

H, C, N, AND O ISOTOPIC SUBSTITUTION STUDIES OF THE 2165 WAVENUMBER (4.62 MICRON) “XCN” FEATURE PRODUCED BY ULTRAVIOLET PHOTOLYSIS OF MIXED MOLECULAR ICES

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Received 2000 May 1; accepted 2000 May 23

ABSTRACT

To better understand the chemical species that gives rise to the 2165 cm⁻¹ (4.62 μm) “XCN” absorption feature seen toward embedded protostars such as W33A, we have performed laboratory studies using deuterium (²H) isotopic labeling. We report the observation of a small but significant deuterium isotope shift for the “XCN” peak which demonstrates that the atomic motion(s) causing the “XCN” band in the laboratory samples must involve hydrogen. We also report the results of ¹³C, ¹⁵N, and ¹⁸O labeling experiments that are consistent with previously reported values.

Subject headings: infrared: ISM: lines and bands — ISM: lines and bands — ISM: molecules — methods: laboratory

1. INTRODUCTION

The absorption at 2165 cm⁻¹ (4.62 μm), commonly referred to as the “XCN” feature, was first observed in the spectrum of the embedded protostar W33A (Soifer et al. 1979), although it was not until later that the feature was clearly shown to be distinct from the nearby CO ice feature (Lacy et al. 1984). It has since been detected toward a number of other protostars (Pendleton et al. 1999). While various laboratory studies have produced peaks remarkably similar to the astronomical feature (Moore et al. 1983; Lacy et al. 1984; Grim & Greenberg 1987; Tegler et al. 1993; Bernstein et al. 1994; Schutte & Greenberg 1997; Demyk et al. 1998; Palumbo et al. 2000b; Hudson & Moore 2000), the identity of the specific molecule that causes this absorption remains uncertain. Lacy et al. (1984) noted that the location of the peak was consistent with a C≡N functional group, and, as a result, the carrier of the feature was referred to by the label “XCN” (hereafter without the quotes), denoting a nitrile or isonitrile group (CN) attached to an unknown molecular structure (X). (See Bernstein, Sandford, & Allamandola 1997 and Pendleton et al. 1999 for assessments of the viability of nitriles, isonitriles, and other classes of compounds as the cause of this feature.) The most recent laboratory work has focused on support (Schutte & Greenberg 1997; Demyk et al. 1998) or criticism (Palumbo et al. 2000b) of the idea that the carrier of the XCN feature is the isocyanate anion (OCN⁻).

To help constrain the chemical nature of the compound(s) that give(s) rise to the XCN feature, we have performed four separate kinds of isotopic-labeling experiments in which the H, C, N, or O atoms in the starting materials were each individually replaced with ²H, ¹³C, ¹⁵N, or ¹⁸O, respectively. Labeling experiments using ¹³C, ¹⁵N, and ¹⁸O have been previously reported in the literature (Grim & Greenberg 1987; Schutte & Greenberg 1997), but the replacement of hydrogen with deuterium (²H or D) appears for the first time here and in a companion paper (Palumbo, Pendleton, & Strazzulla 2000a). These new measurements demonstrate that the atomic motion(s)

causing the XCN feature involve hydrogen, as well as C, N, and O.

2. MATERIALS AND METHODS

The XCN feature appears in the spectra of many protostars embedded in dense molecular clouds but does not appear in the spectra of background stars behind dense clouds (see Pendleton et al. 1999). This suggests that the carrier of the XCN band is formed when interstellar ices are processed and subsequently warmed. In order to simulate this evolutionary history, we formed and irradiated our ices at 12 K, a temperature characteristic of the environments where ices form in dense interstellar molecular clouds. After irradiation, the ices were warmed to simulate the thermal evolution of ices in the vicinity of a protostar.

In most of the experiments reported here, the XCN feature was generated by the UV irradiation of CO:NH₃ = 1:1 ices frozen onto a CsI window at ~12 K. However, a limited number of experiments using more astrophysically relevant mixtures containing H₂O, CH₃OH, and NH₃ gave the same results. The window was suspended in a vacuum chamber and infrared spectra were taken from the CO:NH₃ samples in situ both before and after UV irradiation and after subsequent warm-up of the samples to various temperatures. Spectral data were sampled at 0.1 cm⁻¹ intervals at a resolution of 1 cm⁻¹ (the observed width of an unresolved line). Despite the spectral oversampling, the reported XCN band positions are only accurate to within about 0.5 cm⁻¹, due to the difficulty associated with establishing the exact center of this relatively wide feature. The apparatus and method for the low-temperature ultraviolet irradiation experiments that we used to produce the XCN feature are identical to those described elsewhere (Allamandola, Sandford, & Valero 1988; Bernstein et al. 1994, 1995, 1997) and are very similar to those employed in other laboratories where UV is employed as the radiation source. The companion paper to this one (Palumbo et al. 2000a) contains the results of ²H isotopic labeling experiments on the XCN feature generated from 60 keV Ar⁺⁺ ion bombardment of N₂-containing ices.

The isotopic labeling experiments reported here were performed using ¹³CO (¹³C = 99%), C¹⁸O (¹⁸O = 99%), ¹⁵NH₃ (¹⁵N = 99%), and ND₃ (D = 99%). We also carried out a limited number of alternative experiments using D₂O (D = 99%), CD₃OD (D = 99%), and ¹³CH₃OH

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($^{13}\text{C} = 99\%$). All these compounds were obtained from Cambridge Isotope Laboratories, except the ND_3 , which was obtained from MSD Isotopes. All samples were introduced into the stainless steel vacuum system as gases that were previously mixed in glass bulbs using a glass manifold at room temperature. All gas samples were allowed to equilibrate in the bulb for at least 24 hr before use. The background pressure in the glass gas-handling system was $\sim 10^{-5}$ mbar. The total starting pressure in the sample bulbs varied from 20 to 40 mbar of total pressure. Thus, the contaminant levels in the bulbs associated with the mixing process were always less than about one part in 10^6 , negligible compared to the original impurities of our starting materials.

3. ISOTOPIC SHIFT DATA

Table 1 lists the shifts in the XCN feature caused by the replacement of all the H, C, N, or O with D, ^{13}C , ^{15}N , or ^{18}O in the starting materials in the form of ND_3 , ^{13}CO , $^{15}\text{NH}_3$, or C^{18}O (one substitution at a time) in UV-irradiated $\text{CO}:\text{NH}_3 = 1:1$ ices. The infrared spectra resulting from deuterium substitution are seen in Figure 1 and from ^{15}N and ^{18}O substitution in Figure 2. The shifts produced by substituting ^1H , ^{14}N , and ^{16}O with ^2H , ^{15}N , and ^{18}O are about 8, 19–22, and 9 cm^{-1} , respectively, all to lower frequencies. The 3 cm^{-1} uncertainty range reported for the ^{15}N shift is due to an overlap of the XCN peak with that of residual CO trapped in the sample. This CO produces some absorption near 2137 cm^{-1} that produces the slight asymmetry seen in the XC^{15}N band profile in Figure 2. The value of 22 cm^{-1} results when this effect is ignored, but removal of a typical CO ice band profile until the XC^{15}N band becomes symmetric results in a residual band having an isotopic shift of $\sim 19\text{ cm}^{-1}$. The smaller shift is in better agreement with the value reported earlier by Grim & Greenberg (1987).

Figure 3 shows the dual XCN bands that are formed when an $\text{NH}_3 : ^{12}\text{CO} : ^{13}\text{CO} = 2:1:1$ ice is UV irradiated and warmed. The two bands are separated by approximately 58 cm^{-1} , the same shift that is seen between the XCN bands produced by the irradiation of separate $\text{NH}_3 : ^{12}\text{CO} = 1:1$ and $\text{NH}_3 : ^{13}\text{CO} = 1:1$ ices. Our mea-

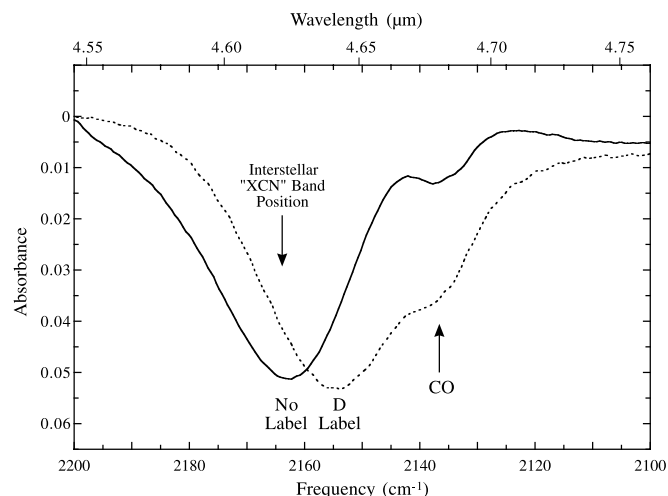


FIG. 1.—The 2200–2100 cm^{-1} (4.55–4.76 μm) infrared spectra of the XCN feature produced in the laboratory by UV irradiating 12 K $\text{CO}:\text{NH}_3 = 1:1$ (solid line) and $\text{CO}:\text{ND}_3 = 1:1$ (dashed line) ice mixtures subsequently warmed to 100 K. The same shifts are observed at 150 K and for irradiated ice mixtures of $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3$ vs. $\text{D}_2\text{O}:\text{CD}_3\text{OD}:\text{ND}_3$. The band seen near 2140 cm^{-1} (4.67 μm) is due to small amounts of trapped CO.

sured isotopic shifts for H, C, N, and O substitutions in $\text{CO}:\text{NH}_3$ ices are summarized in Table 1.

A limited number of experiments using ice compositions other than $\text{CO}:\text{NH}_3$ resulted in the same H, C, N, and O isotopic spectral shifts when the same isotopic substitutions were made. For example, if H, C, N, or O isotopic substitutions are made to more astrophysically relevant $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3$ ices ($\text{H}_2\text{O} \rightarrow \text{D}_2\text{O}$, $\text{CH}_3\text{OH} \rightarrow \text{CD}_3\text{OD}$, $\text{NH}_3 \rightarrow \text{ND}_3$, $^{14}\text{NH}_3 \rightarrow ^{15}\text{NH}_3$, etc.), the same isotopic shifts are observed.

The isotopic shifts observed for ^{13}C , ^{15}N , and ^{18}O substitutions have been previously reported in the literature for a variety of irradiated ice mixtures (Grim & Greenberg 1987; Schutte & Greenberg 1997) and our results are in good agreement with theirs. Our reported deuterium shift of about 8 cm^{-1} is in excellent agreement with that reported in

TABLE 1
POSITION AND SHIFT IN THE XCN BAND POSITION WITH ISOTOPIC SUBSTITUTION^a

Isotopes Present	Isotopic Substitution	Band Position (cm^{-1})	Band Shift (cm^{-1})
^{12}C , ^1H , ^{16}O , ^{14}N	None, normal isotopes	2163	0
^{12}C , ^{13}C , ^1H , ^{16}O , ^{14}N	$^{12}\text{C} \rightarrow ^{13}\text{C}$	2154, 2096 ^a	-58 ^b
^{12}C , ^2H , ^{16}O , ^{14}N	$^1\text{H} \rightarrow ^2\text{H}$	2155	-8 ^c
^{12}C , ^1H , ^{18}O , ^{14}N	$^{16}\text{O} \rightarrow ^{18}\text{O}$	2154	-9 ^d
^{12}C , ^1H , ^{16}O , ^{15}N	$^{14}\text{N} \rightarrow ^{15}\text{N}$	2144	-19 ^e

^a All band shift values were measured from $\text{CO}:\text{NH}_3$ ices after UV irradiation and warm-up to 100 K. Band positions were all measured at 100 K, except for those in the $^{12}\text{C}:\text{C}^{13}$ substitution, which were measured at 150 K.

^b Value in good agreement with the value of 57 cm^{-1} reported by Grim & Greenberg 1987.

^c Value in good agreement with Palumbo et al. 2000a. The same shift is seen when a $\text{D}_2\text{O}:\text{CD}_3\text{OD}:\text{ND}_3 = 20:10:2$ ice mixture is UV irradiated and warmed to 100 K.

^d Value in good agreement with the value of $8.7 \pm 0.6\text{ cm}^{-1}$ reported by Schutte & Greenberg 1997.

^e Value in reasonable agreement with the value of 17 cm^{-1} reported by Grim & Greenberg 1987. Note that the slight asymmetry in the XC^{15}N band seen in Fig. 2 is likely due to small amounts of residual CO trapped in the residue which produce additional absorption centered near 2137 cm^{-1} (see § 3).

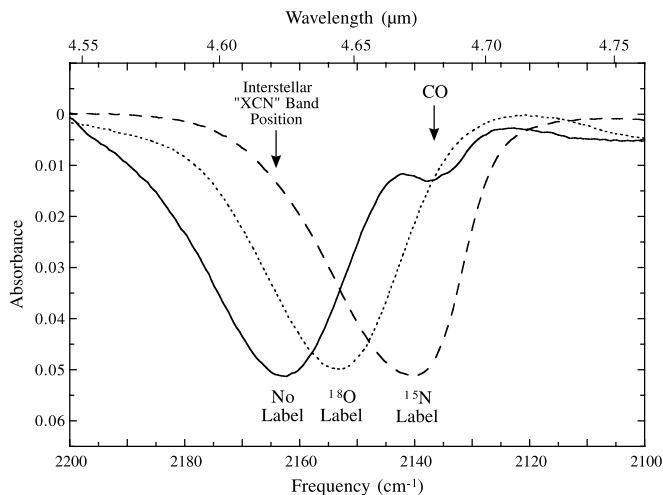


FIG. 2.—The 2200–2100 cm^{-1} (4.55–4.76 μm) infrared spectra of the XCN feature produced in the laboratory by UV irradiating 12 K $\text{CO}:\text{NH}_3 = 1:1$ (solid line), $\text{C}^{18}\text{O}:\text{NH}_3 = 1:1$ (short-dashed line), and $\text{CO}:\text{N}^{15}\text{H}_3 = 1:1$ (long-dashed line) ice mixtures. All the spectra were taken after the ice was subsequently warmed to 100 K. The band seen near 2140 cm^{-1} (4.67 μm) in some of the spectra is due to small amounts of trapped CO.

a companion paper in which ion irradiation was used on ices of different composition (Palumbo et al. 2000a).

Finally, while it has long been known that the *position* of the XCN band can shift somewhat as the temperature of the sample is raised, with the extent of the shift depending on the starting mixture (Lacy et al. 1984; Pendleton et al. 1999), we note that the *isotopic shift* of the peak does not change with temperature. That is, different starting ice compositions can lead to slightly different temperature behaviors in the band position, but the isotopic shifts are everywhere the same as those listed in Table 1.

Thus, the deuterium isotope shift is independent of the starting mixture, temperature, and radiation source, and thus can be entirely attributed to isotopic substitution.

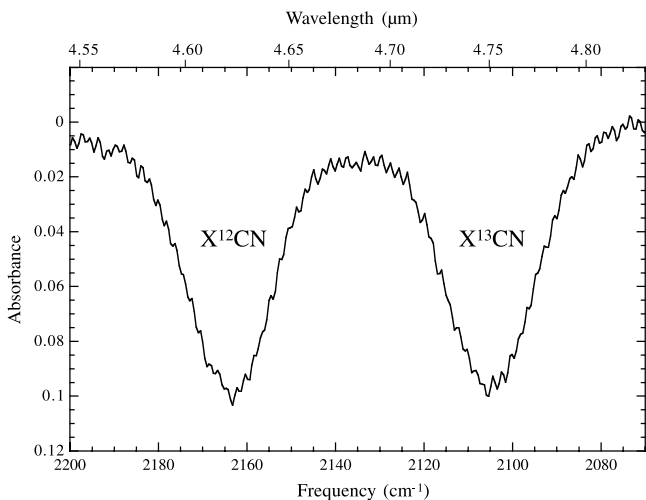


FIG. 3.—The 2200–2070 cm^{-1} (4.55–4.83 μm) infrared spectra of the XCN feature produced in the laboratory by UV irradiating a 12 K $\text{NH}_3 : \text{C}^{12}\text{CO} : \text{C}^{13}\text{CO} = 2:1:1$ ice mixture. The spectrum was taken after the ice was subsequently warmed to 150 K. The same shifts are observed at 100 K.

4. DISCUSSION

4.1. Isotopic Substitutions in General

The shift in position of an infrared band upon isotopic replacement of an atom represents indisputable evidence for the involvement of that atom in the molecular motion giving rise to the infrared feature. The positions of molecular infrared absorption peaks correspond to the frequencies of the vibrational motions of atoms, and a change in the mass of an atom involved in a molecular motion results in a change in the peak position of its associated infrared absorption band. The magnitude of the change in the peak position depends on the kind of motion, the change in reduced mass, and the extent of the involvement of the atom being replaced in the associated molecular motion.

Thus, the magnitude of the isotopic shift provides information about the location of the atoms within the molecule. Atoms that are directly involved in the vibrational motion create the largest isotopic shifts, while those that are more distant cause smaller ones. All else being equal, replacing hydrogen with deuterium should produce the largest shift because this involves a relative increase in mass of a factor of 2, whereas substitution by ^{13}C , ^{15}N , and ^{18}O represents fractional increases in mass of only about 8%, 7%, and 12%, respectively. When isotopic substitution of an element produces shifts smaller than expected, the implication is that the atom is not directly involved in the motion, usually because it is removed some distance from the atomic motions giving rise to the band.

In an ice that is isotopically mixed (such as the ice that produced the spectrum in Fig. 3, which contains both ^{12}C and ^{13}C), one expects to see at least two peaks: one arising from the isotopically normal molecule and one from the labeled molecule. However, if the molecule contains multiple atoms of the type being substituted, additional peaks may show up due to different substitutional combinations. For example, a molecule with two C atoms would have four possible isotopic variants ($^{12}\text{C}:\text{C}^{12}$, $^{12}\text{C}:\text{C}^{13}$, $^{13}\text{C}:\text{C}^{12}$, and $^{13}\text{C}:\text{C}^{13}$).

4.2. Isotopic Substitutions in XCN

It is clear from the observation of H, C, N, and O isotopic shifts reported in Table 1 that the molecular motion producing the XCN feature must involve the elements H, C, N, and O. This is consistent with the observation that the 4.62 μm XCN band is produced only from starting ice mixtures where *all* of the four elements are present. In our experiments these elements must originate in molecules that can be disrupted by UV photons. For example, NH_3 is a very good source of nitrogen for UV-driven experiments, but molecular nitrogen (N_2) is not. This contrasts with ion irradiation experiments, for which N_2 represents a useful source of nitrogen (Palumbo et al. 2000b, 2000a). These isotopic shifts are independent of the starting mixture, temperature, and radiation source and thus can be entirely attributed to isotopic substitution.

4.2.1. Deuterium (^2H) Labeling in XCN

Even though the substitution of deuterium for hydrogen involves a twofold increase in atomic mass, the shift is quite small (8 cm^{-1} ; Fig. 1 and Table 1). This indicates that the hydrogen atom's motion itself is *not* the source of the 2165 cm^{-1} (4.62 μm) peak, but that it is somewhat removed from the fundamental vibration producing the band.

One explanation for the small but significant D-isotope shift is that the species that produces the XCN feature contains at least one covalently bound hydrogen atom that is located fairly close to the $C\equiv N$ group producing the 4.62 μm band. A molecular species having a covalently bound hydrogen atom is inconsistent with previous assertions that the XCN feature can be attributed *solely* to the isocyanate anion (OCN^-). Other, more unusual molecular interactions could conceivably cause such a deuterium shift. Although rarely reported, solvent isotope effects (when H is replaced with D in the solvent, as opposed to the compound itself) on band positions have been reported on certain occasions. For example, a 4 cm^{-1} shift in the position of the $C-O^-$ stretch of a phenolate group was observed when the CH_3OH solvent was replaced with CD_3OD (Zhong & McHale 1997).

In the case of the XCN band, proponents of the OCN^- identification for the band have suggested the counter ion might be NH_4^+ (Grim & Greenberg 1987). Perhaps replacing the hydrogen in an $\text{NH}_4^+ \text{OCN}^-$ complex with deuterium might produce a measurable shift in the OCN^- stretch. Work on the $\text{ND}_4^+ \text{OCN}^-$ system in liquid water at room temperature is currently underway (M. H. Moore 2000, private communication). However, in such a complex the transfer of an H from NH_4^+ to the OCN^- should be very facile, so if the deuterium from the ND_4^+ were interacting strongly enough with the OCN^- to cause a deuterium shift, then presumably the species giving rise to the XCN feature would be more like DOCN or DNCO and less like unperturbed OCN^- . As a result, one might expect the behavior of the CN stretch in such a species to be nearer to that in HOCN or HNCO , species that produce $C\equiv N$ bands at 2290 and 2260 cm^{-1} , respectively (Jacox & Milligan 1964), positions that are quite different from the observed position of 2165 cm^{-1} for the XCN band. This observation and line of reasoning does not necessarily obviate the carrier being an ion (Demyk et al. 1998), but the presence of hydrogen must be involved to yield an isotopic shift in the XCN feature.

4.2.2. ^{13}C , ^{15}N , and ^{18}O Labeling in XCN

The magnitude of the ^{13}C and ^{15}N shifts reported in Table 1 and seen in Figures 2 and 3 indicate that both C and N are *direct* components of the vibrational atomic motion that causes the XCN feature. This is consistent with previous suggestions that the 4.62 μm band is the $C\equiv N$ stretch of a nitrile ($X-C\equiv N$) or isonitrile ($X-N\equiv C$) group (Lacy et al. 1984; Bernstein et al. 1997) and with

previously reported ^{13}C and ^{15}N labeling experiments (Grim & Greenberg 1987).

Furthermore, the absence of any extra peaks (in addition to the two XCN bands in Fig. 2) produced from the irradiation of an isotopically mixed $\text{NH}_3 : ^{12}\text{CO} : ^{13}\text{CO} = 2:1:1$ ice suggests that if the carrier contains C atoms in addition to the one involved in the primary $C\equiv N$ group, they must be removed by several bond distances (see § 4.1).

Despite the fact that substitution of ^{16}O with ^{18}O represents a fractional mass change slightly larger than that of the C and N substitutions, the oxygen isotope produces a band shift that is smaller than those produced by either ^{13}C or ^{15}N . Although this suggests that oxygen it is not among the atoms directly participating in the fundamental vibrational motion causing the XCN feature, it cannot be many bonds removed or the shift would be too small to measure. This is consistent with a previously reported ^{18}O -labeling experiment (Schutte & Greenberg 1997).

5. CONCLUSIONS

The observed isotopic shifts in the XCN band position when H, ^{12}C , ^{14}N , and ^{16}O are replaced with D, ^{13}C , ^{15}N , and ^{18}O (Table 1) unambiguously demonstrate that the elements hydrogen, carbon, nitrogen, and oxygen are all involved in the molecular motion that gives rise to the 2165 cm^{-1} (4.62 μm) XCN feature observed in the laboratory.

The 8 cm^{-1} shift observed when hydrogen is replaced with deuterium is independent of the starting mixture, temperature, and radiation source and thus can be entirely attributed to isotopic substitution. The relatively small size of the shift caused by H \rightarrow D substitution indicates that H is not directly involved in the principal motion producing the XCN band, but it must also be relatively near the $C\equiv N$ group to influence its vibrational frequency.

The ^{13}C , ^{15}N , and ^{18}O shifts (approximately 58, 19, and 9 cm^{-1} , respectively) are all in reasonable agreement with previously published values, and are consistent with a species bearing some type of $C\equiv N$ functional group and an oxygen atom that is near (and likely adjacent to) the $C\equiv N$ group.

This work was supported by NASA grants 344-37-44-01 (Origins of Solar Systems Program) and 344-38-12-04 (Exobiology Program). The authors are grateful for useful discussions with Professor J. McHale, J. Dworkin, Y. Pendleton, and D. Hudgins and excellent technical support from R. Walker.

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