \cdot 10^{16}$.8	.005	.08
MONR2:IRS2 ^b	.05	23.5	-	80^*	$4.5 \cdot 10^{18}$	2.74^{16}	.6	.004	.07

Column 7 and 8 indicate respectively the OCN⁻ column density calculated with $\mathcal{A}_{OCN^-} = 4.28 \times 10^{-17}$ cm/molecule and the percentage it represents compared to water. Column 9 and 10 give the optical depth of NH₄⁺ at 6.85 μm if $N_{NH_4^+}$ is assumed to be equal to N_{OCN^-} , calculated respectively with the value of $\mathcal{A}_{NH_4^+}$ we derived and the value adopted by Grim et al. 1989a.

Ref: ^ad'Hendecourt et al. 1996, ^bChiar et al. 1998, ^cLacy et al. 1984, ^dTielens et al. 1984, ^eTegler et al. 1993, ^fSchutte et al. 1996, ^gWhittet et al. 1996, ^hWientraub et al. 1994, ⁱAllamandola et al. 1992, the two values correspond respectively to the estimate from the 3 and 6 μm band, *laboratory width.

4. Astrophysical implications

4.1. OCN⁻ in RAFGL 7009S

In the spectrum of RAFGL 7009S, the 4.62 μm band is strong. The observed optical depth is 0.65 (compared to 1.53 for the CO which represent about 15% of the water abundance) and the FWHM is about 32 cm⁻¹ (see Table 1). Comparison with laboratory spectra are shown in Figs. 6 and 7. The position of the OCN⁻ band in the experiments is in good agreement with the interstellar spectrum. The best laboratory fit of both the OCN⁻ and CO bands is found for the CO:NH₃ mixture annealed to about 30-40K. The maximum abundance derived for OCN⁻ is 4.75×10^{17} cm⁻². This represents about 4% of the water abundance found in RAFGL 7009S, a very reasonable

estimate, in agreement with cosmic abundance constraints. Thus the identification of the 4.62 μm band with OCN⁻ is confident.

4.2. NH₄⁺ in RAFGL 7009S

Because when OCN⁻ is produced, a positive counterion is produced in the same amount, the assignment of the 4.62 μm feature to OCN⁻ implies that a positive ion is present in the same amount as OCN⁻ in interstellar ices. The counterion of OCN⁻ produced in laboratory by photolysis of mixture containing astrophysically relevant molecules (CO, NH₃) is NH₄⁺. It must thus be present in interstellar ices unless other positive ions are identified which is not the case in RAFGL 7009S. The position of the main NH₄⁺ band at 6.85 μm (Figs. 6 and 8) implies that it participates to the interstellar 6.85 μm band. This band is very

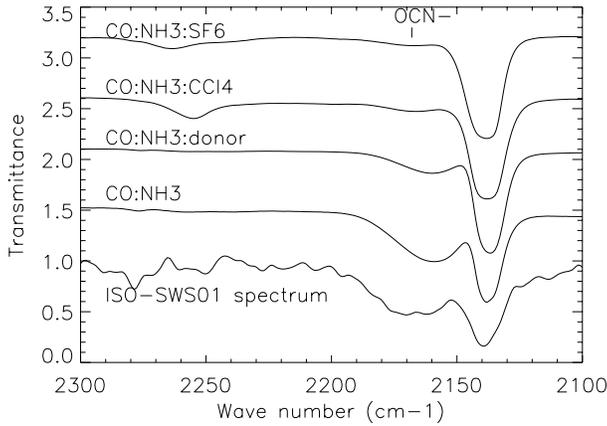


Fig. 7. Comparison of the ISO-SWS01 spectrum of the protostellar object RAFGL 7009S with spectra of photolysed laboratory mixtures CO:NH₃ (1:1), CO:NH₃:e⁻ donor (10:10:1), CO:NH₃:SF₆ (10:10:1) and CO:NH₃:CCl₄ (10:10:2). Position of the OCN⁻ band in the laboratory mixtures has been indicated.

strong in RAFGL 7009S. It is as deep as the H₂O bending mode at 6.0 μm and the lack of candidate for the identification of this strong band is puzzling. Clearly NH₄⁺ cannot be the only carrier of the interstellar 6.85 μm band since in the CO:NH₃ mixture, the optical depth of this band is not reproduced although the optical depth of the 4.62 μm band is (Fig. 6). Using our value of $\mathcal{A}_{NH_4^+}$ (1.3×10^{-17} cm/molecule) and assuming that there is the same amount of NH₄⁺ as OCN⁻ in the source, we found that the optical depth of the 6.85 μm band of NH₄⁺ is 0.07 i.e. it represents 6.5% of the interstellar feature (Table 1). With the value for $\mathcal{A}_{NH_4^+}$ of Grim et al. (1989a) we found that NH₄⁺ explains 100% of the interstellar band, illustrating the necessity of deriving accurate integrated cross section value for NH₄⁺. Methanol is a plausible candidate for this band since it has a vibration at 6.87 μm and since it has been detected in several similar sources due to its CH vibration at 3.53 μm (Grim et al. 1991, Allamandola et al. 1992).

4.3. Identification in other sources

Observations of the 4.62 and 6.85 μm features in several protostellar objects allow us to test the validity of the identification of the 4.62 μm with OCN⁻. Table 1 summarizes the observations of several sources. The upper limit on the abundance of OCN⁻ and its percentage relative to H₂O calculated with the integrated cross section we derived are given. The last two columns give the contribution of NH₄⁺ to the 6.85 μm band, calculated with our derived integrated cross section and with the one of Grim et al. (1989a), assuming that there is the same amount of NH₄⁺ as OCN⁻. The derived abundances of OCN⁻ in all the sources are coherent with cosmic abundances constraints and none of them contradicts the assignment of this band to OCN⁻, reinforcing this identification.

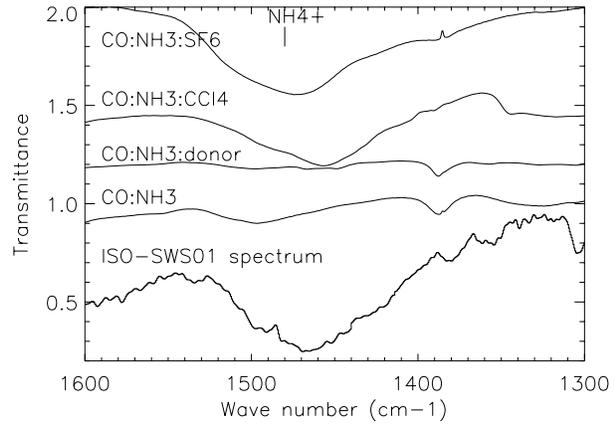


Fig. 8. Comparison of the ISO-SWS01 spectrum of the protostellar object RAFGL 7009S with spectra of photolysed laboratory mixtures CO:NH₃ (1:1), CO:NH₃:e⁻ donor (10:10:1), CO:NH₃:SF₆ (10:10:1) and CO:NH₃:CCl₄ (10:10:2). Position of the NH₄⁺ band in the laboratory mixtures has been indicated.

The expected optical depth of NH₄⁺ at 6.85 μm is coherent with the value observed (when available) except for W33A where it exceeds the observed value if one adopts the integrated cross section of Grim et al. (1989a), indicating that this value is too high. From ground based observations of NGC7538:IRS9 Allamandola et al. (1992) derived an abundance of methanol of 9.1×10^{17} cm⁻². This corresponds to a contribution to the 6.85 μm feature of ~30-45%. The rest of the band may be explained by NH₄⁺ but a firm conclusion cannot be reached because of the uncertainty on $\mathcal{A}_{NH_4^+}$. The situation is identical in W33A where methanol has been estimated to 3.3×10^{18} cm⁻² by Grim et al (1991) and to 3.9×10^{18} cm⁻² by Allamandola et al. (1992) corresponding to a contribution of ~20-30% to the 6.8 μm band. However uncertainties on the integrated cross sections of NH₄⁺ but also of CH₃OH (whose integrated cross section varies with the composition of the ice, e.g. with the water ice content) does not allow to give any secure quantitative conclusions. One can only say that NH₄⁺ necessarily contributes to the 6.85 μm feature if OCN⁻ is assigned to the 4.62 μm band as does CH₃OH if it is present in the grain mantles.

4.4. The presence of ammonia

The production of OCN⁻ and NH₄⁺ is only possible if ammonia, or some other nitrogenous species, is present in the ice. Thus, the identification of OCN⁻ and NH₄⁺ in astrophysical sources implies the presence of nitrogen, most likely in the form of ammonia (because N₂ is quite unreactive under photolysis), in interstellar ices. This is an important result because nitrogenous species have rarely been directly detected in interstellar ices. Vibrational transitions of NH₃ are situated at 2.96, 6.17 and 9.1 μm and fall close to the absorption bands of H₂O and silicates, its detection is therefore difficult. N₂ has a very weak infrared vibration in a region where CO₂ absorption occurs (Ehrenfreund et al. 1992, Quirico et al. 1996) and its detection is without chance. However Knacke et al. (1982)

detected NH_3 in the Becklin-Neugebauer object by its absorption band at $2.96\mu\text{m}$. Recently Lacy et al. (1998) observed the $9.1\mu\text{m}$ band of NH_3 in NGC7538:IRS9 and found an abundance of 10% relative to H_2O . NH_3 has not been detected in the ISO-SWS spectrum of RAFGL 7009S because the water ice and silicate bands are saturated. The detection of ammonia in NGC7538:IRS9, an object similar to RAFGL 7009S suggests that ammonia should also be present in RAFGL 7009S with part of it converted into OCN^- and NH_4^+ .

5. Conclusion

The identification of the 4.62 and $6.85\mu\text{m}$ bands with OCN^- and NH_4^+ in the spectrum of photolysed $\text{CO}:\text{NH}_3$ mixtures has been confirmed. The annealing of the mixtures containing an electron acceptor, and the relationship between the HNCO and OCN^- bands show that these ions are certainly produced via acid-base reactions between HNCO and NH_3 . This mechanism of formation implies that if OCN^- is present in interstellar ices, the counterion NH_4^+ is also present.

The abundance derived for OCN^- (and thus for NH_4^+) in RAFGL 7009S (4% of the water abundance) is coherent with cosmic abundance constraints. We therefore conclude that OCN^- is the most likely identification for the XCN band in this object. NH_4^+ does contribute to the $6.85\mu\text{m}$ feature but it is difficult to give a quantitative estimate of its contribution because of the strong uncertainties on its integrated cross section. Assignment of the $4.62\mu\text{m}$ band to OCN^- in other protostellar objects in which the composition of the ice mantle should be similar to the one of RAFGL 7009S seems to hold and abundances derived for OCN^- are of a few percent. The presence of NH_4^+ in W33A and NGC7538:IRS9 could explain part of the $6.85\mu\text{m}$ band which cannot be accounted for only with the observed abundance of methanol. However more accurate integrated cross section of NH_4^+ is needed in order to be able to give secure quantitative results.

Acknowledgements. We wish to thank F. and N. Legay for their help and discussion on the chemical aspects of this work. We thank an anonymous referee for his comments that have greatly helped to improve this paper.

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