R—O—C≡N SPECIES PRODUCED BY ION IRRADIATION OF ICE MIXTURES: COMPARISON WITH ASTRONOMICAL OBSERVATIONS

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ABSTRACT

We have investigated the effects induced by ion bombardment of mixtures containing nitrogen-bearing compounds at low temperatures. The results show the formation of a band at $2080 \, cm^{-1}$ in binary mixtures, $NH_3:CH_4$ and $N_2:CH_4$, which we attribute to HCN embedded in the organic residue formed by ion irradiation. In addition to this band, ternary mixtures containing an oxygen-bearing species (i.e., H_2O) form a compound with a prominent absorption band at about $2165 \, cm^{-1}$ ($4.62 \, \mu m$). We ascribe this band to a nitrile compound containing O that is bonded to the organic residue. A detailed comparison of the laboratory results with astronomical data of the $4.62 \, \mu m$ absorption band in protostellar spectra shows good agreement in peak position and profile. Our experimental studies show that N_2, which is a more likely interstellar ice component than NH_3, can be the molecular progenitor of the carrier of the interstellar band. This is an alternative to the pathway by which UV photolysis of NH_3-containing ices produces the $4.62 \, \mu m$ band and implies that ion bombardment may well play an important role in the evolution of interstellar ices. Here, we discuss the implications of our studies for the chemical route by which the carrier of the $4.62 \, \mu m$ band is formed in these laboratory experiments.

Subject headings: infrared: ISM: lines and bands — ISM: clouds — ISM: molecules — line: identification — molecular processes — stars: pre–main-sequence

1. INTRODUCTION

Infrared spectra of many protostars show an absorption feature at $4.62 \, \mu m$ ($2165 \, cm^{-1}$; Lacy et al. 1984; Tegler et al. 1993, 1995; Weintraub et al. 1994; Pendleton et al. 1999). Although the feature has not yet been unambiguously identified, a nitrogen-bearing species has been implicated through comparisons to laboratory data. Proposed identifications and various production pathways for the interstellar $4.62 \, \mu m$ band have recently been reviewed by Pendleton et al. (1999).

Over the past two decades, there have been searches for reservoirs of solid-phase nitrogen in molecular cloud regions where there is a significant depletion of the gas. The identification of the interstellar $4.62 \, \mu m$ ($2165 \, cm^{-1}$) band, with a specific nitrogen-bearing species, should therefore contribute to the solution of the problem of the "missing" nitrogen in dense clouds.

Often referred to in the literature as the "X—C≡N" band, the association with nitriles developed because laboratory results of far-ultraviolet (FUV) photolyzed, ammonia-containing ice mixtures revealed a similar band (Hagen 1982; d'Hendecourt et al. 1986). Early studies of ion-bombarded nitrogen-containing mixtures also revealed a band at $4.62 \, \mu m$ ($2165 \, cm^{-1}$; Moore et al. 1983). The FUV experiments have concentrated on NH_3 as the progenitor of the $4.62 \, \mu m$ ($2165 \, cm^{-1}$) band because ammonia has often been proposed as a major reservoir of nitrogen in interstellar ices (cf. van de Hulst 1949) and because NH_3 is readily photolyzed by FUV photons. However, observational reports of solid-state ammonia have been controversial over the years (Knacke et al. 1982; Knacke &

McCorkle 1987; Smith, Sellgren, & Tokunaga 1989; Smith, Sellgren, & Brooke 1993; Graham & Chen 1991; Whittet et al. 1996a). Upper limits for the abundance of NH_3 relative to H_2O of 5% are given by Tielens & Whittet (1997). Recently Lacy et al. (1998) have identified an absorption feature at $9.01 \, \mu m$ ($1110 \, cm^{-1}$) toward the embedded source NGC 7538 IRS9, which they attribute to frozen NH_3 giving a NH_3/H_2O ratio of 0.1 toward that line of sight. Solid N_2, which cannot be easily observed directly since it is a homonuclear molecule, is the more likely reservoir of the nitrogen depleted from the gas phase in molecular clouds (Tielens & Hagen 1982; Whittet et al. 1996b; Charnley 1997; Elsila, Allamandola, & Sandford 1997). Because of its high bond energy, N_2 is not readily photolyzed by FUV photons. In the case of ion bombardment, the high linear energy transfer implies no such constraint. Hence, if nitrogen is in the form of N_2, the $4.62 \, \mu m$ band may provide a discriminant between the energetic processing of interstellar ice mantles by ion bombardment or FUV photons.

The purposes of this paper are (1) to further study the formation of —C≡N-bearing species by looking at the IR spectra in the $2000–2300 \, cm^{-1}$ range produced via ion bombardment experiments of the following ice mixtures: $CH_4:NH_3$ (1:1), $CH_4:N_2$ (1:1), $CO:N_2$ (1:1), $H_2O:NH_3:CH_4$ (2.5:1:2), and $H_2O:N_2:CH_4$ (1:1:1) and (2) to compare laboratory spectra with observations. Our results demonstrate that ion irradiation is an effective pathway that can play a crucial role in the development of interstellar ices. This paper is organized as follows: § 2 contains a review of the experimental technique and results, § 3 discusses the experimental results and a comparison with

previous results, § 4 discusses the relevance of the results to the identification of the interstellar 4.62 μm band, and a summary is given in § 5.

2. EXPERIMENTAL TECHNIQUES AND RESULTS

2.1. Experimental Setup

A high-vacuum chamber ($P \sim 10^{-7}$ mbar) is placed in the sample compartment of either a Perkin-Elmer (model 1710) (4400–400 cm^{-1} = 2.27–25 μm) or a Bruker Equinox 55 (7500–400 cm^{-1} = 1.33–25 μm) Fourier Transform Infrared (FTIR) spectrophotometer. The infrared (IR) beam enters and leaves the chamber through two KBr windows. A silicon crystal substrate is cooled to 10–300 K by a closed-cycle helium refrigerator. Gas mixtures, prepared by premixing the component gases in the chosen ratio, are admitted into the chamber, and they accrete onto the cold silicon substrate in the form of frozen films. All of the spectra shown in the following sections are ratioed to the background spectrum and have been obtained with a resolution of 2 cm^{-1} (except when differently specified). The substrate plane forms an angle of 45° with the IR beam and the ion beam so that before, during, and after irradiation, spectra can be taken without tilting the sample. After irradiation, targets can be warmed at a rate of a few degrees per minute, and spectra are taken at selected temperatures in the range 10–300 K.

Ion beams are obtained from an ion implanter (30 kV) or an ion gun (3 kV). The beam sweeps on the target and produces a 2×2 cm^2 spot (greater than the spot of the IR beam). Doubly ionized beams reaching energy up to 60 keV can also be obtained from the ion implanter. We have irradiated our icy samples with He$^+$ (3 keV and 30 keV), Ar$^+$ (30 keV), and Ar^{++} (60 keV) ions. Experiments with 30–60 keV ions have been performed by depositing species (thickness $\sim 10^{18}$ molecules cm^{-2}) and then irradiating with the beam passing through the target. The deposited energy (eV/16 amu) has been calculated from the knowledge of the stopping power (energy loss per unit path length) of the used ions and from the measurement of the number of impinging ions (ion current times irradiation time). Experiments with 3 keV ions have been performed by depositing species at a known rate (previously calibrated; see Palumbo & Strazzulla 1993) and irradiating at the same time. In this case thicker samples can be obtained. The deposited energy (eV/16 amu) has been calculated from the knowledge of the deposition rate and the ion current.

Doses are given in eV/16 amu because this is a convenient way to compare the results of experiments performed with species of different molecular weights and for mixtures. Ion current densities in the range 10^2 nA cm^{-2} to a few microamperes per square centimeter have been used in order to avoid macroscopic heating of the target.

2.2. Binary Mixtures $NH_3:CH_4$, $N_2:CH_4$, and $N_2:CO$

In Figure 1 we report the results obtained for $NH_3:CH_4$ ($\simeq 1:1$) and $N_2:CH_4$ ($\simeq 1:1$) mixtures in the 2300–1800 cm^{-1} spectral region. In the bottom three panels we report the spectra of the $NH_3:CH_4$ sample as deposited at 10 K (thickness of the sample is $\simeq 1.2 \times 10^{18}$ molecules cm^{-2}), after irradiation with 30 keV He$^+$ at 10 K (80 eV/16 amu), and after warm-up to 200 K. In the top two panels we report the spectra of the $N_2:CH_4$ mixture: at 10 K after irradiation with 60 keV Ar^{++} (60 eV/16 amu) and after

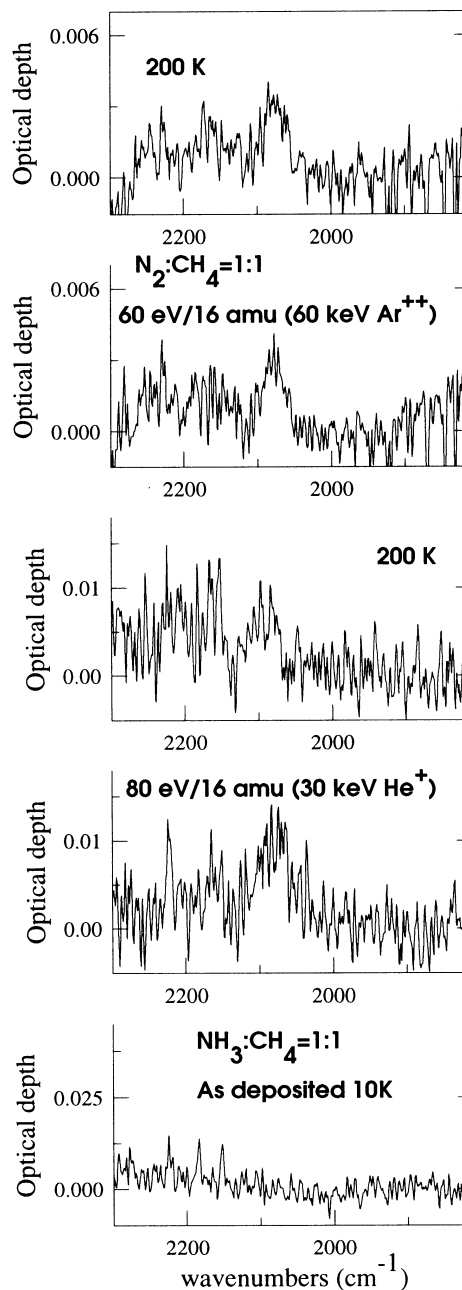FIG. 1.—IR spectra obtained for mixtures $NH_3:CH_4$ ($\simeq 1:1$) and $N_2:CH_4$ ($\simeq 1:1$) in the spectral region 2300–1800 cm^{-1}. *From bottom to top*: $NH_3:CH_4$ as deposited at 10 K, after irradiation at 10 K with 30 keV He$^+$ (80 eV/16 amu), and after warm-up to 200 K. In the two upper panels we report the spectra of the $N_2:CH_4$ mixture at 10 K after irradiation with 60 keV Ar^{++} (60 eV/16 amu) and after warm-up to 200 K.

warm-up to 200 K. Upon ion irradiation, the formation of a weak band centered at about 2080 cm^{-1} is apparent in both mixtures. The feature is still present after warm-up to 200 K. From the whole spectrum (not shown here) other species are observed, some of which are identified (e.g., C_2H_6, from the band at 2975 cm^{-1}). Other species (absorbing in particular in the 1800–1400 cm^{-1} spectral range) are difficult to identify by thin layer infrared spectroscopy and will be investigated in a future study.

After ion irradiation at 10 K of a $N_2:CO = 1:1$ mixture with 30 keV Ar$^+$ (~ 20 eV/16 amu) a weak feature appears at 2181 cm^{-1} along with the carbon dioxide bands at 2347

cm^{-1} and 660 cm^{-1} and the suboxides band at about 2240 cm^{-1} (Strazzulla et al. 1997). The 2180 cm^{-1} feature is very weak in our sample and disappears after warm-up at about 200 K along with the feature attributed to suboxides.

2.3. Ternary Mixtures H_2O:NH_3:CH_4 and H_2O:N_2:CH_4

In Figures 2 and 3 we report the results obtained for H_2O:NH_3:CH_4 ($\simeq 2.5$:1:2) and H_2O:N_2:CH_4 ($\simeq$1:1:1) mixtures in the 2300–2000 cm^{-1} spectral region.

In the bottom panel of Figure 2 we report the spectrum obtained at 10 K of the H_2O:NH_3:CH_4 mixture after irradiation with 30 keV He$^+$ at 120 eV/16 amu. The original thickness of the sample was $\simeq 1.1 \times 10^{18}$ molecules cm^{-2}.
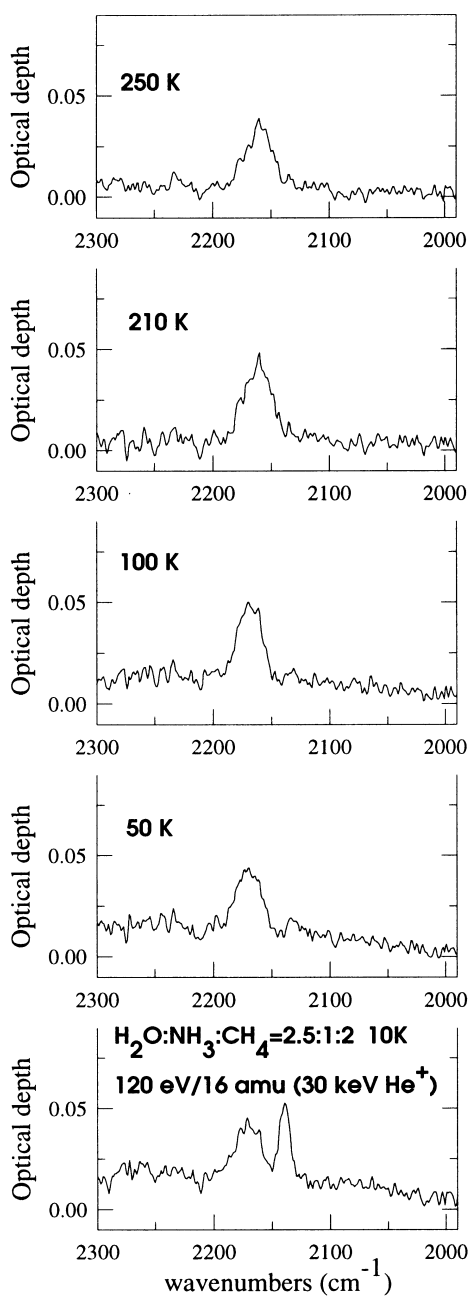
FIG. 2.—IR spectra of a mixture H_2O:NH_3:CH_4 ($\simeq 2.5$:1:2) in the spectral region 2300–2000 cm^{-1}. *Bottom:* Spectrum obtained at 10 K after irradiation with 30 keV He$^+$ at 120 eV/16 amu. *Remaining panels, from bottom to top:* Spectra obtained after warm-up to 50, 100, 210, and 250 K.
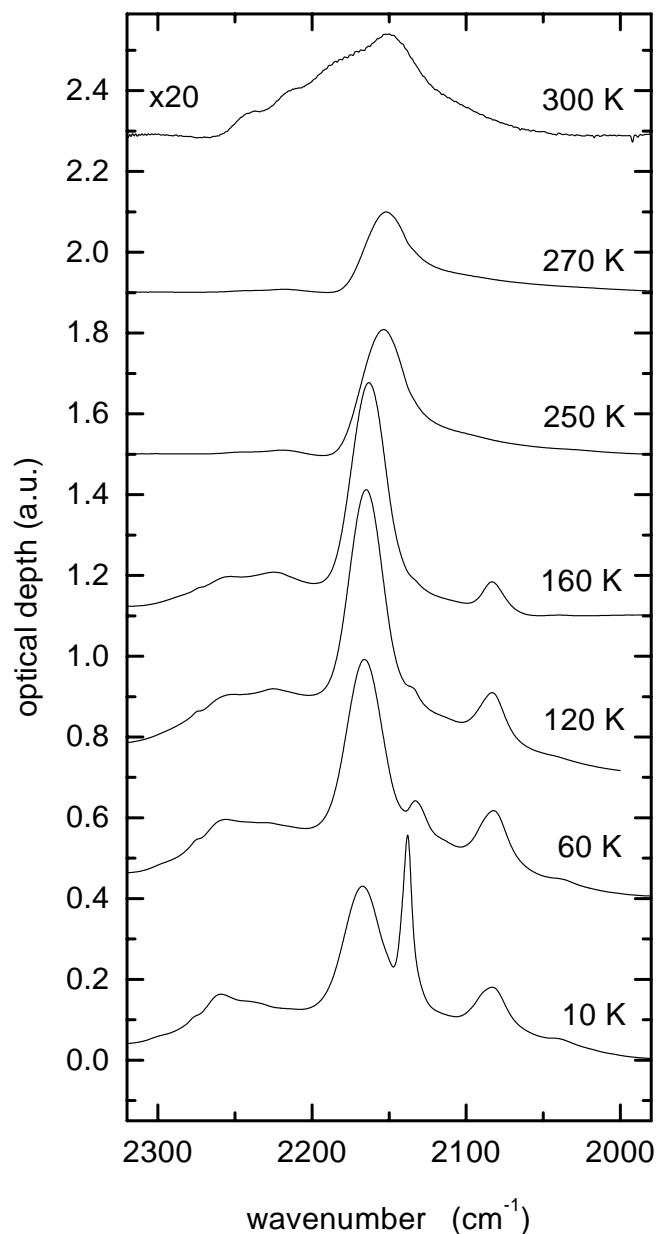
FIG. 3.—IR spectra (taken with a resolution of 1 cm^{-1}) of a mixture H_2O:N_2:CH_4 ($\simeq$1:1:1) in the spectral region 2300–2000 cm^{-1}. *Bottom:* Spectrum obtained at 10 K after irradiation with 60 keV Ar^{++} at 12 eV/16 amu. *Remaining panels, from bottom to top:* Spectra obtained after warm-up to 60, 120, 160, 250, 270, and 300 K. This latter spectrum was taken after the sample had been left overnight, under vacuum, at room temperature.

The appearance of two bands centered at about 2140 and 2165 cm^{-1} is evident. Spectra have also been taken after irradiation with different doses, and it is interesting to note that the profile of the 2165 cm^{-1} band does not depend on the dose. The other panels from bottom to top show the spectra obtained after warm-up to 50, 100, 210, and 250 K, respectively.

In the bottom panel of Figure 3 we report the spectrum taken at 10 K of the H_2O:N_2:CH_4 mixture after irradiation with 60 keV Ar^{++} at 12 eV/16 amu. The appearance of new bands centered at about 2085, 2140, 2165, and 2260 cm^{-1} is also evident in this case. The other panels show from bottom to top the spectra obtained after warm-up to
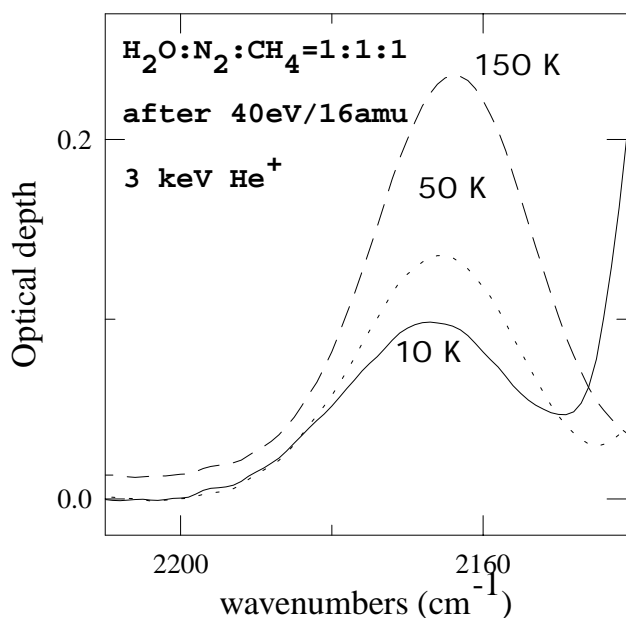
FIG. 4.—Comparison, at three different temperatures, of the profile of the 2165 cm^{-1} band obtained after irradiation of the $H_2O:N_2:CH_4$ mixture with 3 keV He$^+$ at 40 eV/16 amu. The spectra at 10 (*solid line*), 50 (*dotted line*), and 150 K (*dashed line*) are shown.

60, 120, 160, 250, 270, and 300 K. This latter spectrum was taken after the sample was left overnight, under vacuum, at room temperature.

In both mixtures, among the new bands formed, the 2140 cm^{-1} is attributed to solid CO and the 2085 cm^{-1} band is similar to the band observed after ion irradiation of the binary mixtures shown in Figure 1. The broad band at about 2260 cm^{-1} is probably due to a blend of more than one feature. Among these the peak at 2235 cm^{-1} could be due to N_2O (Elsila et al. 1997). The band at 2165 cm^{-1} is attributed, as we discuss below, to an X—C≡N species.

Figures 2 and 3 show that analogous results are obtained by substituting NH_3 with N_2; this means that the new band attributed to X—C≡N is insensitive to the original species that carries the nitrogen atoms.

Upon warm-up, the CO band disappears (because of sublimation), while the carrier of the XCN feature remains. The shape of the band, including intensity, peak position, and FWHM, exhibits relevant variations with the temperature. Figure 4 shows the spectra obtained for a $H_2O:N_2:CH_4 = 1:1:1$ mixture after irradiation at 10 K with 3 keV He$^+$ (40 eV/16 amu) and upon warm-up to 50 and 150 K. In addition to changes in the band profile, the peak position shifts from 2167 cm^{-1} at 10 K to 2164 cm^{-1} at 150 K and, in particular, the integrated band intensity increases by a factor of about 2 as temperature increases. Furthermore, this feature is still present in the spectra after the sample has been left overnight, under vacuum, at room temperature (Fig. 3).

3. DISCUSSION OF THE EXPERIMENTS

3.1. *The Carrier of the* 2165 cm^{-1} *Band in Ion-irradiated Mixtures*

A band at about 2170 cm^{-1} has already been detected by Moore et al. (1983) after irradiation of a mixture $H_2O:NH_3:CH_4$ ($\simeq 1:3:2$) with $\simeq$MeV protons. These

authors also found that ion irradiation of $H_2O:N_2:CO_2$ ($\simeq 1:1:1$) and $H_2O:N_2:CO$ ($\simeq 5:1:1$) mixtures produces a band at about 2180 cm^{-1} (Moore et al. 1983). A band centered at about 2165 cm^{-1} also appears after UV irradiation of mixtures containing ammonia, water, and methanol (e.g., Allamandola, Sandford, & Valero 1988) and ammonia and carbon monoxide (e.g., Lacy et al. 1984; Grim & Greenberg 1987).

We note that this band does not appear when we irradiate the binary mixtures $NH_3:CH_4$ ($\simeq 1:1$) and $N_2:CH_4$ ($\simeq 1:1$), and thus it is sensitive to the presence of oxygen (or, at least, water) in the irradiated mixture. A similar result pertains to the UV photolysis experiments (Bernstein, Sandford, & Allamandola 1997; Schutte & Greenberg 1997). Lacy et al. (1984) report the appearance of a weak band at about 2165 cm^{-1} after photolysis of a binary mixture of $NH_3:CH_4$. While we cannot exclude that the disagreement could be due to the different kind of processing (UV versus ions), we believe that the Lacy et al. (1984) result could be due to a modest contamination of O-bearing species (see also Grim & Greenberg 1987).

Dello Russo & Khanna (1996) present laboratory spectra of crystalline frozen nitriles. The majority of the studied species exhibit the (C≡N) stretch at wavenumbers around 2250–2230 cm^{-1}, too far from our band for an identification. Cyanogen (C_2N_2) has a band at about 2165 cm^{-1}, although it appears as a doublet in the spectrum by Dello Russo & Khanna (1996) because of the crystalline structure of their samples. Cyanopropyne (CH_3C_3N) absorbs at 2154 cm^{-1} and hydrogen cyanide (HCN) at about 2080 cm^{-1}. Recently, Bernstein et al. (1997) have presented the 2320–2050 cm^{-1} infrared spectra (at 12 K) of 16 solid-state nitriles, isonitriles, and related compounds. They found that the C≡N stretching bands of the majority of nitriles fall in the 2300–2200 cm^{-1} region; in contrast, the isonitriles and a few exceptional nitriles produce bands at lower frequencies spanning the 2200–2080 cm^{-1} range.

On the other hand, it is well established (e.g., Strazzulla & Johnson 1991; Strazzulla 1997, 1998) that ion irradiation not only drives the formation of specific molecules, depending on the particular target, but also of refractory residues. Thus, at present, our preferred solution is that the band at 2165 cm^{-1} is due to —C≡N groups bonded to oxygen-containing end groups (here named R—O) of the disordered tridimensional structure (often referred to as refractory organic residue) that is formed upon irradiation of hydrocarbon-containing ices. In the binary mixtures —C≡N groups would be bonded, but in a lower number and/or producing bands of lower absorbance, to H atoms and embedded in the tridimensional disordered network giving rise to the band at 2080 cm^{-1}.

Laboratory experiments have also shown that the profile of the 2165 cm^{-1} band does not depend on the initial composition (nitrogen or ammonia) or on the amount of energy deposited by ions. This result is interesting, particularly in view of the comparison with astrophysical observations (discussed in § 4).

A comparison among the results obtained after ion irradiation experiments performed by different groups gives a very good agreement. In fact after irradiation of $H_2O:CH_4:NH_3$ (Moore et al. 1983) and $H_2O:CH_4:NH_3$ (N_2) (this work) mixtures, a feature is formed at about 2165 cm^{-1}. After ion irradiation of $H_2O:CO_2(CO):N_2$ (Moore et al. 1983) and $CO:N_2$ (this work) mixtures, the feature

formed peaks at about 2180 cm^{-1}. We suggest that the two features are due to the same carrier and that the different peak position is due to the different matrix (i.e., the organic residue in the former case and suboxides in the latter). Furthermore, in the latter case the feature is weaker even in the presence of water (Moore et al. 1983). This could be due to a different efficiency of the —C≡N formation process or to the effect of the different matrix.

3.2. Comparison with FUV Results

The feature observed at about 2165 cm^{-1} after FUV photolysis of icy mixtures containing CO and NH$_3$ has been attributed to the OCN$^-$ ion (e.g., Grim & Greenberg 1987; Schutte & Greenberg 1997). Grim et al. (1989) 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. However, the acid HNCO has never been observed after photolysis of ice mixtures, and it seems unlikely that the absence is due to 100% efficiency in the acid-base reaction. Thus, some doubt about the actual reaction mechanism persists.

As concerns the identification of the carrier of the 2165 cm^{-1} band, while both processes (FUV photolysis and ion bombardment) yield a species containing the same basic *ingredients* (nitrogen, carbon, and oxygen), the ion irradiation experiments indicate that the carrier of this feature is a refractory species well bonded to the residue that also formed as a result of the irradiation. Thus, we suggest the R—OCN identification indicating that the —C≡N group is part of the residue. However, at this stage, it is not possible to exclude that R can also be named R$^+$.

Grim & Greenberg (1987) report that after warm-up above 240 K the 2165 cm^{-1} band disappears and a new absorption feature appears in the spectra at about 2217 cm^{-1}. They attribute this feature to the OCN stretching vibration in ammoniumcyanate, indicating that at this temperature the ions combine to form NH$_4$NCO.

After warm-up above 240 K of ion-irradiated mixtures the 2165 cm^{-1} band does not disappear, and only a weak feature, if any, is present at about 2220 cm^{-1}, which seems to be already present before warm-up (Fig. 3). We suggest that this is due to the fact that in the ion bombardment experiments the —C≡N group is already bonded to the residue. This different behavior after UV and ion irradiation could depend on the different nature of the residue formed.

As concerns the formation mechanism, chemical and physical modifications induced by ion irradiation occur along the ion track, and we are not able to investigate the chemistry along the ion track while the ion is passing through the sample. At this stage we cannot exclude the possibility that acid-base reactions take place along the ion track; however, from the infrared spectra taken after ion irradiation, we have no evidence of the formation of a base (e.g., NH$_3$), if N$_2$ is the nitrogen-bearing species, and an acid (e.g., HNCO). Moreover, two sets of experimental data described below support the hypothesis that the formation mechanism of the 2165 cm^{-1} feature after ion irradiation is different from that suggested as occurring after UV photolysis.

1. Strazzulla (1999) studied the effects of N implantation in H$_2$O:CH$_4$ = 1:1 ice mixtures. In these experiments the ice thickness is greater than the penetration depth of 15 keV N$^+$ ions, so that ions stop in the sample and can form chemical bonds with other species present. After implantation new bands appear among which is a feature at about 2170 cm^{-1}, which is very similar to the feature formed after ion irradiation of the H$_2$O:CH$_4$:N$_2$ (or NH$_3$) mixtures and which similarly shifts to lower wavenumbers after warm-up. Therefore, this feature can be attributed to the same carrier of the 2165 cm^{-1} band as discussed in this paper.

2. The second experiment develops in several steps: first a C$_2$H$_4$ (or CH$_4$):H$_2$O mixture was irradiated at 10 K in order to form the organic refractory residue; then the sample was warmed up to 200 K to let the volatile species (C$_2$H$_4$ [or CH$_4$] and others formed) sublimate; then the sample was cooled down to 10 K again and a film of N$_2$ was deposited on it; the N$_2$ sample is thin enough that incoming ions have a larger penetration depth; after ion irradiation of this sample (organic residue + N$_2$ ice) a feature at about 2165 cm^{-1} is formed as a result of ion-induced mixing. The profile of this feature is very similar to that observed after ion irradiation of the H$_2$O:CH$_4$:N$_2$ (or NH$_3$) mixtures. Again we attribute the two similar features to the same carrier. Furthermore, this experiment shows that the formation of the 2165 cm^{-1} band does not depend on the presence of CH$_4$ in the mixture but on the formation of the organic residue after ion irradiation.

4. RELEVANCE TO IDENTIFICATION OF INTERSTELLAR BAND

Firm detections of the interstellar 4.62 μm band have been made toward eight luminous, dust-embedded protostars (Lacy et al. 1984; Tegler et al. 1993, 1995; Weintraub et al. 1994; Pendleton et al. 1999). Although extensive searches have not been made, the band does not appear to be present in the general, quiescent cloud medium or in the diffuse interstellar medium (ISM). The peak position and width of the interstellar absorption bands do not vary by more than 2.5 and 5 cm^{-1}, respectively, among the sources, suggesting that either the conditions are very similar along the line of sight toward each of the different protostellar clouds or that the carrier of the band is rather insensitive to its environment. The different evolutionary stages of the different protostars make it rather unlikely that the former is the case.

Table 1 gives the optical depths for the sources that have been reported in the literature as having 4.62 μm absorption. The data include the 3.1 μm water ice band, the 4.62 μm band, and the polar and nonpolar components of CO (4.67 μm). These data have been collected from a number of resources (Willner et al. 1982; Whittet et al. 1988; Smith et al. 1989; Weintraub et al. 1994; Chiar et al. 1995, 1998; Tegler et al. 1995; Hough et al. 1989; Pendleton et al. 1999; Tielens et al. 1991; Sato et al. 1990).

A comparison of the optical depths of the absorption features seen in the spectra of protostars where the 4.62 μm band is present reveals a lack of correlation between the 4.62 μm band and any other band. There is also no correlation among the absorption bands in general (including water, CO, and silicate), which may simply be stating that the formation of these species is more critically dependent upon their environmental conditions.

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TABLE 1

OPTICAL DEPTHS

Source	$\tau_{3.1}$ (H$_2$O)	$\tau_{4.62}$	$\tau_{4.67(CO)}$ Nonpolar 2140 cm^{-1}	$\tau_{4.67(CO)}$ Polar 2136 cm^{-1}
AFGL 2136............	2.72[a]	0.06[b]	0[c]	0.22[c]
AFGL 961 E	2.46[d]	0.06[b]	0.22[e]	0.20[e]
Mon R2 IRS 2	2.54[d]	0.029[b]	0.37[e]	0.16[e]
Elias 18.................	0.80[f]	0.05[g]	0.26[e]	0.14[e]
W33A...................	>5.4[h]	1.5[b]	0.79[e]	0.68[e]
L 1551 IRS 5	2.1[i]	0.16[g]	0.80[g]	0.16[g]
NGC 7538 IRS 9......	3.28[h]	0.31[b]	2.5[e]	0.2[e]
Elias 16.................	1.6[g]	<0.05[g]	1.22[j]	0.11[e]
RNO 91	1.29[k]	0.19[k]	0.33[k]	...
PV Cep.................	0.44[g]	<0.04[g]	0.13[g]	...
Elias 1-12	0.66[g]	<0.04[g]	0.23[g]	0.1[g]

[a] From Hough et al. 1989.
[b] From Pendleton et al. 1999.
[c] From Tielens et al. 1991.
[d] From Smith et al. 1989.
[e] From Chiar et al. 1998.
[f] From Whittet et al. 1988.
[g] From Tegler et al. 1995.
[h] From Willner et al. 1982.
[i] From Sato et al. 1990.
[j] From Chiar et al. 1995.
[k] From Weintraub et al. 1994.

In Figure 5 we show a comparison of the 2165 cm^{-1} band observed toward the embedded source W33A and laboratory spectra of the H$_2$O:N$_2$:CH$_4$ ($\simeq$1:1:1) mixture irradiated with 40 eV/16 amu at 10 K and warmed up to 50, 110, 150, and 220 K. We can see that a very good spectral match is obtained at a temperature between 50 and 150 K. Similarly, a good comparison is given by the laboratory spectrum of the H$_2$O:NH$_3$:CH$_4$ ($\simeq$2.5:1:2) mixture irradiated with 120 eV/16 amu and warmed up to 170 K.

This result seems to indicate that icy mantles suffer from energetic processing during their lifetimes. Recently, similar conclusions have been drawn by Teixeira, Emerson, & Palumbo (1998) after a detailed analysis of new observations of the solid CO feature compared with a large number of laboratory data of deposited or processed (by energetic ion irradiation) ices. It has been shown that the nonpolar component of the CO ices seems to be well constrained with irradiated CO ices producing excellent fits to the observed features as previously suggested by Palumbo & Strazzulla (1993). As concerns the polar component, it is not possible to uniquely define its carrier; however, a promising solution is that it is due to CO produced after ion irradiation of polar ices (e.g., H$_2$O:CH$_3$OH mixtures; see also Palumbo & Strazzulla 1993; Chiar et al. 1995).

The ion flux in molecular clouds and in the environment of young stellar objects is not well known. Jenniskens et al. (1993) estimated the proton flux (J) in the diffuse medium to be $J(E \sim 1$ MeV$) \simeq 0.6$–3 cm^{-2} s^{-1}. If we assume that icy mantles survive for 10^5–10^8 years (3×10^{12}–3×10^{15} s), the dose they suffer ranges between 0.01 and 50 eV atom^{-1} (C, N, O, Si).

Finally, we want to emphasize the following points. First, ion irradiation opens the possibility that N$_2$ is the nitrogen-bearing molecular progenitor of the interstellar 4.62 μm band, while FUV laboratory experiments have exclusively considered NH$_3$ as the molecular precursor of nitrogen.

Second, we have presented laboratory results that consider CH$_4$ to be the carbon-bearing species in the ice

mixture, while astronomical observations indicate that methane is not among the most abundant species in icy grain mantles (Boogert et al. 1996). However, laboratory experiments described in § 3.2 show that the formation of the 2165 cm^{-1} band does not depend on the presence of CH$_4$ in the ice sample but on the refractory organic residue produced by ion irradiation. Thus, methane could be substituted and/or added to any other hydrocarbon (e.g., methanol) and/or a carbon-rich refractory material. It could be argued that the 3.4 μm feature due to the organic residue has not been detected in dense molecular clouds (Allamandola et al. 1993) while it has been observed in the diffuse interstellar medium (Sandford et al. 1991; Pendleton et al. 1994) and in circumstellar shells of carbon-rich stars (Chiar et al. 1998). The fate of the 3.4 μm feature in dense molecular clouds is a puzzling problem, which we will not address here. On the basis of the observational results the hypothesis that the organic mantles, implied by the 3.4 μm feature observed in the diffuse interstellar medium, are formed in dense molecular clouds after processing of simple ices has been seriously questioned (Chiar et al. 1998). However, we want to stress that the intensity of the 3.4 μm feature in laboratory spectra depends on the starting mixture and on the total dose of irradiation. As the dose increases, the intensity of the 3.4 μm band decreases due to a progressive carbonization (i.e., loss of hydrogen; e.g., Strazzulla 1997) of the refractory material. Furthermore, the 2165 cm^{-1} band is much more intense than the 3.4 μm feature in the laboratory spectra (see also Moore et al. 1983), and it is present in our laboratory spectra even if the 3.4 μm feature is undetectable. In addition, an important observational test is to search for the other features present in the laboratory spectra of ion-irradiated mixtures. In fact, the laboratory spectra we have presented show some other features that we have not here discussed. The most intense (at higher temperature) are in the O—H stretch and 1600–1400 cm^{-1} spectral regions. In contrast with what happens for the 4.62 μm band, the profiles and intensities of these
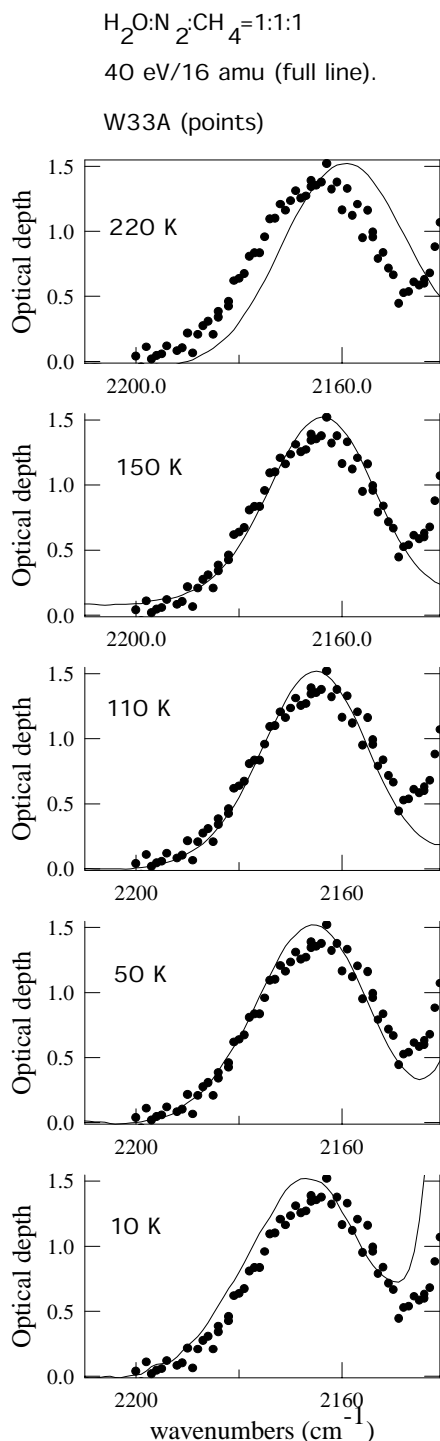
$H_2O:N_2:CH_4 = 1:1:1$

40 eV/16 amu (full line).

W33A (points)

FIG. 5.—IR spectra of a mixture $H_2O:N_2:CH_4$ ($\simeq 1:1:1$) in the spectral region 2300–2000 cm^{-1} (*lines*) are compared with that observed toward W33A (*circles*). *From bottom to top:* Spectra obtained at 10 K after irradiation with 3 keV He$^+$ at 40 eV/16 amu and after warm-up to 50, 110, 150, and 220 K.

features strongly depend on the initial mixture. Thus, a much more detailed study is necessary before these bands can be used for any astronomical speculation.

Third, according to current models CO is much more abundant than CH_4 in interstellar ices. If ion bombardment plays an important role in the evolution of interstellar ices, the absorption bands that appear in laboratory spectra

after ion irradiation of $H_2O:CO:N_2$ (NH_3) and $CO:N_2$ mixtures should also be present in astronomical spectra. However, laboratory experiments have shown that the feature that appears at about 2180 cm^{-1} after ion irradiation is weak because either it has a low intrinsic intensity or its formation efficiency is low. Therefore, we expect that a weak feature, not detectable or not yet detected, is present at this position.

5. SUMMARY

We have presented laboratory experiments on the formation of $-C\equiv N$ groups bonded to O-bearing end groups of the refractory organic residue produced through ion irradiation of $H_2O:NH_3:CH_4$ and $H_2O:N_2:CH_4$ ice mixtures. These give rise to an absorption feature centered at about 2165 cm^{-1} in the infrared spectra.

An interstellar absorption band at 4.62 μm (2165 cm^{-1}) has been detected toward several protostellar objects and has often been attributed to a nitrogen-bearing species. As recently reviewed by Pendleton et al. (1999) the carrier of the interstellar 4.62 μm band almost certainly involves C, N, and O, and of the possible reservoirs for the solid nitrogen-bearing species, N_2 is a strong candidate. Energetic processing of interstellar ices and/or grain surface reactions are among the most likely production pathways leading to the interstellar 4.62 μm band. Of the forms of energetic processing, ion bombardment offers the distinct advantage over UV photolysis by enabling N_2 to participate in the chemistry of interstellar grain mantles (if N_2 is the dominant N-bearing molecule in interstellar ices).

Our experiments on the ion bombardment of ices suggest that the interstellar 4.62 μm feature is due to $-C\equiv N$ groups bonded to O-bearing end groups of the disordered tridimensional structure of a refractory matrix on grains. This differs from the suggestion that this feature is due to OCN^- based on experiments in which the band is produced by ultraviolet radiation.

The ultimate identification of the 4.62 μm band will help solve the case of the missing nitrogen in dense molecular clouds. Interstellar ices are likely to contain substantial amounts of solid N_2, as nitrogen is depleted from the gas phase in molecular clouds; the molecular form is quite stable and no other reservoir of solid nitrogen has emerged. Upper limits (5%–10%) have been placed on the amount of ammonia that is present along lines of sight to some objects, so it seems doubtful that much of the nitrogen is hiding in the form of ammonia. The discovery that solid N_2 comprises the majority of the ice present on bodies (e.g., Pluto, Triton) in the outer solar system (Cruikshank et al. 1993; Quirico et al. 1999) suggests that N_2 may be hiding in the interstellar ices as well.

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