

*Letter to the Editor***Further evidence for the OCN^- assignment to the XCN band in astrophysical ice analogs****W.A. Schutte and J.M. Greenberg**

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Abstract. The well-known “XCN” feature near 2167 cm^{-1} observed towards various low- and high-mass embedded protostars can be well matched with a feature produced by photolysis of astrophysical ice analogs containing CO and NH_3 . An assignment of this laboratory XCN band to OCN^- was earlier proposed based on the correspondence in position and in the ^{13}C and ^{15}N isotopic shifts. We report here a further experimental study of this identification. First, the isotope shift of the XCN band obtained by irradiating ^{18}O labelled ice samples equals $8.7 \pm 0.6\text{ cm}^{-1}$, in good agreement with OCN^- . Second, highly sensitive spectroscopy reveals three additional weak features which can be assigned to the OCN^- ion. Together with the earlier work, these results leave little doubt to the correctness of the identification of the laboratory XCN feature with OCN^- .

Key words: ISM: clouds – ISM: dust, extinction – ISM: molecules – stars: pre-main-sequence

1. Introduction

Infrared observations towards a number of low and high mass embedded protostellar sources have revealed a broad absorption feature near 2167 cm^{-1} (Lacy et al. 1984; Tegler et al. 1993, henceforth T93; Tegler et al 1995, henceforth T95). The width of this feature indicates a solid state origin. Since its position is indicative of the stretching mode of a doubly or triply bonded CN group, the band became generally known as the XCN feature. A similar feature can be obtained under laboratory conditions by ultraviolet (UV) photolysis of astrophysical ice analogs containing CO and NH_3 (Lacy et al. 1984). A detailed fit of the XCN feature towards the highly obscured source W33A is obtained when the ice mixture is dominated by H_2O (Grim & Greenberg 1987, henceforth GG87; T93). While alternative assignments have been proposed (e.g., the Si–H stretching mode; Moore et

al. 1991), no other candidate has yet been shown to produce a satisfactory match to the interstellar XCN band.

Ultraviolet processing may modify the composition of the icy dust mantles in dense clouds (Greenberg et al. 1972). In view of the importance of the XCN feature as an indicator of such processing, the issue of the identification of the corresponding laboratory band generated considerable interest. While the laboratory feature was observed already in 1982 (Hagen 1982), no firm assignment could initially be given. This was an especially vexing problem, since the feature is quite strong and is already obtained at short irradiation times, indicating a simple product that is efficiently formed from the CO and NH_3 precursors. d’Hendecourt et al. (1986) considered a number of candidates, either nitriles (R-CN) or iso-nitriles (R-NC), in various forms, but none of these could satisfy the spectroscopic constraints. In a recent study, Bernstein et al. (1994), produced XCN by UV photolysis of Hexamethylene Tetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) in the presence of H_2O . However, it is plausible that the formation of XCN in these experiments was preceded by the photochemical production of CO and NH_3 as the true parents (Bernstein et al. 1994, 1995).

Important constraints on the identity of XCN became available from the study of the isotope shifts obtained by including $^{15}\text{NH}_3$ and ^{13}CO in the ice sample (GG87). On this basis an assignment to the strong ν_3 mode of the OCN^- ion was proposed. Further indications for this identification were the good coincidence of the XCN band with the OCN^- stretching feature in various salt matrices, and the formation of a feature at 2217 cm^{-1} upon warm-up to 240 K, close to the position of the OCN^- stretching vibration of ammoniumcyanate (NH_4NCO ; GG87). In a subsequent paper, Grim et al. (1989; henceforth G89) proposed that the production of ions could take place by acid–base reactions in the presence of NH_3 after acids are formed by photochemical reactions. In this view, the formation of the acid HNCO from the addition of the ammonia dissociation product NH to CO is the step preceding the OCN^- formation. Based on the position and the observed isotope shifts, a broad feature

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near 1500 cm^{-1} was assigned to the counterion, NH_4^+ . The viability of acid–base reactions under cryogenic conditions has a firm basis in the physical/chemical literature (e.g., Ritzhaupt & Devlin 1977). Indeed, Zundel & Fritsch (1984) wrote that “In the condensed phase the equilibrium may shift to the right [towards acid–base proton transfer; authors], and this shift is particularly pronounced at low temperatures.” Nevertheless, the OCN^- identification and the viability of acid–base reactions in astrophysical ice analogs has not met general acceptance (e.g., T93; Bernstein et al. 1995). Tielens (1989) argued that the lack of a large band shift upon warm-up of the laboratory ices and during sublimation of the ice matrix excludes identification with an ion. However, this argument was not supported by a quantitative estimate of the shift which would be expected. Indeed, the position of the XCN band does show a 6 cm^{-1} shift during warm-up from 10 to 150 K (T93). Furthermore, there is an $\sim 10\text{ cm}^{-1}$ difference in the position in CO/NH_3 matrices as opposed to H_2O dominated ices (GG87). While in various salt matrices considerably larger shifts of up to 67 cm^{-1} are found (Maki & Decius 1959, Gordon & Foss Smith 1974), it does not seem unreasonable that in the much less polarizing environment of ices, matrix shifts are considerably smaller.

In this paper we present additional laboratory research on the identification of the XCN feature with OCN^- . In the first place, we searched additional, weaker, features of OCN^- . Second, we have measured the ^{18}O isotope shift of the XCN band. Third, a number of additional criteria for the ion identification; e.g., charge balance between the proposed negative and positive species, are verified.

2. Experimental

Our general experimental procedures have been outlined in Gerakines et al. (1995; 1996). To produce astrophysical ice analogs, gas mixtures were prepared in a glass vacuum manifold and subsequently deposited on a 10 K substrate mounted in a vacuum chamber. For UV photolysis a microwave discharge hydrogen flow lamp was employed which was operated at a pressure of 0.6 mbar. The output of the lamp equals $\sim 1\ 10^{15}\text{ photons cm}^{-2}\text{ s}^{-1}$ ($E_{\text{photon}} \geq 6\text{ eV}$). C^{18}O (MSD isotopes) had 99 % isotopic purity, H_2^{18}O (Aldrich) was of 95 % isotopic purity, while all other gases exceeded 99.9 % purity. The compositions of the various ice samples were directly determined from the band intensities in the infrared spectra, using band strengths from the literature (d’Hendecourt & Allamandola 1986; Gerakines et al. 1995). For the stretching mode of C^{18}O near 2086 cm^{-1} we used $A = 1.6 \times 10^{-17}\text{ cm molec.}^{-1}$. This value is derived from the relative intensities of the modes of C^{16}O and C^{18}O for a sample of isotopically normal CO (^{18}O abundance 0.20 %) and using $A = 1.1 \times 10^{-17}\text{ cm molec.}^{-1}$ for the C^{16}O stretching mode (Gerakines et al. 1995).

3. Results

3.1. The ^{18}O induced isotope shift

The ^{18}O isotope shift of the XCN band was studied by irradiating the ice mixture $\text{H}_2\text{O}:\text{CO}:\text{NH}_3 = 100:22:22$, unlabelled as well as with H_2^{18}O and with C^{18}O . The benefit of an H_2O dominated mixture is that, contrary to CO/NH_3 binary ices, the position of the XCN band shows little variation with dose; i.e., the position of the feature varies only by 0.6 cm^{-1} between 3 and 30 minutes irradiation. Thus a possible source of error in the shift measurement is avoided. Figure 1 shows the XCN features produced by 30 min. irradiation of the labelled and the unlabelled ice. Clearly an isotope shift is present, showing that the XCN carrier definitely contains oxygen. The magnitude of the shift equals $8.7 \pm 0.6\text{ cm}^{-1}$, in good agreement with the shift of 8.3 cm^{-1} reported for OCN^- (Schettino & Hisatsune 1970, henceforth SH70).

Earlier, an ^{18}O isotope shift of 0 cm^{-1} was reported for the XCN band (G89). Inspection of the original spectra from which this result was obtained however showed that these experiments suffered from very poor reproducibility of the ice matrix (Up to a factor 4 from the purported composition $\text{H}_2\text{O}/\text{NH}_3/\text{CO}/\text{O}_2 = 10/1/1/0.25$). Due to the sensitivity of the XCN position to the ice composition, such discrepancies between the composition of the labelled and unlabelled samples could well have been responsible for a large error in the shift measurement.

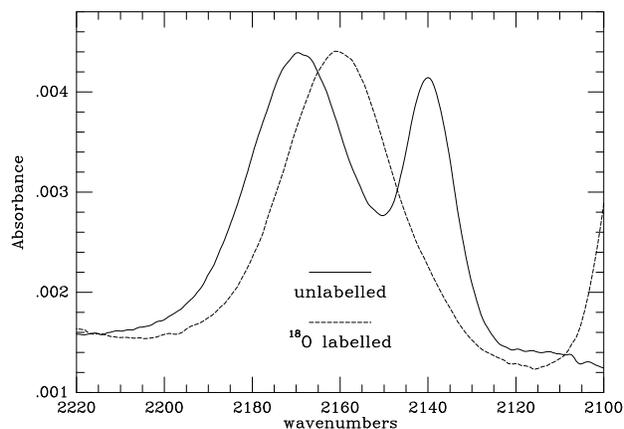


Fig. 1. XCN features obtained upon UV photolysis of $\text{H}_2\text{O}/\text{CO}/\text{NH}_3 = 100/22/22$ at 10 K. Solid line: unlabelled. Dashed line: With H_2^{18}O and C^{18}O . The feature at 2140 cm^{-1} in the unlabelled sample is due to CO

3.2. Weak OCN^- bands

Besides the very strong ν_3 band, OCN^- has three weak features each with a relative intensity of a few percent which are due to the ν_1 and ν_2 fundamentals and the $2\nu_2$ overtone. In a KI matrix these fall at 1201 , 628 , and 1288 cm^{-1} , respectively, while the main ν_3 band falls at 2156 cm^{-1} (SH70). To achieve a sensitive search for these features, we simultaneously deposited and irradiated a $\text{CO}:\text{NH}_3 = 1:1$ mixture over a period of 2 hours. While

such a mixture is not a very likely analog of the interstellar ice (e.g., T93), it is the simplest ice in which XCN can be produced. We chose this mixture to minimize the number of features which could interfere with the search for the weak OCN^- bands. For an extensive account of the photochemistry of CO/NH_3 binary ices we refer to G89. The simultaneous deposition/irradiation technique yields a sample with a ~ 10 x higher column density of XCN than the amount that is obtained by the usual procedure of first depositing and subsequently irradiating, because in the latter case the quantity produced is constrained by the requirement that the sample is transparent to UV radiation.

Figure 2 shows the spectrum in the relevant regions, after warm-up to 120 K. At this temperature some photochemically produced CO_2 , which absorbs near 650 cm^{-1} , has sublimed. Besides the XCN band which in this sample falls at 2155 cm^{-1} , small features at 1206, 630, and 1296 cm^{-1} (henceforth, the “weak bands”) are present close to the positions of the weak OCN^- bands. In salt matrices the weak OCN^- features have an intensity of 4 - 5 % of the main feature (SH70), consistent with the intensity of the weak bands in our experiment. The moderate shifts relative to the OCN^- bands in KI are similar to the shifts seen for OCN^- in various salt matrices (SH70). During warm-up to 240 K the XCN band and the weak bands decrease in intensity and finally disappear simultaneously. We conclude that the weak bands show good correspondence with the ν_1 , ν_2 , and $2\nu_2$ modes of OCN^- .

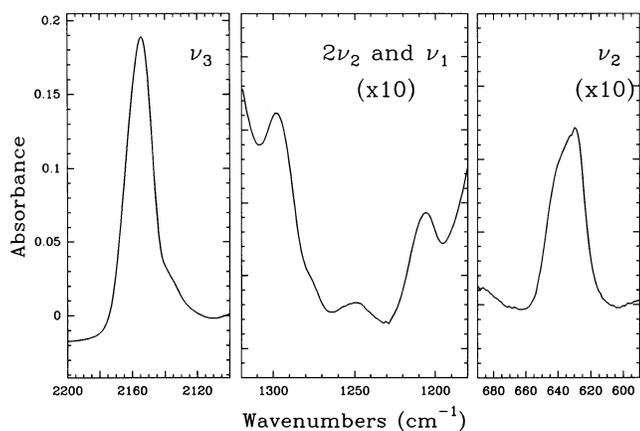


Fig. 2. Selected spectral regions for a sample obtained by simultaneous deposition and irradiation of $\text{CO}/\text{NH}_3=1:1$. Shown are bands that are attributable to various vibrational modes of OCN^- ; i.e., the XCN feature at 2155 cm^{-1} (attributable to $\text{OCN}^- \nu_3$), and the weak bands at 1296 , 1206 , and 630 cm^{-1} (attributable to $2\nu_2$, ν_1 and ν_2 , respectively). The size of the weak bands have been enhanced by a factor 10.

3.3. Miscellaneous considerations

In the framework of the proposed formation of OCN^- through acid–base interaction at cryogenic temperature, some additional criteria need to be satisfied. First, production of the acid; i.e., HNCO and/or HOCN, should precede ion formation. Second,

charge balance should hold throughout the photolysis. Finally, no XCN feature should be obtained when irradiating ices with carbon and nitrogen carriers other than CO and NH_3 (although some may be produced at high UV dose, if CO and NH_3 can be photochemically obtained from the original molecules).

The formation of the acid precursors is most easily studied in an Ar matrix. First, the positions of the vibrational transitions of the HNCO and HOCN acids depends sensitively on the matrix, and have only been extensively studied for noble gas matrices. Second, production of the acids should be optimized in an inert matrix since acid–base interaction is minimized in this case. The formation of HNCO has earlier been reported for photolysis of CO/NH_3 in an Ar matrix (Milligan & Jacox 1965, G89). We have photolysed $\text{H}_2\text{O}/\text{CO}/\text{NH}_3/\text{Ar} = 100/25/25/20,000$. As in the earlier work a double structure was observed at 2265 and 2260 cm^{-1} , matching the position of the ν_2 mode of HNCO (Teles et al. 1989). Other features of HNCO are much weaker (Teles et al. 1989) and fell below the detection limit. No trace of HOCN was found in our as well as in the earlier experiments. After the Ar sublimation at $\sim 30\text{ K}$, the double structure disappears while a feature grows at 2232 cm^{-1} . While this structure could be due to HNCO in the H_2O dominated matrix, such an assignment is uncertain due to the lack of comparison data for similar matrices.

Charge balance is most easily identifiable for simple ices. The possible presence of many different ions in complex mixtures makes it difficult to establish charge balance because of the large uncertainties in the band strengths (G89). In a mixture $\text{CO}/\text{NH}_3 = 56/20$, the XCN feature and the purported band of NH_4^+ near 1500 cm^{-1} showed a constant ratio of their integrated intensities within 10 % (the measurement error) between 1 min. and 1 hour of irradiation. During this time the intensities of both features varied together by up to a factor 10.

Mixtures of N- and C- bearing molecules other than NH_3 with CO were monitored for photochemical formation of XCN. We compared the efficiency of the XCN formation as expressed in conversion of carbon to XCN after 30 min. of photolysis with that for $\text{CO}/\text{NH}_3 = 1/1$. For the ices $\text{CO}/\text{N}_2 = 1/1$ and $\text{H}_2\text{O}/\text{CO}/\text{N}_2 = 3/1/1$ an upper limit of 5 % was found for the XCN formation efficiency relative to $\text{CO}/\text{NH}_3 = 1/1$. For the mixture $\text{CH}_4/\text{NH}_3 = 1/1$ a very small quantity of XCN is formed at an efficiency of 4 % of that for $\text{CO}/\text{NH}_3 = 1/1$. However, some CO is also produced during the irradiation, apparently originating from photochemical reactions of CH_4 and condensing residual H_2O vapor in the set-up (Gerakines et al. 1995). Thus, it appears probable that the minor XCN production in this experiment is due to some contamination of the sample.

We conclude that all additional criteria for the OCN^- assignment of XCN; i.e., observation of the acid precursor, charge balance throughout the photolysis, and the absence of XCN upon photolysis of mixtures in which either CO or NH_3 is absent, appear to be satisfied.

4. The acid–base interaction in cryogenic solids

In a solid matrix acids and bases form a hydrogen bonded complex. Depending on the nature of the species, this could lead either to transfer of the proton and the formation of ions or to the proton being more or less equally shared by the acid and the base (e.g., Zundel & Fritsch 1984). Surprisingly, there is no straightforward relationship between the strength of the acid at room temperature and the degree of proton transfer under cryogenic (10 K) conditions; e.g., the $\text{HCl}\cdot\text{NH}_3$ complex contains a mutually shared proton, while upon formation of the $\text{HNO}_3\cdot\text{NH}_3$ complex ion formation readily proceeds (Ault & Pimentel 1973, Ritzhaupt & Devlin 1977). However, in the case of the XCN feature the coincidences in the isotope shifts as well as of the infrared features (Section 3; GG87) clearly points to the formation of OCN^- rather than some acid–base complex involving HNCO or HOCN.

It is not clear whether the positive and negative ions are exclusively found in complexes, or whether they can also become isolated inside the H_2O matrix, as was proposed by G89. The great symmetry of the XCN feature in irradiated $\text{H}_2\text{O}/\text{CO}/\text{NH}_3 = 100/22/22$ (Fig. 1) suggests that no two distinct OCN^- components are present, and it is therefore perhaps more likely that the ions only reside in complexes.

5. Discussion

Our experimental results provide strong support to the original assignment by GG87 of the XCN feature obtained by UV photolysis of astrophysical ice analogs containing CO and NH_3 to the OCN^- ion. The ^{18}O isotope shift of the XCN band closely corresponds with that of the ν_3 mode of OCN^- (Section 3.1). Furthermore, a photolysed CO/NH_3 sample gives, besides the XCN band, weak features at 1206, 630, and 1296 cm^{-1} , attributable to the weak ν_1 , ν_2 , and $2\nu_2$ OCN^- modes (Section 3.2). The close agreement of the ^{13}C and ^{15}N isotope shifts of the XCN band with those of OCN^- constitutes further support for this assignment (GG87). Finally, some additional criteria for the formation of OCN^- by acid–base reactions appear to be met: formation of the HNCO acid prior to OCN^- , charge balance between NH_4^+ and OCN^- during photolysis as reflected by the constant ratio of their respective IR bands, and the absence of XCN in analogs without either CO or NH_3 (Section 3.3). The new experimental results combined with the older ones leave little doubt as to the correctness of the OCN^- assignment to the XCN band produced by UV photolysis of astrophysical ice analogs, as originally proposed by GG87.

The excellent match of the interstellar XCN band with the ν_3 mode of OCN^- makes the ion a prime candidate for its identification. While in laboratory studies the ion is generally produced by photolysis of CO with NH_3 , in dense clouds the HNCO acid is perhaps directly incorporated in the ice mantles (Hasegawa & Herbst 1993). In view of the, in some cases, great ease of ion formation through acid–base reactions under cryogenic conditions (e.g., Ritzhaupt & Devlin 1977), OCN^- production could then possibly be stimulated not only by UV radiation but also by the

energy freed if HNCO is formed by exothermic grain surface reactions, or even by the heat of condensation. Spectroscopy by the Infrared Space Observatory of HNCO, or, alternatively, of the products of CO/NH_3 irradiation (e.g., HCONH_2 ; GG89) could reveal how OCN^- may be produced in interstellar ices.

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References

- Ault B.S., Pimentel G.C., 1973, *J. Phys. Chem.* 77, 1649
 Bernstein M.P., Sandford S.A., Allamandola L.J., Chang S., 1994, *J. Phys. Chem.*, 98, 12206
 Bernstein M.P., Sandford S.A., Allamandola L.J., Chang S., Scharberg M.A., 1995, *ApJ* 454, 327
 d'Hendecourt L.B., Allamandola L.J., 1986, *A&AS* 64, 453
 Gerakines P.A., Schutte W.A., Greenberg J.M., van Dishoeck E.F., 1995, *A&A* 296, 810
 Gerakines P.A., Schutte W.A., Ehrenfreund P. 1996, *A&A* 312, 289
 Goldanskii V.I., 1977, *Nature* 268, 612
 Gordon D.J., Foss Smith D., 1974, *Spectrochimica Acta* 30A, 2047
 Greenberg J.M., Yench A.J., Corbett J.W., Frisch H.L., 1972, *Mémoires Société Royale de Sciences de Liège*, 6^e série, tome III, p. 425
 Grim R.J.A., Greenberg J.M., 1987, *ApJ* 321, L91 (GG87)
 Grim R.J.A., Greenberg J.M., de Groot M.S., Baas F., Schutte W.A., Schmitt B., 1989, *A&AS* 78, 161 (G89)
 Hagen W., 1982, Ph.D. thesis. University of Leiden
 Hasegawa T.I., Herbst E., 1993, *MNRAS* 261, 83
 Ito K., Bernstein H.J., 1956, *Canadian Journal of Chemistry* 34, 170
 Lacy J.H., Baas F., Allamandola L.J., Persson S.E., McGregor P.J., Lonsdale C.J., Geballe T.R., van de Bult C.E.P., 1984, *ApJ* 276, 543
 Maki A., Decius J.C., 1959, *J. Chem. Phys.* 31, 772
 Milligan D.E., Jacox M.E., 1965, *J. Chem. Phys.* 43, 4487
 Moore M.H., Tanabe T., Nuth J.A., 1991, *ApJ* 373, L31
 Okabe H., 1978, *Photochemistry of Small Molecules*. Wiley, New York
 Ritzhaupt G., Devlin J.P., 1977, *J. Phys. Chem.* 81, 521
 Schettino V., Hisatsune I.C., 1970, *J. Chem. Phys.* 52, 9 (SH70)
 Tegler S.C., Weintraub D.A., Allamandola L.J., Sandford S.A., Rettig T.W., Campins H., 1993, *ApJ* 411, 260 (T93)
 Tegler S.C., Weintraub D.A., Rettig T.W., Pendleton Y.J., Whittet D.C.B., Kulesa C.A., 1995, *ApJ* 439, 279 (T95)
 Teles J.H., Maier G., Hess Jr. B.A., Schaad L.J., Winnewisser M., Winnewisser B.P., 1989, *Chem. Ber.* 122, 753
 Tielens A.G.G.M., 1989, in: *IAU symp. 135: Interstellar dust*, Allamandola, L.J., Tielens, A.G.G.M. (eds.). Kluwer, Dordrecht, p. 239
 Zundel G., Fritsch J., 1984, *J. Phys. Chem.* 88, 6295

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