

HYDROGEN ISOTOPIC SUBSTITUTION STUDIES OF THE 2165 WAVENUMBER (4.62 MICRON) “XCN” FEATURE PRODUCED BY ION BOMBARDMENT

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ABSTRACT

The interstellar 4.62 μm absorption band, commonly seen toward embedded protostellar objects, has not yet been unambiguously identified; here we report new results which further elucidate the components of the band carrier, which is often referred to in the literature as the “XCN” band due to previous implications of carbon and nitrogen. If the atmosphere of the early Earth was not overly reducing, as some studies indicate, production of prebiotic molecules containing the cyanogen bond would have been difficult. In that case, CN-bearing molecules, necessary for the origin of life, may have come primarily from extraterrestrial sources, and the interstellar medium may be an important source of those molecules. Laboratory studies show that energetic processing of ice mixtures containing H, C, N, and O atoms readily reproduce a band similar in peak position and profile to that seen in the interstellar spectra. Earlier isotopic labeling experiments clearly identified carbon, nitrogen, and oxygen as active participants of the XCN species. In this paper, results of ion bombardment of $\text{CH}_3\text{OH}:\text{N}_2$ and $\text{CD}_3\text{OD}:\text{N}_2$ ices are presented. A shift in band position resulting from deuterium substitution demonstrates that hydrogen is also a component of the carrier in the laboratory-produced 4.62 μm band. Irradiation of ices through ion bombardment allows the testing of mixtures which include N_2 , a possible source of the available nitrogen in dense cloud ices that cannot be probed through UV photolysis experiments.

Subject headings: dust, extinction — ISM: lines and bands — ISM: molecules — line: identification — methods: laboratory — molecular processes

1. INTRODUCTION

The identification of absorption bands detected in the spectra of interstellar dust is important because it enables an accurate assessment of the content of the dust and of the distribution of the biogenic elements in space. Interstellar dust, incorporated into primitive solar system bodies and subsequently delivered to the early Earth, may have contributed to the origin of life on our planet. Of particular interest in this regard are those components of interstellar dust that involve the biogenic elements. The interstellar 4.62 μm (2165 cm^{-1}) absorption band, seen toward luminous protostars embedded in dense molecular clouds and commonly referred to as the “XCN” band, is one example. The delivery of CN-bearing molecules to the early Earth may have been necessary for the origin of life as the production of prebiotic molecules containing the cyanogen bond is difficult in an environment that is not overly reducing (Whittet, Gibb, & Nummelin 2000a), as several studies have suggested (Schopf 1992; Kasting 1993; Delano 1993, 2000). Therefore, the identification of the interstellar 4.62 μm band may include the identification of an extraterrestrial source of carbon and nitrogen.

First observed toward the massive protostar W33A (Soifer et al. 1979), the 4.62 μm band peak was later identified with a $\text{C}\equiv\text{N}$ functional group (Lacy et al. 1984). This band has now been detected toward a number of other deeply embedded protostars (Weintraub et al. 1994; Tegler et al. 1995; Pendleton et al. 1999) in dense molecular clouds, but it does not appear in the spectra of diffuse interstellar

medium (ISM) dust (Whittet et al. 2000b). Laboratory studies have investigated the production mechanism and starting mixtures necessary to reproduce the interstellar band (see Pendleton et al. 1999 for a review), but there are problems with the candidates suggested thus far. In order to move toward an identification of this elusive interstellar band, we report here isotopic labeling experiments which are additional steps along this path.

Energetic processing (both UV photolysis and ion irradiation) of several ice mixtures containing hydrogen, carbon, nitrogen, and oxygen produces an organic residue in which the carrier of the 4.62 μm band lies. In many cases, an absorption band results which is remarkably similar to that seen in the interstellar medium in both profile and peak position (Moore et al. 1983; Lacy et al. 1984; Grim & Greenberg 1987; Tegler et al. 1993; Schutte & Greenberg 1997; Demyk et al. 1998; Palumbo et al. 2000; Hudson & Moore 2000). Here we report irradiation experiments using ion bombardment of $\text{CH}_3\text{OH}:\text{N}_2$ and $\text{CD}_3\text{OD}:\text{N}_2$ ices. Ion bombardment delivers sufficient energy to break apart the strong N_2 bond, which allowed the use of N_2 as the source of nitrogen in the starting ice mixture. Theoretical models of interstellar ices suggest N_2 as a component of the icy grain mantles (Tielens & Hagen 1982; Brown & Charnley 1990; Hasegawa, Herbst, & Leung 1992), as do laboratory studies (d’Hendecourt, Allamandola, & Greenberg 1985). We also note that solid N_2 is prevalent on the two largest icy bodies of the outer solar system: Pluto and Triton (Cruikshank et al. 1998).

Based on isotopic substitutions involving carbon, nitrogen, and oxygen, laboratory experiments leading to the production of an interstellar-like XCN band have previously identified the isocyanate anion, OCN^- , as the carrier of the laboratory band (Schutte & Greenberg 1997; Demyk et al. 1998). While the shifts measured in these experiments

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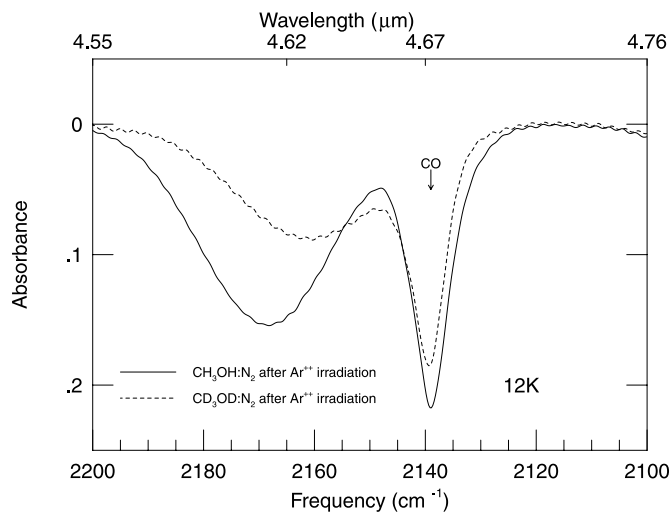


FIG. 1.—IR spectra in the 2200–2100 cm⁻¹ region of the mixtures CH₃OH:N₂ (solid line) and CD₃OD:N₂ (dashed line) after ion irradiation at 12 K with 60 keV Ar⁺⁺ at 57 eV/16 amu and 50 eV/16 amu, respectively.

undoubtedly implicate C, N, and O as components of the carrier of the 4.62 μm band, results reported here and in the companion paper by Bernstein, Sandford, & Allamandola (2000) indicate that hydrogen is also contained in the carrier molecule.

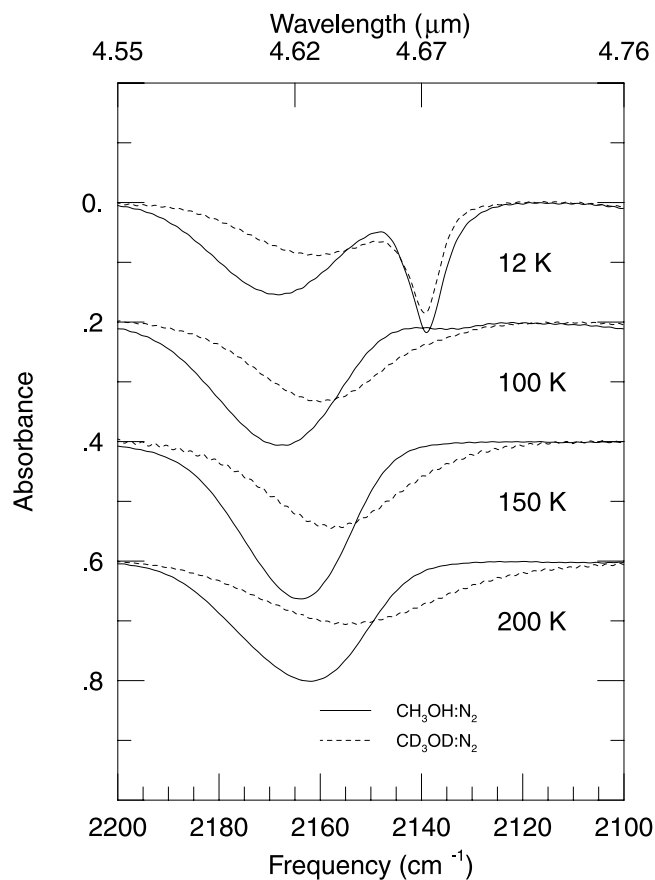


FIG. 2.—IR spectra in the 2200–2100 cm⁻¹ region of the irradiated mixtures CH₃OH:N₂ (solid line) and CD₃OD:N₂ (dashed line) at 12 K and after warm up to 100, 150, and 200 K. Spectra have been offset for clarity.

2. MATERIALS AND METHODS

A detailed description of the experimental apparatus used to obtain in situ IR spectra of irradiated and unirradiated frozen gases can be found elsewhere (Baratta & Palumbo 1998; Palumbo et al. 2000). In a stainless steel vacuum chamber, frosts were accreted onto a cooled (10–300 K) substrate. In the studies described here, a silicon crystal was used. The vacuum chamber was placed in the sample compartment of the IR spectrometer (Bruker Equinox 55) and spectra were taken in the 2.27–20 μm (4400–500 cm⁻¹) range with a resolution of 1 cm⁻¹. During condensation, samples were bombarded by 60 keV Ar⁺⁺ ions. The ion beam produced a spot in the target which was greater than the IR beam and low currents were used in order to avoid macroscopic heating of the target. The energy released to the sample by impinging ions (the dose) is given in eV per small molecule (16 amu). In our apparatus, the substrate plane forms an angle of 45° with the IR beam and the ion beam. Thus, before, during, and after irradiation, spectra can be taken without tilting the sample. After irradiation (at 12 K), the samples were warmed up and spectra were taken at different temperatures.

3. ISOTOPIC SHIFT DATA

We have previously studied the profile of the feature at 4.62 μm (2165 cm⁻¹) formed after ion irradiation of a variety of icy mixtures containing H, C, N, and O (e.g., Palumbo et al. 2000). Here we present the results relative to the mixtures CH₃OH:N₂ and CD₃OD:N₂. Figure 1 shows the IR spectrum of the mixture CH₃OH:N₂ = 1:1 after ion irradiation with 60 keV Ar⁺⁺ (dose: 57 eV/16 amu) in the 4.54–4.76 μm (2200–2100 cm⁻¹) spectral range. This spectrum is compared with that of the CD₃OD:N₂ = 1:1 mixture after ion irradiation at a dose of 50 eV/16 amu. In both spectra, an absorption feature is present at about 4.68 μm (2138 cm⁻¹) which is attributed to solid carbon monoxide (CO) formed after ion irradiation (Sandford et al. 1988; Palumbo & Strazzulla 1992). The interstellar CO feature has been well studied and compares well with laboratory-produced bands (see Chiar et al. 1998; Teixeira, Emerson, & Palumbo 1998).

Irradiation of the CH₃OH:N₂ mixture also produces a feature at 2168 cm⁻¹ whose profile (shape, width, and peak position) is nearly identical to that presented by Palumbo et al. (2000) after ion irradiation of other ice mixtures which span a variety of C, H, O, and N sources. When deuterium is substituted for hydrogen, the feature shifts to 2160 cm⁻¹, thereby implicating hydrogen in the carrier of the band.

Figure 2 shows a comparison of the 4.62 μm (2165 cm⁻¹) feature in the CH₃OH:N₂ and CD₃OD:N₂ mixtures at 12 K and after warm-up to 100, 150, and 200 K. As the temperature increased, the peak position shifted to lower wavenumbers in both mixtures. The result is an isotopic shift of 0.017 μm (8 cm⁻¹) at all temperatures.

4. SIGNIFICANCE OF RESULTS

Based on isotopic substitutions involving carbon, nitrogen, and oxygen, laboratory experiments leading to the production of an interstellar-like XCN band have implicated C, N, and O as components of the carrier of the 4.62 μm (2165

cm^{-1}) band (Schutte & Greenberg 1997; Demyk et al. 1998; Palumbo et al. 2000; Bernstein et al. 2000). The results reported here and in the companion paper by Bernstein et al. (2000) indicate that hydrogen is also contained in the carrier molecule. Replacing hydrogen with deuterium produces a peak shift in frequency because the change in mass results in a spectral shift in the vibrational modes of the carrier. The detection of a shift indicates the atom replaced is an active participant in the species responsible for the feature, so in this case hydrogen is implicated as a component of the carrier of the $4.62 \mu\text{m}$ band. However, the magnitude of the shift indicates the proximity of the atom to the molecular motion of the band, so the observation of a small, 8 cm^{-1} shift, such as that seen with the deuterium substitution, indicates that while hydrogen may be located fairly close to the nitrile or isonitrile producing the $4.62 \mu\text{m}$ band, the hydrogen atom's motion itself is not the source of the $4.62 \mu\text{m}$ band.

The use of ion bombardment as the energetic process responsible for the restructuring of the molecular components in the initial ice mixture has a twofold significance. First, the duplication of the observed shift by two different laboratory groups using two different processes and different ice mixtures instills confidence that the shift, although small, is real. Second, the use of ion bombardment as the energy production technique allows the nitrogen source to derive from solid N_2 instead of ammonia. N_2 is a likely component of interstellar ices and ion bombardment allows the strong N_2 bond to be broken, thereby freeing the nitrogen to participate in the development of other chemical entities.

Identifying the components in the band carrier is the first step in the identification process. Investigating the structure of the atoms within the component has proven to be a more difficult task. Although the magnitude of the shift in isotopic-labeling experiments reveals something about the distances of the atoms from the central action, there are complications that can be envisaged. First attempts at identifying the structure of the $4.62 \mu\text{m}$ band were made by Lacy et al. 1984, who suggested that the carrier contains nitrile ($-\text{C}\equiv\text{N}$) groups. Upon further study, Bernstein, Sandford, & Allamandola (1997) presented arguments that isonitriles ($-\text{N}\equiv\text{C}$) are slightly favored over nitriles. Palumbo et al. (2000), based on the results of ion irradiation of icy mixtures such as $\text{H}_2\text{O}:\text{CH}_4:\text{N}_2$ or NH_3 , suggested that the $4.62 \mu\text{m}$ (2165 cm^{-1}) feature is due to $\text{C}\equiv\text{N}$ groups bonded to oxygen containing end groups (named $\text{R}-\text{O}$) of the disordered tridimensional structure (an organic refractory residue) that is formed upon irradiation of hydrocarbon-containing ices. In that case, hydrogen, which is part of the refractory residue formed after ion irradiation, was presumed present in the carrier.

5. CONCLUSIONS

The interstellar $4.62 \mu\text{m}$ (2165 cm^{-1}) band, seen in absorption along lines of sight which pass through icy grains in front of embedded protostars, may be an important contributor to the CN inventory of material available for incorporation into newly forming planetary systems. The identification of the interstellar band is important, therefore, not only for the astrophysical understanding of organic material in the dense cloud environment, but also for the potential relevance to the origin of life, as extraterrestrial sources of carbon and nitrogen may have been required. Here we have reported new information that will help in the determination of the carrier of the interstellar $4.62 \mu\text{m}$ band through comparison to similar bands produced in the laboratory.

The results presented here reveal that hydrogen, along with oxygen, nitrogen, and carbon, is a component in the carrier of the $4.62 \mu\text{m}$ (2165 cm^{-1}) laboratory band because a substitution of deuterium for hydrogen in the starting mixtures produces an 8 cm^{-1} shift in the peak position of the band.

In the experiment reported here, ion bombardment of N_2 -containing ices resulted in a deuterium shift. An identical result has been obtained by an independent laboratory experiment using UV photolysis of NH_3 -containing ices (Bernstein et al. 2000). The isotopic shift is seen in both cases, demonstrating that, although small, the shift is real. The magnitude of the shift indicates that while hydrogen is located fairly close to the nitrile or isonitrile producing the $4.62 \mu\text{m}$ band, the hydrogen atom's motion itself is not the source of the $4.62 \mu\text{m}$ band. However, confirmation of the presence of hydrogen means that it must be included in any identification of the molecular species responsible for the $4.62 \mu\text{m}$ band.

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