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Astrophysics

Further evidence for the assignment of the XCN band in astrophysical ice analogs to OCN⁻

Spectroscopy and deuterium shift

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Abstract. The ν_3 feature of the OCN⁻ ion near 2160 cm⁻¹ which is produced by acid-base reactions in cryogenic HNCO/NH$_3$ samples shows a small matrix induced deuterium shift. A similar shift is found for the "XCN" band near this position produced by photolysis of CO/NH$_3$ ice. This agreement, together with the abundant evidence already in the literature, clearly demonstrates that the XCN feature can be assigned to OCN⁻.

Key words. methods: laboratory – ISM: molecules – infrared: ISM: lines and bands

1. Introduction

Infrared observations towards many embedded protostellar sources show an absorption band near 2161 cm⁻¹ (4.63 μm; e.g., Pendleton et al. 1999; Whittet et al. 2001). Its position is indicative of the stretching mode of a CN group, and so this feature became known as the XCN feature. It was already shown in the discovery paper that UV irradiation of cryogenic ice mixtures containing CO and NH$_3$ produces a very similar feature (Lacy et al. 1984). To constrain its identity, Grim & Greenberg (1987) and Schutte & Greenberg (1997) measured three isotope shifts by labelling the ice sample with ^{13}C, ^{15}N or ^{18}O. The shifts coincided with those of the ν_3 CN stretching band of OCN⁻ in alkali halide matrices. Such an agreement is strong evidence for an identification, since isotope shifts depend only weakly on the nature of the matrix, even though the position of a feature itself may shift considerably (Maki & Decius 1959; Gordon & Foss Smith 1974). It was proposed that the formation of OCN⁻ is preceeded by photochemical formation of isocyanic acid (HNCO), followed by proton transfer to NH$_3$ (Grim et al. 1989).

A very similar feature is produced through irradiation with energetic ions of ices containing (at least) CO and NH$_3$, or H$_2$O, CO and N$_2$ (Palumbo et al. 2000). Recently it was demonstrated that this feature gives identical ^{13}C and ^{15}N isotope shift as the XCN feature produced by UV photolysis (Hudson et al. 2001), and thus should arise from the same species. We will therefore throughout this

paper use the designation "XCN" for the carrier of the feature produced by photolysis as well as by irradiation.

Besides the magnitude of the three isotope shifts, other results also pointed to OCN⁻. First, the growth of the XCN feature during photolysis of CO/NH$_3$ mixtures is strongly correlated with the growth of a feature at 1500 cm⁻¹ which can be ascribed to NH$_4^+$ (Schutte & Greenberg 1997). Next, additional features are produced at 1206, 630 and 1296 cm⁻¹ which are close to the other infrared active modes of OCN⁻ (Schutte & Greenberg 1997). Next, upon warm-up to 240 K, a feature forms at 2217 cm⁻¹, near the position of the OCN stretching vibration of ammoniumcyanate (NH$_4$NCO; Grim & Greenberg 1987). Next, photolysis of isotopically mixed ^{13}CO/^{12}CO/NH$_3$ samples produced no more than one labelled XCN feature, consistent with the carrier having only one C atom (Bernstein et al. 2000; Hudson et al. 2001). Next, the behaviour of the XCN feature when the ice matrix was doped by electron donor or electron acceptor molecules gave direct evidence that the carrier is a negative ion (Demyk et al. 1998; Hudson & Moore 2000). Next, Hudson et al. (2001) investigated the production of the XCN band by irradiation of a large sample of ice mixtures with a wide variety of composition. In each case, the production or non-production of the XCN band in these mixtures was consistent with the OCN⁻ assignment. This wealth of evidence appears to make OCN⁻ the best identified product of energetic processing of interstellar ice analogs.

Recently, Bernstein et al. (2000) and Palumbo et al. (2000) measured a deuterium (D) shift of 8 cm⁻¹ for the XCN feature obtained by photolysis of unlabelled and

deuterated CO/NH$_3$ = 1/1 ice. From this they concluded that the carrier should contain hydrogen and that therefore the feature cannot be solely due to OCN$^-$. This conclusion however seems at odds with the overwhelming evidence in favor of this assignment summarized above. In addition, the XCN feature having several carriers seems unlikely, since the various isotopically labelled experiments in each case produced only a single feature (Grim & Greenberg 1987; Schutte & Greenberg 1997; Bernstein et al. 2000; Palumbo et al. 2000; Hudson et al. 2001). Alternatively, the shift could be caused by the interaction of the OCN$^-$ ion with the matrix, causing some coupling of its vibrational motion to the H atoms of its neighbors. As noticed already by Bernstein et al. and Hudson et al., matrix induced D shifts are not unprecedented (e.g., Nelander & Nord 1982; Zong & McHale 1997).

In this paper we investigate whether a matrix induced D shift occurs for OCN$^-$. We produce the ion by acid base reactions in ice samples of isocyanic acid (HNCO) and NH$_3$. The results are compared with the D shift of the XCN band produced by UV photolysis of CO/NH$_3$ ices. Furthermore we investigate whether the D shift of the XCN band depends on the nature of the matrix. We will first however make a close comparison between the spectral properties of "XCN" and OCN$^-$.

2. Experimental

Detailed descriptions of the general procedure for creation and UV photolysis of ice samples have been published earlier (Gerakines et al. 1995, 1996). The reagents used in these experiments were NH$_3$ (Praxair, 99.99% purity), ND$_3$ (Cambridge Isotope Laboratories, D/H = 99) and CO (99.997% purity). The gas samples were prepared in a glass manifold at a background pressure of $\sim 1 \times 10^{-4}$ mbar. Before preparation of a ND$_3$ containing mixture, the glass manifold as well as the glass bulb in which the sample is prepared was neutralized with 30 mbar ND$_3$ for 12 hr. The vacuum system was neutralized by flushing with ND$_3$ at 5×10^{15} molecules s^{-1} for 90 min. The spectrum of the deuterated samples showed, besides the umbrella mode of ND$_3$ at 830 cm^{-1}, a weak feature at 927 cm^{-1} due to the umbrella mode of ND$_2$H. The relative intensity of these peaks, assuming equal intrinsic strength, showed that the final amount of H in our deuterated experiments was $\sim 2.5\%$. NH$_3$/ND$_3$ and HNCO were deposited through seperate deposition tubes (Gerakines et al. 1995). To ensure transparency for UV, the thickness of samples in photolysis experiments was ≤ 0.1 μm.

To produce isocyanic acid (HNCO) we used the technique of Linhard (1938). This involves the thermal cracking of cyanuric acid (C$_3$H$_3$N$_3$O$_3$, Aldrich, purity 98%). After its production the HNCO was stored in liquid nitrogen. Before making a deposition, the tube was placed in an octane slush to enhance the HNCO vapor pressure.

To measure the matrix induced D shift of OCN$^-$, we selected matrices strongly dominated by NH$_3$. This

is essential for a meaningful comparison of the D shifts of OCN$^-$ in HNCO/NH$_3$ and of XCN in photolysed CO/NH$_3$, because otherwise the nature of the matrix would be very different in these two sets of experiments, and no agreement could be expected. An additional benefit of such matrices is that their composition remains stable during photolysis or warm-up. As a result, features shift very little over the course of the experiment, allowing a more accurate measurement of the D shift. To produce OCN$^-$ by direct acid-base reactions we used NH$_3$/HNCO = 100/1. For photolysis NH$_3$/CO = 40/1 was used. Since for photolysis the sample thickness is limited to ≤ 0.1 μm, the amount of XCN that is produced becomes too low for accurate spectroscopy if the CO fraction is smaller. To investigate the dependency of the D shift on sample composition we furthermore photolysed NH$_3$/CO = 1/1.

3. Results

3.1. Spectroscopic properties of OCN$^-$ and XCN

To investigate the spectroscopic properties of OCN$^-$, we deposited an ice mixture NH$_3$/HNCO = 1/1, followed by slow warm-up. Figure 1 follows the evolution of the spectrum. Already at 12 K features are present at 3240, 3040, 2820, 2155, 1500, 1295, 1210 and 630 cm^{-1} which cannot be ascribed to the original species. Upon warm-up, these bands grow while the bands of HNCO and NH$_3$ diminish. This shows that proton transfer takes place. The 3240, 3040, 2820 and 1500 cm^{-1} bands can be ascribed to the $\nu_1 + \nu_5$, $\nu_2 + \nu_4$, $2\nu_4$ and ν_4 modes of NH$_4^+$ (Wagner & Hornig 1950). The 2155, 1295, 1210 and 630 cm^{-1} features are identified with the ν_3, $2\nu_2$, ν_1 and ν_2 bands of OCN$^-$ by comparing to its spectrum in salt matrices (Maki & Decius 1959).
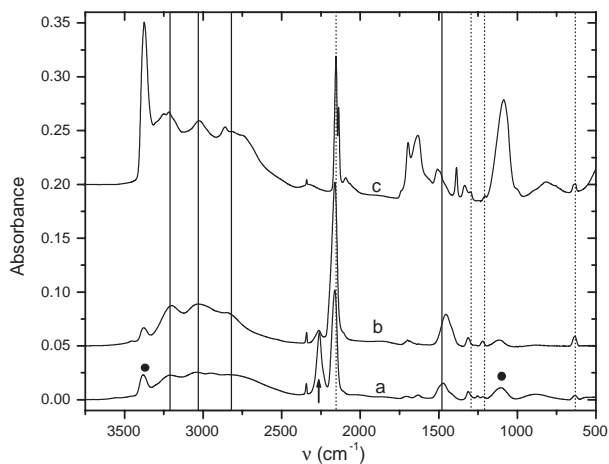

Fig. 1. a) NH$_3$/HNCO (1/1) at 12 K; **b)** idem, after warm-up to 80 K; **c)** NH$_3$/CO (1/1.2) photolysed at 12K, followed by warm-up to 80 K. Dotted vertical lines indicate OCN$^-$ features, solid lines NH$_4^+$ features, the arrow indicates the HNCO feature, dots the NH$_3$ features.

To compare the spectroscopic properties of OCN$^-$ to that of XCN, Fig. 1 furthermore shows the spectrum of NH$_3$/CO = 1/1, deposited and simultaneously photolysed for two hours at 12 K, followed by warm-up to 80 K. We choose similar abundances in the starting mixture to optimize the XCN concentration. It can be seen that all four OCN$^-$ features in the NH$_3$/HNCO ice have counterparts in the photolysed mixture. Furthermore, the features of NH$_4^+$ can be clearly recognized as well. The relative intensity of the NH$_4^+$ and OCN$^-$ features are quite similar in both samples. While a difference of $\sim$15 cm^{-1} can be seen between the position of the $2\nu_2$ and ν_1 features of OCN$^-$ in the warm-up experiment and the corresponding features in the photolysed sample, similar shifts are also seen for OCN$^-$ in different salt matrices (Maki & Decius 1959; Gordon & Foss Smith 1974). The difference of $\sim$40 cm^{-1} of the ν_4 NH$_4^+$ band in the two experiments is consistent with the very strong sensitivity of this feature to temperature and matrix composition (Grim et al. 1989; Schutte et al. 2001).

3.2. The D shift of OCN$^-$ and XCN

3.2.1. Warm-up of NH$_3$ or ND$_3$ with HNCO

Table 1 gives the position of the ν_3 OCN$^-$ band as a function of temperature for the unlabelled and deuterated NH$_3$/HNCO = 100/1 ice mixture, while Fig. 2a compares the features. A clear D-shift is found, which increases from 1.8 to 3.1 cm^{-1} during warm-up from 12 to 60 K. As mentioned in Sect. 1, the deuterium shift should be ascribed to the interaction of the ion with the matrix. The increase of the shift with temperature can be understood in terms of the annealing of the ice matrix, which results in rearranging of the constituents into an energetically more favorable configuration and strengthening of their interaction. The D shift changes only slightly upon re-cooling to 12 K, showing that this effect is irreversible.
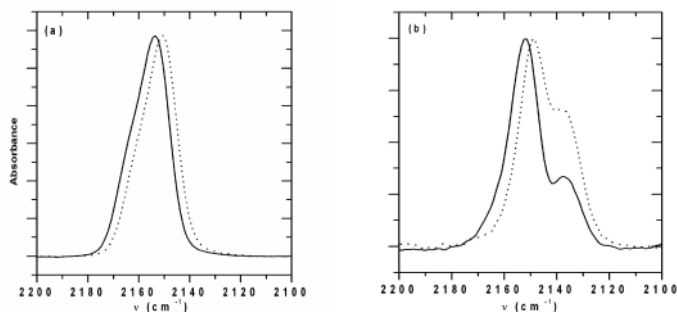

Fig. 2. Comparison of the deuterium shift of the ν_3 feature of OCN$^-$ with the XCN band: **a)** OCN$^-$ in NH$_3$/HNCO = 100/1 (solid line), and ND$_3$/HNCO = 100/1 (dashed line), after warm-up to 60 K, and recooling to 12 K; **b)** XCN in NH$_3$/CO = 40/1, photolysed for 30 min (solid line), and in ND$_3$/CO = 40/1, photolysed for 30 min (dashed line). The peak at 2138 cm^{-1} is due to CO.

Table 1. Position of the XCN/OCN$^-$ feature in various unlabelled and deuterated experiments.

| mixture | | | t_{irr} | T | ν cm^{-1} | ν cm^{-1} | $\Delta\nu$ cm^{-1} |
NH$_3$	HNCO	CO	m	K	H	D	
100	1			12	2155.0	2153.2	1.8
				30	2154.7	2152.5	2.2
				50	2153.6	2151.2	2.4
				60	2153.5	2150.4	3.1
				12[a]	2153.6	2150.7	2.9
40		1	10	12	2152.1		
			30	12	2151.9	2149.0	2.9
1		1	37	50	2158.3	2151.6	6.7
			37	100	2156.9	2150.6	6.3
			37	140	2158.7	2152.6	6.1

[a] Recooled.

3.2.2. UV photolysis of NH$_3$ or ND$_3$ with CO

Table 1 gives the position of the XCN band produced by photolysis at 12 K of unlabelled and deuterated NH$_3$/CO = 40/1, while Fig. 2b compares the features. A clear D shift is apparent of 2.9 $\pm$ 0.1 cm^{-1}.

In a second set of experiments we photolysed unlabelled and deuterated NH$_3$/CO = 1/1, followed by warm-up. For the deuterated experiment an accurate measurement of the XCN position can only be obtained after warm-up to $\geq$50 K, due to the interference with the strong CO feature at lower temperature. The results are listed in Table 1. The D shift equals 6.4 $\pm$ 0.3 cm^{-1}, depending slightly on temperature. This is somewhat lower that the 8 cm^{-1} shift reported by Bernstein et al. (2000) for this mixture. We note however that for matrices with comparable abundances of the initial ice components, the nature of the matrix changes strongly during the photolysis (due to the high concentration of photoproducts). For this reason, the position of the XCN band is rather unstable, i.e., in our NH$_3$/CO = 1/1 experiment the XCN band shifted 5 cm^{-1} over the course of the photolysis. In addition, in such ice mixtures variation in the mixing ratio of the components will cause a significant change in the nature of the matrix. Therefore, errors in the measurement of the D shift may be introduced by imperfect reproducibility between the labelled and unlabelled experiment of the UV lamp intensity, the mixing ratio, the sample thickness, or the spectrum of the UV lamp. The difference of up to 2 cm^{-1} between the measurements of the ^{13}C and ^{15}N isotope shifts for the NH$_3$/CO = 1/1 mixture by Grim & Greenberg (1987) and Bernstein et al. (2000) is probably due to this effect. It seems plausible that the 1.6 cm^{-1} difference between our result and that of Bernstein et al. derives from this effect as well.

4. Discussion

The shift of the OCN$^-$ feature produced by proton transfer between HNCO and NH$_3$ in our unlabelled and

deuterated NH_3/HNCO = 100/1 mixtures clearly shows that OCN$^-$ can produce a D shift even though it does not contain hydrogen. As already explained in Sect. 1, such a behaviour is not unprecedented and can be ascribed to the intermolecular bonding of the ion with species in the matrix. After warm-up to 60 K and recooling the shift equals 2.9 cm^{-1}. This is in excellent agreement with the D shift of 2.9 cm^{-1} for the XCN band produced by photolysis of NH_3/CO = 40/1, giving strong support to the OCN$^-$ assignment.

The NH_3/HNCO = 100/1 experiments were not fully deuterated, because of the hydrogen in the HNCO. If the hydrogen would stay in close contact with the OCN$^-$ ion, e.g., when a NHD_3^+.OCN$^-$ complex is formed, we would expect the D shift for the NH_3/HNCO experiment to be somewhat less than for the photolysis experiments. The good agreement therefore suggests that the H atom is not in the direct neighbourhood of the OCN$^-$. However, this conclusion depends on the extend of annealing caused by the photolysis, since below 60 K the D shift of OCN$^-$ in the NH_3/HNCO sample is smaller.

The D shift of the XCN band in the photolysed CO/NH_3 = 1/1 and 1/40 samples differ considerably, i.e., 6.4 cm^{-1} and 2.9 cm^{-1}, respectively. This demonstrates that the shift depends on the matrix. This seems inconsistent with the shift being caused by a covalently bonded H atom, since in that case the influence of the matrix should be small (e.g., the C, O, and N isotopic shifts of the ν_3 mode of OCN$^-$ remain constant within 2 cm^{-1} in different salt matrices, even though the band position itself shifts by up to 80 cm^{-1}; Maki & Decius 1959; Gordon & Foss Smith 1974). However, if the shift originates from the interaction of the XCN carrier with the matrix, a clear matrix dependency is plausible.

Besides the good agreement in the D shift, the coincidence of *four* spectral features produced in the photolysed ices with the four OCN$^-$ features is "hard evidence" in favor of the OCN$^-$ assignment. This agreement was earlier noticed by Schutte & Greenberg (1997), however, at the time the comparison was only done with literature data of OCN$^-$ in salt matrices.

The evidence presented in this paper, together with the evidence already published earlier (Sect. 1) clearly demonstrates that the XCN band near 2160 cm^{-1} produced by processing of ices containing CO and NH_3 is due to the ν_3 feature of OCN$^-$.

5. Astrophysical implications

The identification of the laboratory XCN feature with OCN$^-$ makes this species a prime candidate for the carrier of the interstellar XCN band. While it has been thought that organic nitriles or iso-nitriles could also be candidates, a thorough investigation of a large variety of such species showed that none satisfied the spectroscopic constraints (Bernstein et al. 1997). Another argument in favor of OCN$^-$ is the ease with which this species could be produced under interstellar conditions. Besides through

photolysis or irradiation of ices with CO and NH_3 (see also Hudson et al. 2001), isocyanic acid (HNCO) may be produced directly by grain surface chemistry (Hasegawa & Herbst 1993). In the presence of NH_3, proton transfer would be straightforward if a modest amount of energy is supplied to the ice matrix, e.g., through some warm-up (Fig. 1). Therefore it appears that the identification of the interstellar 4.62 μm "XCN" feature with OCN$^-$ is secure. We therefore propose to hereafter designate it accordingly.

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