

THE INFRARED SPECTRA OF NITRILES AND RELATED COMPOUNDS FROZEN IN Ar AND H₂O

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ABSTRACT

We present the 2320–2050 cm⁻¹ (4.31–4.88 μm) infrared spectra of 16 solid-state nitriles, isonitriles, and related compounds in order to facilitate the assignment of absorption features in a spectral region now becoming accessible to astronomers for the first time through the Infrared Space Observatory (ISO). This frequency range spans the positions of the strong C≡N stretching vibration of these compounds and is inaccessible from the ground due to absorption by CO₂ in the terrestrial atmosphere. Band positions, profiles, and intrinsic strengths (*A* values) were measured for compounds frozen in Ar and H₂O matrices at 12 K. The molecular species examined included acetonitrile, benzonitrile (phenylcyanide), 9-anthracenecarbonitrile, dimethylcyanamide, isopropyl nitrile (isobutyronitrile), methylacrylonitrile, crotononitrile, acrylonitrile (vinyl cyanide), 3-aminocrotononitrile, pyruvonitrile, dicyandiamide, cyanamide, *n*-butylisocyanide, methylisocyanoacetate, diisopropylcarbodiimide, and hydrogen cyanide. The C≡N stretching bands of the majority of nitriles fall in the 2300–2200 cm⁻¹ (4.35–4.55 μm) range and have similar positions in both Ar and H₂O matrices, although the bands are generally considerably broader in the H₂O matrices. In contrast, the isonitriles and a few exceptional nitriles and related species produce bands at lower frequencies spanning the 2200–2080 cm⁻¹ (4.55–4.81 μm) range. These features also have similar positions in both Ar and H₂O matrices, and the bands are broader in the H₂O matrices. Three of the compounds (pyruvonitrile, dicyandiamide, and cyanamide) show unusually large shifts of their C≡N stretching frequencies when changing from Ar to H₂O matrices. We attribute these shifts to the formation of H₂O:nitrile complexes with these compounds. The implications of these results for the identification of the 2165 cm⁻¹ (4.62 μm) “XCN” interstellar feature and the 4550 cm⁻¹ (2.2 μm) feature of various objects in the solar system are discussed.

Subject headings: infrared: general — methods: laboratory — molecular data

1. INTRODUCTION

Astronomers are unable to make ground-based measurements in certain portions of the infrared spectrum because of strong absorption produced by telluric CO₂. This is particularly true in the 2400–2200 cm⁻¹ (4.17–4.55 μm) spectral region in which the asymmetric O=C=O stretching fundamental produces a strong feature. Since the large intrinsic strength of this absorption and the large scale height of CO₂ preclude a solution to this problem using airborne platforms like the Kuiper Airborne Observatory, astronomical observations in this spectral region require observations be made with space-borne telescopes.

With the recent successful launch of the European Infrared Space Observatory (ISO) (see Encrenaz & Kessler 1992), the 2400–2200 cm⁻¹ portion of the infrared spectrum has become accessible for the first time. There are a wide variety of compounds that produce infrared absorption features in this range and, despite the rather limited extent of this spectral region, it is anticipated that ISO will detect a number of new features here (Allamandola 1993). Examples of molecular fundamentals that produce bands at these frequencies include the stretching vibrations of oxides of nitrogen and carbon, the CD stretch, and various CN stretches.

Here we focus on the absorption bands produced by the CN stretching vibrations of nitriles, isonitriles, and related compounds. Nitriles are compounds that contain one or more —C≡N functional groups that typically produce a strong absorption feature or features in the 2400–2200 cm⁻¹ range due to stretching vibrations of the C≡N group. There are a number of reasons to expect that ISO will detect bands due to nitriles in the interstellar medium (ISM), espe-

cially in the spectra of ices in dense molecular clouds. First, a number of nitriles and related compounds like HCN, HNC, NH₂CN, CH₂CN, CH₃CN, CH₂CHCN, and CH₃CH₂CN have been detected in the gas phase in dense clouds using radio spectral techniques (see Mann & Williams 1980; Irvine, Goldsmith, & Hjalmarsen 1987; van Dishoeck et al. 1993 for reviews). At the low temperatures typical of dense interstellar clouds (*T* < 40 K), these molecules will be frozen out efficiently onto dust grains in the clouds (see Sandford & Allamandola 1993). Infrared spectroscopic studies have shown already that mixed molecular ices in these clouds contain H₂O, CO, CH₃OH, H₂, and a host of other molecular species that were either condensed out of the gas phase or formed *in situ* (see Sandford 1996 for a recent review). The nitriles seen in the gas phase in these clouds should be present in the ices as well.

Indeed, there is some direct observational evidence that interstellar solids do contain nitriles or related species. Spectra obtained from a limited number of lines of sight through dense clouds contain a broad, often weak, feature centered at about 2165 cm⁻¹ (4.62 μm) near the CO ice feature (Lacy et al. 1984; Tegler et al. 1993). The specific molecule or molecules responsible for this absorption have yet to be identified conclusively. While a variety of assignments for this band have been proposed, including the Si-H stretching vibration (Nuth & Moore 1988; Moore, Tanabé, & Nuth 1991) and the CN stretch in the OCN⁻ ion (Grim & Greenberg 1987), most work has focused on the possibility of nitrile or isonitrile carriers. Early laboratory experiments by Moore et al. (1983) and Lacy et al. (1984) demonstrated that a feature similar to the observed inter-

stellar band was produced when laboratory ice mixtures were exposed to ionizing radiation. Lacy et al. noted further that the feature was produced only by ices containing C and N. This, in conjunction with the feature's position, lead them to suggest that the absorption is due to the stretching vibration of a C≡N functional group in a larger molecule, i.e., a nitrile or isonitrile [usually designated as X(CN), X(C≡N), or XCN], and that some sort of energetic processing is required to produce it.

Subsequent laboratory irradiation experiments have confirmed the importance of C and N for the formation of the 2165 cm⁻¹ band and have demonstrated that excellent spectral fits to the astronomical data can be obtained using more astrophysically relevant ice mixtures (Tegler et al. 1993; Bernstein et al. 1995). In addition, some of these laboratory experiments showed that energetic processing produces simultaneously a host of other related CN-bearing species (Bernstein et al. 1995). Thus, there are many reasons to expect that the infrared spectra of dense molecular clouds will contain a feature or features due to nitriles or related compounds in the 2300–2200 cm⁻¹ spectral region.

Finally, there are indications that nitriles may also be present in a variety of solar system objects. Low-resolution infrared spectra of the comets Panther (1981 II) and Bowell (1982 I) contained absorption features centered near 4420 cm⁻¹ (2.26 μm) (Jewitt et al. 1982). Cruikshank et al. (1991) noted that absorption features in this region could be due to overtones of the fundamental C≡N stretch in nitriles or isonitriles. Recently, Cruikshank et al. (1996) have discovered a well-defined feature near 4400 cm⁻¹ (2.27 μm) in the spectrum of the icy planetesimal 5145 Pholus. The possibility that nitriles and related compounds could be present in the solar system has motivated some recent laboratory work to characterize the spectral properties of these materials (Khare et al. 1995; Russo & Khanna 1996).

Interpretation of any features found in this spectral region will require comparison to appropriate laboratory data. Although there is a large chemical literature on the infrared spectral properties of nitriles, nitrile complexes, and related compounds (see Freedman & Nixon 1972; Hunt & Andrews 1987; Bohn & Andrews 1989; Jacobs, Willner, & Pawelke 1992; Kubelková, Kotrla, & Florián 1995; and references therein), these studies cover only a small range of nitrile compounds, and there is a dearth of spectral information on nitriles frozen into astrophysically relevant, H₂O-rich ices at low temperature. In this paper we present the infrared spectra of 16 nitriles and related compounds (see Fig. 1) frozen in both argon and H₂O matrices to facilitate the search for and assignment of any features observed by ISO in the 2400–2200 cm⁻¹ (4.17–4.55 μm) region of the spectrum. The methods and materials used in this study are described in the following section (§ 2). In § 3, spectra, frequencies, and intrinsic strengths of the C≡N stretching bands of the compounds studied are presented. Finally, the implications of the results for infrared astronomy and astrochemistry are discussed in § 4.

2. EXPERIMENTAL TECHNIQUES

The techniques and equipment employed for this study were typical of those used in matrix isolation studies. Since both have been described in detail elsewhere (Allamandola, Sandford, & Valero 1988; Hudgins, Sandford, & Allamandola 1994; Hudgins & Allamandola 1995), we will provide only a brief overview of the general techniques and

equipment used. This overview is then followed by more detailed discussion of points unique to the samples studied in this work.

In general, samples were prepared by freezing gas samples onto a CsI window cooled to 12 K by a closed cycle helium refrigerator (Air Products Displex CSW 202). The window is suspended in a high-vacuum chamber (~10⁻⁸ mbar), which is part of a continuously pumped stainless steel manifold, to minimize the accumulation of contaminant gases. Infrared spectra over the mid-infrared range (5000–500 cm⁻¹; 2–20 μm) were measured from the samples at a resolution of 0.9 cm⁻¹ (the observed FWHM of an unresolved feature) using a Nicolet 7000 FTIR spectrometer. Because of oversampling (two points per resolution element), the positions for sharp bands can be determined with an accuracy to ±0.2 cm⁻¹. We report positions to tenths of a wavenumber for features produced by the compounds in Ar matrices, since these absorptions were in general quite narrow. However, this precision was not attainable when H₂O matrices were used. Most of the bands produced using H₂O matrices were sufficiently broad (see § 3.1 and Table 1) that the uncertainty in the band center was much greater than our precision. Thus, positions are only reported to the nearest wavenumber for features produced by the compounds in H₂O matrices.

More detailed discussions of the sample preparation techniques used for the specific materials studied in this work can be found in the next two sections.

2.1. Materials

The argon (Matheson 99.999% pure) used for the Ar matrix isolation studies was prepared by passing it through a liquid nitrogen-cooled trap to remove condensable contaminants and was then used without further purification. The H₂O (distilled) used for the H₂O matrix studies was purified further by three freeze pump thaw cycles under vacuum ($P < 10^{-5}$ mbar) before use in order to remove dissolved gases. With the exception of HCN, all the other compounds discussed in this paper were purchased from the Aldrich Chemical Company. The compounds and their purities are acetonitrile (1; 99.8%), benzonitrile (2; 99+%), 9-anthracenecarbonitrile (3; 97%), dimethylcyanamide (4; 99%), isopropyl nitrile (5; 99%), methylacrylonitrile (6; 99%), crotononitrile (7; 99%), acrylonitrile (8; 99+%), 3-aminocrotonitrile (9; 96%), pyruvonnitrile (10; 95%), dicyandiamide (11; 99%), cyanamide (12; 99%), *n*-butylisocyanide (13; 97%), methylisocyanoacetate (14; 95%), and diisopropylcarbodiimide (15; 99%). The hydrogen cyanide (16; 99+%) was graciously provided to us by the Brauman group in the Chemistry Department of Stanford University. A summary of the structures of these compounds is given in Figure 1. Each of the samples was subjected to three freeze pump thaw cycles under vacuum ($P < 10^{-5}$ mbar) and then used without further purification.

2.2. Sample Preparation

All the compounds except 3, 9, and 11–14 had sufficient volatility at room temperature that samples could be prepared by mixing, in the gas phase, appropriate amounts of Ar or H₂O with the sample compound of interest. The relative gas abundances were controlled using a glass gas handling system (see Allamandola et al. 1988), and the gases were mixed in volume-calibrated greaseless, glass bulbs. Bulbs prepared for argon matrix studies were mixed at room tem-

TABLE 1
POSITIONS, FWHMS, AND STRENGTHS OF THE C≡N STRETCHING FEATURE IN Ar AND H₂O MATRICES^a

Number	Compound Name	Position (FWHM ^b) in Ar (cm ⁻¹)	Position (FWHM ^b) in H ₂ O (cm ⁻¹)	Integrated Absorbance in H ₂ O (cm molecule ⁻¹)
1	Acetonitrile [CH ₃ CN]	2293.0, 2258.3 (1.3, 1.5)	2296, 2264 (15, 15)	1.1 × 10 ⁻¹⁷
2	Benzonitrile [C ₆ H ₅ CN]	2241.4, 2237.3 (2.1, 2.2)	2238 (21)	3.1 × 10 ⁻¹⁸
3	9-Anthracene carbonitrile [C ₁₄ H ₉ CN]	2226.0, 2224.5 (4.3 together)	2222 (16)	~5 × 10 ⁻¹⁸
4	Dimethylcyanamide [(CH ₃) ₂ NCN]	2228.4 (1.5)	2224 (24)	1.7 × 10 ⁻¹⁷
5	Isopropyl nitrile [(CH ₃) ₂ CHCN]	2287.8, 2254.0 (2.4, 3.3)	2255 (16)	8.4 × 10 ⁻¹⁸
6	Methylacrylonitrile [CH ₂ C(CH ₃)CN]	2234.7, 2211.6 (1.7, 1.8)	2239 (15)	1.0 × 10 ⁻¹⁷
7	Crotonitrile [CH ₃ CH ₂ CN]	2232.8, 2229.9 (2.1, 1.1, 2.1)	2232 (17)	1.5 × 10 ⁻¹⁷
8	Acrylonitrile [CH ₂ CHCN]	2229.9 (10.0)	2240 (16)	7.7 × 10 ⁻¹⁸
9	3-Aminocrotonitrile [(CH ₃ (NH ₂)CCHCN]	2215.4, 2207.4 (1.8, 2.5)	2192 (28)	?
10	Pyruvonnitrile [CH ₃ C(=O)CN]	2225.5 (1.5)	2092 (18)	5.1 × 10 ⁻¹⁸
11	Dicyandiamide [NHC(NH ₂)NHCN]	2207.7, 2203.3 (5.9 together)	2204, 2159.5 (21, 21)	?
12	Cyanamide [H ₂ N-CN]	2264.3 (1.5)	2267, 2224 (~40, ~25)	?
13	<i>n</i> -Butylisocyanide [CH ₃ (CH ₂) ₃ NC]	2152.2, 2150.3, 2147.6 (6.1 together)	2154 (13)	~3 × 10 ⁻¹⁷
14	Methylisocyanacetate [CH ₃ OC(=O)CH ₂ NC]	2162.3, 2157.7 (2.9, 1.0)	2172 (19)	1-4 × 10 ⁻¹⁷
15	Disopropylcarbodiimide [(CH ₃) ₂ CHNCNCH(CH ₃) ₂]	2144.3, 2137.5, 2128.5, 2123.7, 2118.6, 2112.7 (14.3 together)	2112 (31)	1.7 × 10 ⁻¹⁶
16	Hydrogen cyanide [HCN]	2093.4 (<1) ^c	2092 (18)	5.1 × 10 ⁻¹⁸

^a The values for Ar and H₂O matrices correspond to typical sample concentrations of Ar: compound ≈ 750:1 and H₂O: compound ≈ 10:1 (see text).

^b The FWHMs were measured from transmittance spectra.

^c Values taken from Bohn & Andrews 1989

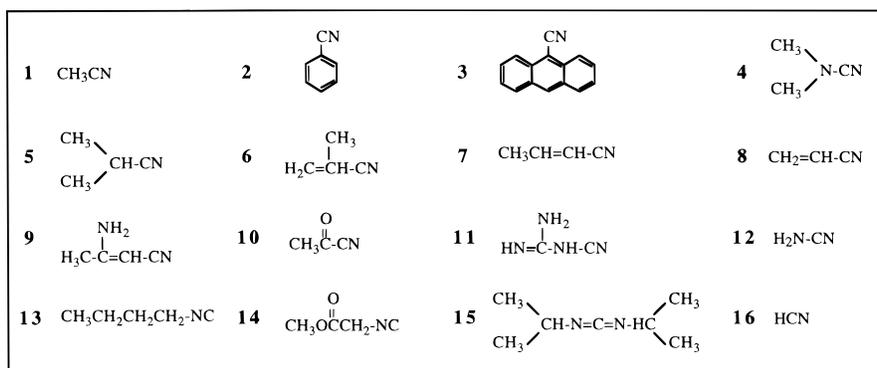


FIG. 1.—Structures of the nitriles, isonitriles, and related compounds studied in this work

perature with Ar-to-sample ratios of 750:1 and had total pressures of ~ 750 mbar. Bulbs prepared for H₂O matrix studies were mixed at room temperature with H₂O-to-sample ratios of 10:1 and had total pressures of ~ 22 mbar. The higher sample concentrations in H₂O matrices were necessary in order to be able to discern the sample features which were obscured by the strong H₂O features (see § 3.1). The background pressure in the glass line used for mixing the samples was typically $\sim 10^{-6}$ mbar. Thus, the contaminant levels for the Ar and H₂O matrix bulbs must be less than factors of 10^{-8} and 10^{-6} , respectively. Each glass sample bulb was transferred to the stainless steel vacuum manifold. The sample mixture was then deposited onto the 12 K CsI window, and its spectrum was measured.

Because of their low volatilities at room temperature, compounds 3, 9, and 11–14 could not be premixed in the gas phase in glass bulbs. Instead, samples of these compounds frozen in Ar and H₂O matrices were prepared using the same technique described by Hudgins & Allamandola (1995). Deposition of these materials onto the cooled CsI window was achieved in the following manner: A sample of compound 3, 9, or 11–14 was placed into a clean, dry, 12 cm long straight 0.5 O.D. Pyrex tube, with a greaseless glass (Ace glass 8194-69, 0–10 mm) stopcock near the open end, which was inserted into the vacuum chamber facing the cold window. After the tube had been opened and pumped down to vacuum, it could be heated (if necessary) in a controlled manner by running current through a surrounding resistive wire until the enclosed sample began to sublime. The compound was then deposited in a matrix by condensing it onto the CsI window while Ar or H₂O was deposited simultaneously at a controlled rate from a glass bulb through a separate copper inlet tube. Compounds 9 and 12–14 had sufficient vapor pressures at room temperature that heating was unnecessary. The tubes containing compounds 3 and 11 were warmed gently to about 60°C in order to provide a sample deposition rate adequate to produce a CN stretching feature having an absorption depth of $\sim 10\%$ after 30 minutes of deposition.

For argon matrices, the Ar was codeposited at a rate of ~ 10 mmol hr⁻¹, which provided good isolation of the sample compound. The exact Ar to sample ratio is not known when this deposition technique is used. However, based on the rate of Ar flow and assuming that the C≡N stretching bands of the samples have a "typical" nitrile integrated absorbance value of 1×10^{-17} cm molecule⁻¹ (Wexler 1967; see also § 3.2.3), we estimate that the Ar to

compound ratios in these samples fell between 100 and 1000.

For H₂O matrices, typical flow rates were on the order of 0.04 mmol of H₂O hr⁻¹. Based on the relative strengths of the 3250 cm⁻¹ (3.08 μm) O—H stretching band of H₂O and the C≡N stretching band, and assuming $A_{\text{CN}} = 1 \times 10^{-17}$ cm molecule⁻¹ for the C≡N stretching band and $A_{\text{OH}} = 1.7 \times 10^{-16}$ cm molecule⁻¹ for the H₂O O—H stretching band (Hudgins et al. 1993), we estimate that the H₂O-to-compound ratio was ~ 10 –100 for the experiments involving compounds 3, 13, and 14. For those experiments involving compounds that possess an —NH₂ or =NH functional group, (i.e., 9, 11, and 12), the N—H stretching band blends with the O—H stretching feature produced by the H₂O, and estimates could not be made using the 3250 cm⁻¹ H₂O feature. In these cases, we used the 1660 cm⁻¹ (6.02 μm; $A_{\text{HOH}} = 1.0 \times 10^{-17}$ cm molecule⁻¹; Hudgins et al. 1993) H—O—H bending mode and 760 cm⁻¹ (13.2 μm; $A_{\text{lib}} = 2.8 \times 10^{-17}$ cm molecule⁻¹; Hudgins et al. 1993) libration mode features of H₂O (less absorption produced by superimposed nitrile bands) to estimate sample concentrations. We estimate H₂O to nitrile ratios of 5–30 for 3-aminocrotononitrile (9), 10–30 for dicyandiamide (11), and ~ 4 for cyanamide (12).

3. EXPERIMENTAL RESULTS

While the emphasis in this paper is on the CN stretching bands produced in the 2320–2050 cm⁻¹ (4.31–4.88 μm) frequency range by compounds 1–16, complete spectra from 4000 to 500 cm⁻¹ (2.5–20 μm) were obtained in all cases. Before presenting the details associated with the CN stretching features, we provide first a brief discussion of the similarities and differences in the overall spectra of these compounds when they are frozen in Ar and H₂O matrices.

Figure 2 presents the complete 4000–500 cm⁻¹ infrared spectra of acetonitrile (1; CH₃CN) frozen at 12 K in both Ar and H₂O matrices. The large broad features near 3250 (off scale), 1660, and 760 cm⁻¹ (3.08, 6.02, and 13.2 μm) in the lower spectrum are produced by the O—H stretching, H—O—H bending, and H₂O librational vibrations of solid H₂O, respectively. The remaining bands in the spectra are produced by acetonitrile (1). While the same acetonitrile bands are generally visible in both spectra, some of the CH₃CN bands in the H₂O:CH₃CN sample show lower spectral contrast or are obscured partially by strong overlying H₂O absorptions (notice, in particular, the features at ~ 910 and 725 cm⁻¹ [11.0 and 13.8 μm]). Other peaks, such

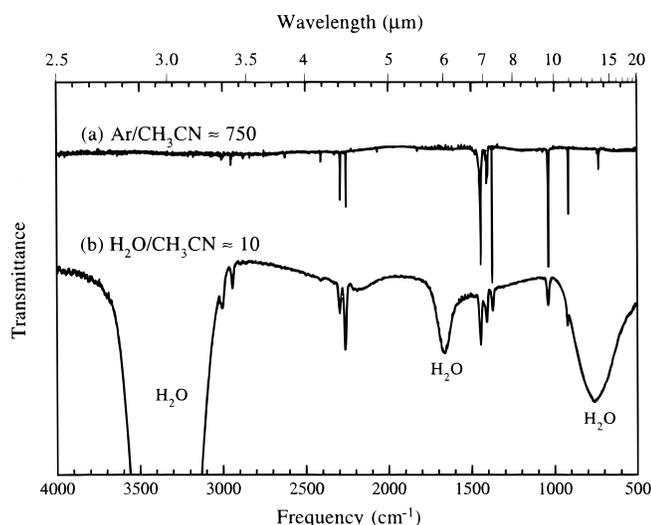


FIG. 2.—The 4000–500 cm^{-1} (2.5–20 μm) infrared spectra of acetonitrile (1) (a) isolated in an argon matrix ($\text{Ar}/\text{CH}_3\text{CN} \approx 750$) at 12 K and (b) frozen in an H_2O ice matrix ($\text{H}_2\text{O}/\text{CH}_3\text{CN} \approx 10$) at 12 K. The broad features near 3250 (off scale), 1660, and 760 cm^{-1} (3.08, 6.02, and $13.2 \mu\text{m}$) in the lower spectrum are produced by the H_2O matrix. The remaining bands in the spectra are due to various vibrational modes of acetonitrile (1). Note the features associated with $\text{C}\equiv\text{N}$ stretching vibrations near 2250 cm^{-1} .

as the C–H stretches at 3006 and 2950 cm^{-1} (3.327 and $3.390 \mu\text{m}$), are more prominent in the spectrum of the H_2O matrix than in the Ar nitrile. In addition, all the nitrile bands in the spectrum of the $\text{H}_2\text{O}:\text{CH}_3\text{CN}$ sample are considerably broader than those in the spectrum of the Ar: CH_3CN sample, and peak positions are displaced frequently (see § 3.1, Fig. 2, and Table 1). Such changes in position, width, and spectral contrast are due to “matrix effects” and are not uncommon when molecules are frozen in different matrices. H_2O , with its ability to form strong hydrogen bonds with neighboring molecules, is well known for its ability to produce large matrix effects.

The spectra in Figure 2 are illustrative of a number of important points. The same spectral differences seen between Ar and H_2O matrices in Figure 2 were seen in the spectra of the other compounds examined: (i) bands produced by compounds in H_2O matrices were typically broader than those produced by the same compounds in Ar, (ii) spectral contrast was lower for most bands in H_2O matrices (even though these samples typically had higher compound-to-matrix abundance ratios), and (iii) the positions of bands associated with the same molecular vibrations differed to varying degrees between the two matrices. In addition, the low spectral contrast of the CH_3CN bands with respect to the H_2O bands in Figure 2b, in conjunction with the fact that the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ratio is ~ 0.1 in Figure 2b but are expected to be orders of magnitude lower in astrophysical ices (see Hasegawa, Herbst, & Leung 1992), illustrates how difficult it will be to identify this class of molecules in solid-state materials in space. To be successful, the detection of these compounds will require very high signal-to-noise ratio infrared spectra taken at a moderately high resolution.

Such a search can be optimized by looking for bands that are characteristic of this class of molecular compounds, the band produced by the $\text{C}\equiv\text{N}$ stretching vibration being the most obvious candidate. All the compounds addressed in

this paper possess at least one peak in the $2300\text{--}2100 \text{ cm}^{-1}$ ($4.35\text{--}4.76 \mu\text{m}$) region, corresponding to the $\text{C}\equiv\text{N}$ stretch (or in the case of diisopropylcarbodiimide [15], an $\text{N}=\text{C}=\text{N}$ functional group). Searches for this band have the advantages that it is one of the strongest absorptions produced by all these molecules and that this spectral region is not obscured by the stronger features of H_2O . The chief disadvantage with searching for the $\text{C}\equiv\text{N}$ stretch is that this spectral region is obscured by telluric CO_2 . Fortunately, data from space-borne telescopes, like ISO, will overcome this limitation.

In the following subsections, we summarize and discuss the spectral properties (positions, widths, and strengths) of the CN stretching features of all the compounds shown in Figure 1 when they are frozen in both Ar and H_2O matrices.

3.1. The CN Stretching Feature

The compounds examined here produce CN stretching features that span the spectral range from about 2300 to 2080 cm^{-1} ($4.35\text{--}4.81 \mu\text{m}$). For convenience, the behaviors of these bands are discussed in three separate sections. First we consider the $2325\text{--}2125 \text{ cm}^{-1}$ ($4.30\text{--}4.71 \mu\text{m}$) range where the $\text{C}\equiv\text{N}$ stretches of most nitriles fall when frozen into both Ar and H_2O matrices. Second, we address the few nitriles whose $\text{C}\equiv\text{N}$ stretching band positions differ dramatically between Ar and H_2O matrices. Then we consider the $2225\text{--}2025 \text{ cm}^{-1}$ ($4.49\text{--}4.94 \mu\text{m}$) range in which the remaining compounds, including the isonitriles, produce their CN stretching bands.

3.1.1. Nitriles and the $2325\text{--}2125 \text{ cm}^{-1}$ ($4.30\text{--}4.71 \mu\text{m}$) Region

Figure 3 shows the $2325\text{--}2125 \text{ cm}^{-1}$ ($4.30\text{--}4.71 \mu\text{m}$) infrared spectra of molecules 1–9 isolated in argon matrices at 12 K. These peaks are caused by the stretching of the $\text{C}\equiv\text{N}$ group in each compound. The frequency of the $\text{C}\equiv\text{N}$ stretching peak(s) depends, in part, on the electron density available to the $\text{C}\equiv\text{N}$ group with higher electron densities generally producing lower frequencies (Nakanishi & Solomon 1977). Thus, the position provides information about the type of molecule to which the group is attached. For example, the $\text{C}\equiv\text{N}$ stretches of acetonitrile (1) appear at a higher frequency than those of benzonitrile (2), and benzonitrile produces bands at higher frequencies than does anthracene carbonitrile (3) (Fig. 3). These frequency shifts reflect, imperfectly (because there are also matrix effects), the capacity of the methyl, benzene, or anthracene functional groups to conjugate with the $\text{C}\equiv\text{N}$ group, thereby altering its bond force constant and thus its vibrational frequency. Similarly, the dimethylcyanamide (4) peak is shifted down $\sim 30 \text{ cm}^{-1}$ ($0.06 \mu\text{m}$) from that of isopropyl nitrile (5) (Fig. 3). The only difference between these molecules is the replacement of a CH in (5) with an N in (4), but the interaction of the lone pair of electrons on the N atom with the $\text{C}\equiv\text{N}$ group shifts the band to lower frequencies.

In many cases, the $\text{C}\equiv\text{N}$ stretch produces more than one band, in spite of the fact that there is only one infrared-active $\text{C}\equiv\text{N}$ stretching mode. These multiple bands are usually the result of the compound occupying several different sites, each with a different geometry, within the matrix. For example, some molecules may have $\text{C}\equiv\text{N}$ groups replacing one or more Ar atoms in the matrix, while others may be partially occupying interstitial sites. As a result, a given sample will include molecules that experience several slightly different neighboring environments that produce

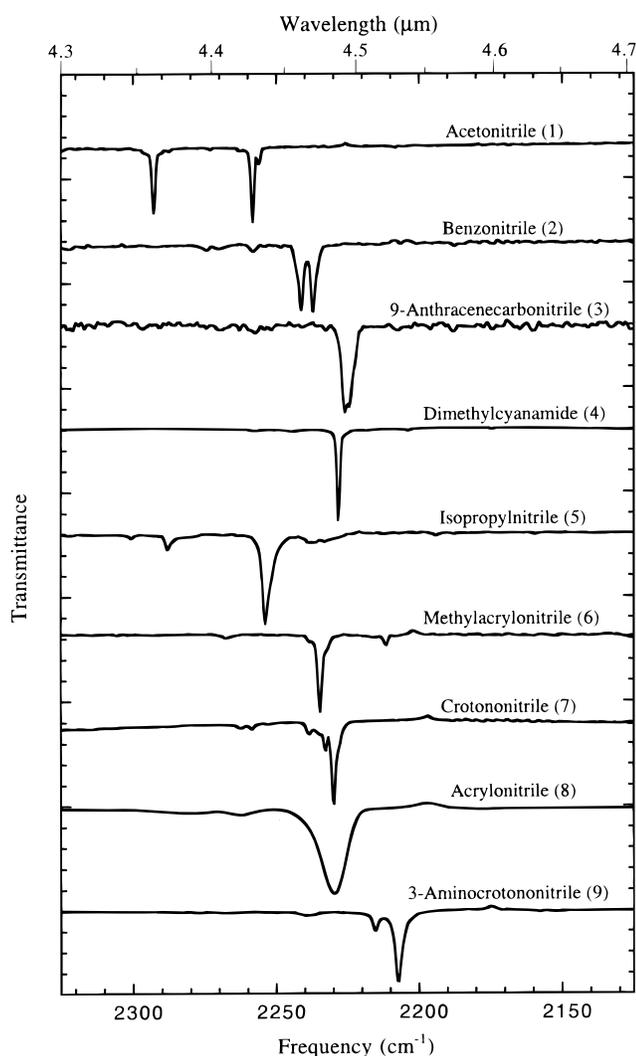


FIG. 3.—The 2325–2125 cm^{-1} (4.30–4.71 μm) infrared spectra of a number of nitriles (compounds 1–9 in Fig. 1) isolated in argon matrices at 12 K. With the exception of compounds 3 and 9, all the samples have nitrile concentrations such that Ar/nitrile \approx 750. Ar/nitrile ratios for compounds 3 and 9 are estimated to lie between 100 and 1000.

slightly different matrix shifts in the band position (Hallam 1973) (benzonitrile in Fig. 3 is a good example of this effect). Site effects generally produce modest shifts of $\sim 20 \text{ cm}^{-1}$ or less. Thus, the two major bands produced by acetonitrile (1) (Fig. 3) are not due to simple site effects on the $\text{C}\equiv\text{N}$ stretching mode. Instead, only the lower frequency band at 2258.3 cm^{-1} is due to $\text{C}\equiv\text{N}$ stretching vibrations. The higher frequency band at 2293.0 cm^{-1} is due to a combination band produced by the strong vibrational modes at 1376 and 917 cm^{-1} (Pace & Noe 1968).

Figure 4 shows the 2325–2125 cm^{-1} (4.30–4.71 μm) infrared spectra of the same molecules (1–9) frozen in H_2O matrices at 12 K. The resulting $-\text{C}\equiv\text{N}$ stretching bands show the general behaviors outlined above, namely, the spectra are similar to the Ar matrix spectra except that the bands are considerably broader and usually show minor position shifts (see Table 1). These effects are largely the result of increased intermolecular interactions and weak chemical complexes formed within the H_2O matrix, an effect that is absent in the Ar matrices. While the site effects that split bands are presumably present in these samples as

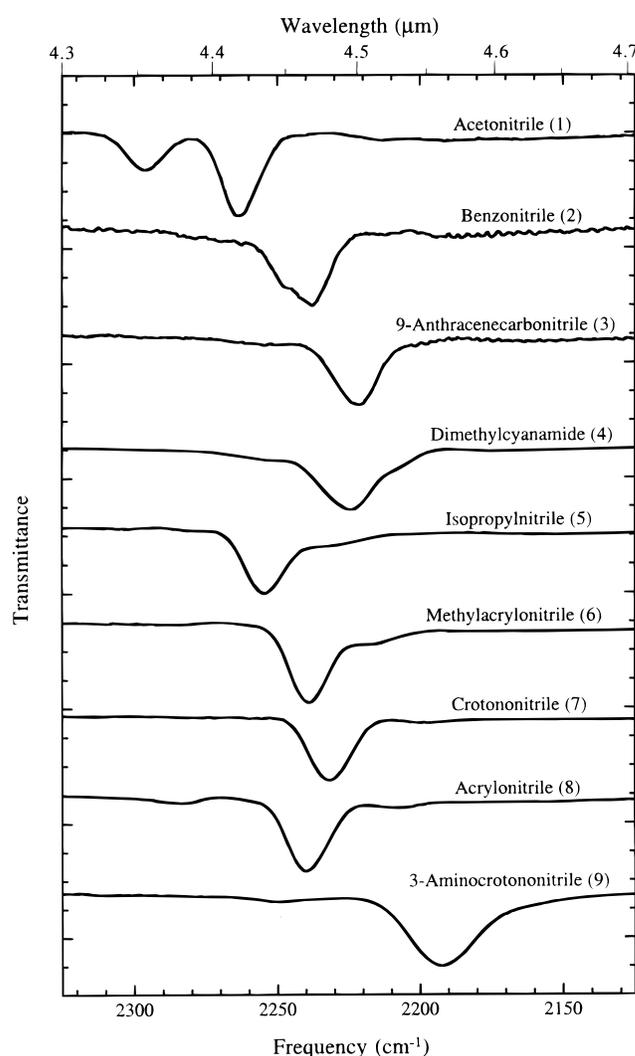


FIG. 4.—The 2325–2125 cm^{-1} (4.3–4.7 μm) infrared spectra of a number of nitriles (compounds 1–9 in Fig. 1) frozen in H_2O -rich ices at 12 K. With the exception of compounds 3 and 9, all these samples have nitrile concentrations such that H_2O /nitrile \approx 10. Ar/nitrile ratios are estimated to lie between 10 and 100 for compound 3 and between 5 and 30 for compound 9.

well, the large widths of the features cause them to overlap. A hint of site-related band blending is apparent in the spectrum of benzonitrile in H_2O (Fig. 4).

3.1.2. Nitriles That Form Strong Complexes with H_2O

The $-\text{C}\equiv\text{N}$ stretching bands shown in Figures 3 and 4, and summarized in Table 1, demonstrate amply that small band shifts (typically $< 20 \text{ cm}^{-1}$) are expected in different matrices because of differences in intermolecular interactions. However, several of the compounds we studied showed considerably more dramatic shifts in band positions between the Ar and H_2O matrix samples. Figure 5 compares the $-\text{C}\equiv\text{N}$ stretching band positions in Ar and H_2O matrices of pyruvonnitrile (10), dicyandiamide (11), and cyanamide (12). These compounds produced bands with shifts of about 133, 45, and 40 cm^{-1} , respectively (see Table 1). In all three cases the shift in H_2O is to lower frequencies. In the case of pyruvonnitrile (10), the entire band shifts downward, while the spectra of dicyandiamide (11) and cyanamide (12) show multiple bands, one near the original Ar matrix position and a new band or bands at lower frequencies. In all

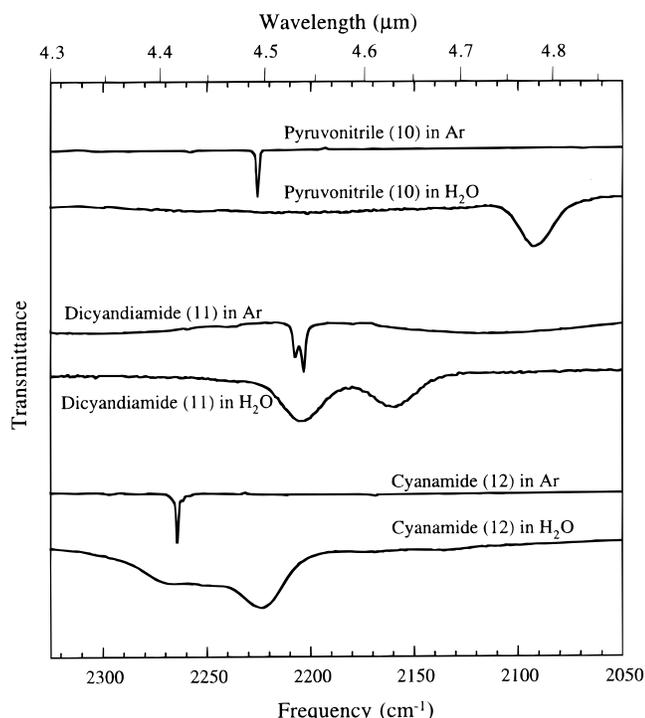


FIG. 5.—The 2325–2050 cm^{-1} (4.3–4.9 μm) infrared spectra of nitriles that show significant redshifts of the $\text{C}\equiv\text{N}$ stretching band when frozen in H_2O at 12 K (compounds 10–12 in Fig. 1). This indicates that these species form moderately strong chemical complexes with H_2O . The pyruvotrile (10) samples have $\text{Ar/nitrile} \approx 750$ and $\text{H}_2\text{O/nitrile} \approx 10$. The dicyandiamide (11) samples have $\text{Ar/nitrile} \approx 100\text{--}1000$ and $\text{H}_2\text{O/nitrile} \approx 10\text{--}30$. The cyanamide (12) samples have $\text{Ar/nitrile} \approx 100\text{--}1000$ and $\text{H}_2\text{O/nitrile} \approx 4$.

three cases, the shifts are large enough that they cannot be attributed solely to simple matrix effects.

It is reasonable to attribute these redshifts to a hydrogen bond interaction that weakens the $-\text{C}\equiv\text{N}$ triple bond. Thus, these shifts may be caused by a direct and strong interaction of H_2O molecules with each of these three nitriles and are not due to the general dielectric effect of the matrix. We remind the reader, however, that the concentrations of these compounds were considerably larger in the H_2O matrices than in the Ar matrices, so the effects could be due to interactions between the nitrile molecules themselves rather than between the nitriles and H_2O .

3.1.3. The 2225–2025 cm^{-1} (4.49–4.94 μm) Region and Isonitriles

Figure 6 shows the 2225–2025 cm^{-1} (4.49–4.94 μm) infrared spectra of *n*-butylisocyanide (13), methylisocyanoacetate (14), diisopropylcarbodiimide (15), and hydrogen cyanide (16) frozen at 12 K in both Ar and H_2O matrices. Compounds 13 and 14 are both isocyanides, and the features observed in this spectral region are due to the CN stretching vibration of their $-\text{N}\equiv\text{C}$ groups. The features in the spectra of diisopropylcarbodiimide (15) and HCN (16) are due to CN stretching vibrations in the $\text{N}=\text{C}=\text{N}$ and $-\text{C}\equiv\text{N}$ groups of these molecules, respectively. (Note: We measured the spectrum of HCN only in H_2O matrices. The data for HCN-isolated in Ar in Fig. 6 and Table 1 are taken from Bohn & Andrews [1989].)

Although molecules 13–16 produce bands at significantly lower frequencies, their CN stretching bands behave like those of the majority of the other compounds discussed in this paper. Like compounds 1–9, all four species exhibit

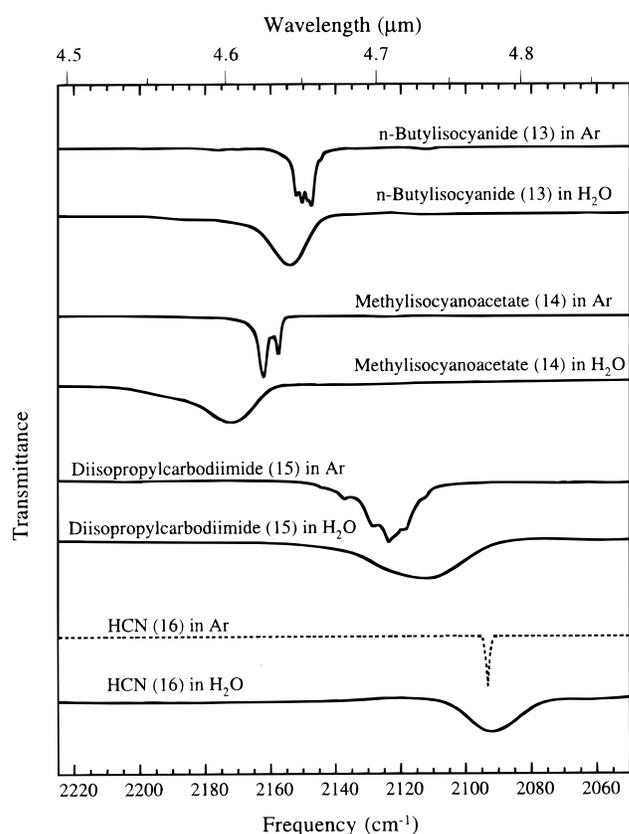


FIG. 6.—The 2225–2050 cm^{-1} (4.5–4.9 μm) infrared spectra of compounds 13–16 isolated in argon and frozen in H_2O -rich ices at 12 K. The *n*-butylisocyanide (13) and methylisocyanoacetate (14) samples have $\text{Ar/isonitrile} \approx 100\text{--}1000$ and $\text{H}_2\text{O/isonitrile} \approx 10\text{--}100$. The diisopropylcarbodiimide (15) samples have $\text{Ar/compound} \approx 750$ and $\text{H}_2\text{O/compound} \approx 10$. The HCN (16) sample in H_2O has $\text{H}_2\text{O/nitrile} \approx 10$. The spectrum of HCN in Ar is adapted from Bohn & Andrews (1989).

small changes in band position between matrices, and broader bands are produced in H_2O matrices.

In summary, the spectral data presented here demonstrate that the $-\text{C}\equiv\text{N}$ stretching bands produced by these compounds in H_2O matrices are broader than those produced in Ar matrices and that the bands generally, but not always, fall at similar positions for both matrices.

3.2. Integrated Absorbances

Should nitriles or related compounds be identified in space, the determination of their abundances will require the intrinsic strengths of their CN stretching bands to be known. Unfortunately, the intrinsic strengths of these bands are notoriously variable. Wexler, in his voluminous review of the absorptivities of many different chemical functional groups (Wexler 1967), notes for nitriles that “ $\text{C}\equiv\text{N}$ stretching vibrations fall within the relatively narrow range 2210–2270 cm^{-1} , whereas the intensity varies over a several hundred-fold range.” He points out that the strength often depends strongly on what adjacent chemical groups are present in the molecule and notes further that the band can vary substantially in strength in the same molecule when it is placed in different solvents or matrices.

This high degree of variability will complicate the interpretation of the abundances of any nitriles detected in space and highlights the need to establish the intrinsic absorption strengths (*A* values) of the CN stretches of a variety of

nitriles and related compounds under astrophysically relevant conditions. Since previous laboratory studies suggest that nitriles will be produced in environments in which H₂O-rich interstellar ices are irradiated by ionizing radiation (see Bernstein et al. 1995), the strengths of the CN stretches of these compounds in H₂O matrices are clearly of interest. Since the *A* values of the compounds shown in Figure 1 have not been reported previously for molecules frozen in H₂O matrices, we devote much of the following sections to their determination. We also discuss estimates of the *A* values for the CN stretches in the same compounds frozen in Ar matrices, since these values will likely be representative of nitriles frozen in nonpolar ices and in the gas phase.

Using absorption spectra and known *A* values, the column density, *N* (in units of molecules cm⁻²), of an absorbing species can be determined from

$$N = \frac{\int \tau_i(\nu) d\nu}{A_i}, \quad (1)$$

where $\tau_i(\nu)$ is the frequency-dependent optical depth of a particular absorption band of the molecule [$\tau = \ln(I_0/I)$], and A_i is the integrated absorbance in units of cm molecule⁻¹. In the following sections we discuss how *A* values were determined for the CN stretching bands produced by the compounds shown in Figure 1. Since the techniques used to determine the *A* values differed depending on whether or not the compound in question had a substantial vapor pressure at room temperature, we will discuss "volatile" and "nonvolatile" species in separate sections below.

3.2.1. Integrated Absorbances of Volatile Nitriles in H₂O Matrices

The *A* values for the CN stretching absorption bands produced by "volatile" nitriles (all the compounds in Fig. 1 except 3, 9, and 11–14) in H₂O matrices were determined as follows. Since these compounds all have substantial vapor pressures at room temperature, it was possible to prepare sample bulbs containing H₂O and the compound of interest mixed in known proportions. As a compromise between having a sufficient sample to be able to detect the nitrile bands in the midst of the much stronger bands of H₂O and having enough H₂O present that the majority of the sample species' neighbors in the matrix were H₂O, we used H₂O-to-compound ratios of 10:1. These sample bulbs were used to produce a 12 K ice from which an infrared spectrum was obtained (see § 2.2). Then we assumed that the strengths of the H₂O ice bands in these mixtures was the same as those produced by pure H₂O ices, i.e., we assumed that the smaller amounts of host molecules did not alter significantly the intrinsic strengths of the more abundant H₂O molecules. The column density of H₂O was determined, using equation (1), from H₂O band areas divided by *A* values from Hudgins et al. (1993). The column density of nitrile is one-tenth that of the H₂O, and the *A* value of the CN stretch is given, using equation (1), by its band area divided by the nitrile column density. The *A* values determined in this manner for the CN stretching vibration bands of compounds 1, 2, 4–8, 10, 15, and 16 are summarized in Table 1. Given the possibility that the strength of the O–H stretch of H₂O may have been affected slightly by the presence of the guest molecules and uncertainties in the gas sample mixing ratios, band area measurements, etc., we estimate these values to be accurate to ~20%.

Examination of the values in Table 1 shows that the strengths of the –C≡N stretch in the majority of the nitriles we examined in H₂O matrices fall within a factor of 2–3 to each other, and the extremes differ only by a factor of less than 6. Thus, the large range of band strength variability reported by Wexler (1967) for nitriles in different solvent and matrix environments is decreased considerably when only low-temperature, H₂O-rich ices are considered. (Note: the CN stretch of diisopropylcarbodiimide [15] is considerably stronger than that of the other compounds, but this compound is not a nitrile; its feature is due to N=C=N stretching vibrations, not –C≡N stretching vibrations.)

3.2.2. Integrated Absorbances of Nonvolatile Nitriles in H₂O Matrices

It was not possible to prepare gas sample bulbs having predetermined H₂O-to-guest mixing ratios for compounds 3, 9, and 11–14, since these molecules have no appreciable vapor pressure at room temperature. Instead, ice samples were prepared by cocondensing the molecule with H₂O vapor directly onto the CsI window at low temperature (see § 2.2). As a result, the ratios of H₂O to guest species in these ice samples were not well constrained, and *A* values could not be determined using the technique described in the previous section.

However, rough estimates of the strengths of the CN stretching bands produced by several of these compounds can be made using functional group analysis. For example, if the C–H stretching absorption of 9-anthracenecarbonitrile (3) near 3050 cm⁻¹ (3.28 μm) has an *A* value similar to that of pure polycyclic aromatic hydrocarbons, its column density is given, from equation (1), by its C–H stretching band area divided by 8 × 10⁻¹⁹ cm per aromatic C–H bond (Wexler 1967). The inferred column density of 9-anthracenecarbonitrile can then be used in conjunction with the measured area of the –C≡N stretching feature and equation (1) to derive *A*_{CN}. A similar procedure was used for *n*-butylisocyanide (13), except in this case we used the *A* values of 4 × 10⁻¹⁸ and 8.5 × 10⁻¹⁹ cm per C–H bond, respectively, for the asymmetric and symmetric aliphatic C–H stretching absorptions bands near 2960 and 2940 cm⁻¹ characteristic of pure alkanes (Sandford et al. 1991).

We expect that *A* values determined in this manner are considerably less accurate than those determined for the more volatile nitriles (see § 3.2.1). Nonetheless, this technique results in a value of *A*_{CN} ≈ 5 × 10⁻¹⁸ cm molecule⁻¹ for 9-anthracenecarbonitrile (3) (see Table 1), a value consistent with the other nitriles and one that compares quite favorably with the canonical value of 4 × 10⁻¹⁸ cm molecule⁻¹ given by Wexler (1967) for aromatic nitriles. In the case of *n*-butylisocyanide (13), this technique yields values of *A*_{CN} = 3.3 × 10⁻¹⁷ and 2.8 × 10⁻¹⁷ cm molecule⁻¹ based on the asymmetric and symmetric C–H stretching bands, respectively, consistent with a value of *A*_{CN} ≈ 3 × 10⁻¹⁷ cm molecule⁻¹ for this molecule. This value is larger than that of all the nitriles considered so far and raises the possibility that isonitriles may produce CN stretches that are intrinsically stronger than those in nitriles (Table 1).

The use of functional group analysis is considerably more problematic for the remaining nonvolatile compounds (9, 11, 12, and 14). In the case of the only other isonitrile we have studied, methylisocynoacetate (14), one can use

several different functional groups. Using the C—O stretching band near 1230 cm^{-1} ($8.13\text{ }\mu\text{m}$) produced by the O=C—O group (assumed $A_{\text{C-O}} = 6 \times 10^{-17}$ cm per C—O bond; Wexler 1967) and the C=O stretching band near 1750 cm^{-1} ($5.71\text{ }\mu\text{m}$) produced by the O=C—O group (assumed $A_{\text{C=O}} = 3 \times 10^{-17}$ cm per C=O bond; Wexler 1967) yields values of $A_{\text{CN}} \approx 4 \times 10^{-17}$ cm molecule $^{-1}$ and $A_{\text{CN}} \approx 1 \times 10^{-17}$ cm molecule $^{-1}$, respectively. The average of these determinations suggests that methylisocyanoacetate (14) may produce a CN stretching band that is somewhat stronger than typical of nitriles, as was the case for *n*-butylisocyanide (13). (We note that a similar determination of the A value using the aliphatic C—H stretching bands is not reliable since it is known that the presence of an O=C—O group perturbs their strength strongly [Wexler 1967].)

Finally, we were unable to estimate A_{CN} values for 3-aminocrotonitrile (9), dicyandiamide (11), and cyanamide (12), since the other features we could use for comparison are associated with $-\text{NH}_2$ and $=\text{NH}$ groups that are sensitive to complexation and that produce absorption features that are overlapped by much stronger H_2O features.

3.2.3. Integrated Absorbances of Nitriles in Ar Matrices

Because argon does not produce any infrared absorption features, it was not possible to determine A values for the CN stretches of the compounds in our Ar matrix studies using the band strength comparison techniques discussed in § 3.2.1, even for compounds that were premixed with Ar in the sample bulbs. We could, however, use the functional group analysis technique described in § 3.2.2 to make rough checks of band strengths for these samples. We found that the average strengths of the CN stretching bands produced by our compounds in Ar usually fell within factors of 2–3 of those determined for the same compounds in H_2O . However, it is apparent from the examples in § 3.2.2 that such computations are not very precise, and it is quite possible that the CN stretches of some of our compounds frozen in Ar could actually differ from those frozen in H_2O by as much as a factor of 10.

4. DISCUSSION OF RESULTS AND ASTROPHYSICAL IMPLICATIONS

The results shown in § 3 illustrate the danger of assigning molecular identifications to bands discovered in astronomical spectra based solely on one feature, especially if published positions are from compounds in pure form or if astrophysically inappropriate matrices are used for comparison. Proper identifications will require comparisons with laboratory spectra taken from compounds studied under astrophysically relevant conditions. Even then there may be significant uncertainties depending on band location.

While one of the primary motivations of obtaining the nitrile spectra presented in this paper was to serve as a database for the interpretation of future astronomical spectra taken by spacecraft like ISO, our results have some immediate implications for several issues of interest to interstellar and solar system materials. These are discussed briefly in the following two sections.

4.1. The 2165 cm^{-1} Band and “XCN”

The spectra of a limited number of lines of sight through dense clouds contain a broad, often weak, feature on the

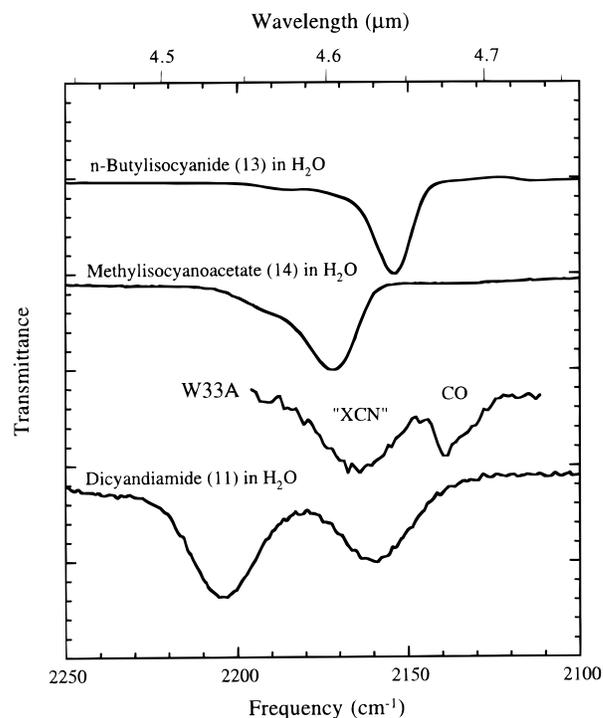


FIG. 7.—The $2250\text{--}2100\text{ cm}^{-1}$ ($4.44\text{--}4.76\text{ }\mu\text{m}$) infrared spectra of the compounds *n*-butylisocyanide (13), methylisocyanoacetate (14), and dicyandiamide (11) frozen in H_2O compared with the infrared spectrum of the protostellar object W33A.

blue side of the CO ice feature (Fig. 7; Lacy et al. 1984; Tegler et al. 1993; Weintraub et al. 1994). This feature is typically centered at about 2165 cm^{-1} ($4.62\text{ }\mu\text{m}$) and has a width of about $\sim 25\text{ cm}^{-1}$ ($\sim 0.05\text{ }\mu\text{m}$). While only a modest number of sources have been studied, there is an indication that this feature is present only in the spectra of objects embedded within the clouds and not in the spectra of background stars (Tegler et al. 1995). This suggests that the carrier of the feature may be associated with the local environment of the embedded star.

The molecule(s) responsible for this absorption have yet to be identified conclusively, although a number of suggestions have been put forward. Laboratory experiments have shown that a feature similar to the observed interstellar band is produced when laboratory ice mixtures containing C and N are exposed to ion bombardment or ultraviolet radiation (Moore et al. 1983; Lacy et al. 1984; d’Hendecourt et al. 1986; Bernstein et al. 1995), suggesting that the absorption is due to the stretching vibration of a $\text{C}\equiv\text{N}$ functional group in a nitrile or isonitrile. Alternate assignments for this band include an Si—H stretch (Nuth & Moore 1988; Moore et al. 1991), although this identification has problems (Tegler et al. 1993), and the CN stretch in the OCN^- ion (Grim & Greenberg 1987). This work will focus on the nitrile-isonitrile interpretation.

It is apparent from Table 1 and Figures 3–6 that most of the compounds addressed in this study do not come close to matching the astronomical “XCN” feature, independent of matrix composition, and these compounds can be eliminated as potential candidates for the carrier of the XCN band. For example, the compounds discussed in § 3.1.1 (Figs. 3 and 4) produce $\text{C}\equiv\text{N}$ stretching features that fall far to the blue of the interstellar feature. However, some nitriles show large red shifts when frozen in H_2O matrices

(§ 3.1.2; Fig. 5), and of these, dicyandiamide (11) is shifted sufficiently to produce a band very near the XCN feature (Fig. 7). The two isonitriles studied, *n*-butylisocyanide (13) and methylisocyanoacetate (14), also produce bands in the vicinity of the XCN feature and provide a better match when in H₂O matrices than in Ar matrices (Fig. 7). Finally, the CN stretching features produced by diisopropylcarbodiimide (15) and HCN (16) do not provide a good fit to the XCN feature, both producing features that fall too far to the red.

Given their proximity to the interstellar 2165 cm⁻¹ XCN feature, the compounds shown in Figure 7 merit additional discussion, since their structures may provide clues to the identity of the interstellar band carrier. Dicyandiamide (11) is a nitrile and normally produces a C≡N stretching feature near 2200 cm⁻¹, but it is also one of the rare nitriles that displays a strong redshift when frozen in H₂O. These nitriles contain a lone electron pair in conjugation with the C≡N bond. Apparently, this lone pair can hydrogen bond with H₂O to form a complex, and this shifts the frequency of the C≡N stretch. Interestingly, dicyandiamide contains alternating C and N throughout its structure, a trait shared by hexamethylenetetramine (HMT; C₆N₄H₁₂), a major product of the UV photolysis of interstellar ice analogs (Bernstein et al. 1995) and a photolytic source of XCN (Bernstein et al. 1994). The biggest objection to dicyandiamide being the actual carrier of the interstellar band is that ¹⁸O-labeling experiments and compositional studies of the XCN band in our laboratory indicate that the carrier contains oxygen (unpublished data), which dicyandiamide does not. In any event, if dicyandiamide is responsible for the interstellar XCN feature, we would predict that objects like W33A, which produce relatively strong 2165 cm⁻¹ XCN bands, should also produce even stronger bands near 2205 cm⁻¹ (4.54 μm) (see Figs. 5 and 7). Data currently being taken by ISO should allow this possibility to be easily tested.

While its match to the interstellar feature is not as good as that provided by dicyandiamide, *n*-butylisocyanide (13) has some attractive features also. This molecule is rich in aliphatic -CH₃ and -CH₂- groups, functional groups that are known to be produced when realistic interstellar ice analogs are photolyzed (Bernstein et al. 1995). Furthermore, aliphatic -CH₃ and -CH₂- groups are common in dust in the diffuse interstellar medium, and the ratio of -CH₂-/-CH₃ = 3 in this molecule is similar to the value of 2.5 ± 0.4 for the interstellar medium (Sandford et al. 1991). Unfortunately, *n*-butylisocyanide fails to meet the same criterion as dicyandiamide; namely, it does not contain oxygen.

Finally, methylisocyanoacetate (14) provides a fit to the interstellar feature that is of intermediate quality to the fits provided by *n*-butylisocyanide and dicyandiamide. The presence of -CH₃ and -CH₂- groups in methylisocyanoacetate are compatible with their production in photolysis experiments on interstellar ice analogs and, unlike the other two species discussed here, it *does* contain oxygen. Indeed, the presence of some of the oxygen in the form of C=O is interesting, since C=O functional groups are also made in the organic residues produced by the UV photolysis of interstellar ice analogs (Bernstein et al. 1995). This type of structural constraint is similar to those discussed by d'Hendecourt et al. (1986) in their attempt to limit the possible identity of XCN. Interestingly, the *A* values for

the CN stretching bands of the possible carrier species discussed by d'Hendecourt et al. fell between 1.8 and 3.6 × 10⁻¹⁷ cm molecule⁻¹, a range similar to that determined here (§ 3.2, Table 1).

We wish to stress that we are not suggesting that one of these specific compounds is the carrier of the XCN band. Their spectra serve simply to illustrate that stable nitrile and isonitrile compounds are plausible candidates for the carrier of the interstellar XCN feature at 2165 cm⁻¹ (4.62 μm).

In summary, the spectra of nitriles, isonitriles, and related compounds presented here provide evidence that *the carrier of the interstellar XCN band near 2165 cm⁻¹ is an isonitrile or one of a limited set of nitriles that form strong complexes with H₂O.*

4.2. Nitriles in the Solar System

As mentioned earlier, it has been suggested that absorption features seen near 4400 cm⁻¹ (2.27 μm) in the reflection spectra of several small solar system bodies could be due to the overtone of a C≡N stretch (Cruikshank et al. 1991).

A number of our spectra contained sufficiently strong fundamental absorption bands and high enough signal-to-noise ratio that we could observe possible overtones of the C≡N stretching fundamental (compounds 6, 7, 8, 11, and 13). In all these cases, it was found that the overtone falls at very nearly twice the frequency of the fundamental, the largest differences between the actual and scaled positions being about 30 cm⁻¹. This indicates that the C≡N stretching vibration in these molecules is fairly harmonic. If this is true of all the compounds we have studied, this would imply that typical nitriles should produce C≡N stretching overtones that span the range from about 4600 to 4400 cm⁻¹ (2.17–2.27 μm), and isonitriles should produce overtones in the 4360–4280 cm⁻¹ (2.29–2.34 μm) range (see Table 1).

As is often the case, the strength of the overtone relative to the fundamental seems to be highly variable. In the cases in which we see the overtone, its strength is found to lie between about 1/10–1/40 that of the fundamental. Since the spectra in which we can see the overtone are likely to be biased toward those having the strongest overtone bands, it is possible that the “average” strength of the C≡N stretching overtone is weaker still.

Given that the C≡N stretching feature seems to be fairly harmonic, simple scaling of the positions of the C≡N stretching fundamentals would suggest that the 4400 cm⁻¹ astronomical features could potentially be associated with normal nitriles, but not with isonitriles or with the nitriles that form strong complexes with H₂O. Since the interstellar 2165 cm⁻¹ “XCN” feature is most likely due to an isonitrile (§ 4.1), this suggests that the 4400 cm⁻¹ features seen in the spectra of comets Panther and Bowell and in 5145 Pholus are not associated with the “XCN” carrier.

While our limited data on the overtone of the fundamental CN stretch suggest that it could contribute to the 4400 cm⁻¹ feature seen in the spectra of these solar system objects, more appropriate laboratory data of this class of compounds taken using reflectance techniques will be needed to address this possibility fully.

5. CONCLUSIONS

We have obtained the infrared spectra of 16 nitriles, isonitriles, and related compounds isolated in Ar matrices and frozen into H₂O-rich ices. The spectra have been used to

determine the positions, profiles, widths, and strengths of the features produced by the CN stretching vibrations in these molecules. These data can be used as a database to assist with the interpretation of infrared features found in the 2320–2030 cm^{-1} (4.31–4.93 μm) range. Such data are currently being obtained by ISO.

The CN stretching bands are considerably broader when these molecules are frozen in H_2O -rich ices than when they are isolated in Ar matrices. In most cases, the positions of the CN stretching bands are very similar in the H_2O and Ar matrices, the differences being characteristic of typical matrix effects. However, there are a small number of exceptions in which the position of the $\text{C}\equiv\text{N}$ stretching feature is shifted dramatically to lower frequencies when the molecule is frozen in H_2O . The $\text{C}\equiv\text{N}$ stretching bands of nitriles typically fall between 2300 and 2200 cm^{-1} (4.35 and 4.55 μm). In contrast, the isonitriles we studied produced bands between 2180 and 2140 cm^{-1} (4.59 and 4.67 μm), i.e., at considerably lower frequencies.

While the intrinsic strength of the $\text{C}\equiv\text{N}$ stretching band in nitriles is notoriously sensitive to the structure and environment of the molecules, we found that the band's intrinsic strength did not vary much between molecules when they were frozen in H_2O -rich ices. Insofar as we can tell, there also do not appear to be major differences in the intrinsic strength of the feature between H_2O and Ar matrices. The strength of the feature may be substantially stronger in isonitriles than in nitriles, i.e., the $-\text{N}\equiv\text{C}$ group is a better absorber than the $-\text{C}\equiv\text{N}$ group, although our limited number of isonitrile spectra leave this uncertain.

In those cases in which it was observed, the overtone of the $\text{C}\equiv\text{N}$ stretching vibration was found to have a peak frequency and width very nearly twice those of the fundamental, indicating that the $\text{C}\equiv\text{N}$ stretching vibration is fairly harmonic. In those cases in which the overtone was evident, it typically had a strength 1/10–1/40 that of the fundamental, but the “average” strength of the overtone could be considerably lower.

The data presented in this paper have several immediate astrophysical implications. First, they demonstrate that the 2165 cm^{-1} (4.62 μm) interstellar “XCN” absorption band seen in the spectra of protostellar objects embedded in dense molecular clouds is *not* due to a normal nitrile. Instead, the carrier of this band is probably an isonitrile, or possibly one of a very limited set of nitriles that can form strong complexes with H_2O . Second, the observed harmonic nature of the $\text{C}\equiv\text{N}$ stretch suggests that the absorption features seen near 4400 cm^{-1} (2.27 μm) in the reflection spectra of several solar system objects are unlikely to be related to the carrier of the interstellar XCN feature, but they could potentially be due to the $\text{C}\equiv\text{N}$ stretching overtone of more typical nitriles.

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