

Preparation, Identification, and Low-Temperature Infrared Spectra of Two Elusive Crystalline Nitrile Ices

by

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Abstract

Infrared (IR) spectra of the alkyl nitrile ices CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$ are relevant to the study of the low-temperature chemistry of objects within and beyond the Solar System, but the thermodynamically favored low-temperature crystalline phases of these compounds have not been presented and identified in the planetary-sciences literature. Moreover, there is a large variation in the published IR spectra of these two icy solids, including spectra that are used for the analyses of spacecraft data from the Voyager and Cassini missions. Here the IR spectra of the low-temperature crystalline forms of CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$, which are the thermodynamically stable phases at Titan temperatures, are presented for the first time with all samples being made by vapor-phase deposition. Conditions are described for producing these ice phases for both compounds, and new measurements are reported of ice density and refractive index, quantities needed to compute IR absorption coefficients, band strengths, optical constants, and, ultimately, nitrile abundances in extraterrestrial environments. Comparisons are drawn between CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$, an earlier prediction on their similar crystallization behaviors is verified, and previous work is examined in light of these new results, including a counter-intuitive observation in which the low-temperature phase of an ice is made by heating a high-temperature phase. Applications and extensions are described.

Key Words: Ices, IR spectroscopy, Titan, organic chemistry, infrared observations

1. Introduction

The identification of molecules and polyatomic ions in planetary and interstellar environments relies on laboratory studies of such species' chemical and physical properties, and particularly spectroscopic data. Although extensive laboratory work has been carried out in this area, uncertainties remain in the relevant literature. In this paper we present new results for crystalline propionitrile ($\text{CH}_3\text{CH}_2\text{CN}$, ethyl cyanide), an organic compound that has been proposed (Dello Russo and Khanna, 1996) as a solid-phase component of Titan's atmosphere, that has been observed there in the gas phase (Cordiner et al., 2015), and that has been found in the interstellar medium (Johnson et al., 1977), but for which there appears to be a considerable divergence among published low-temperature spectroscopic results.

Infrared (IR) spectra of solid $\text{CH}_3\text{CH}_2\text{CN}$ have been presented in this journal and elsewhere in recent years for application to studies of Titan (Ennis et al., 2017, 2018; Couturier-Tamburelli et al., 2018; Nna-Mvondo et al., 2019). Earlier IR work includes that of Dello Russo and Khanna (1996), Khanna (2005), and Moore et al. (2010), but other spectroscopic results can be found in the literature going back at least 40 years (Wurrey et al., 1976), with calorimetric studies of the solid being published even earlier (Weber and Kilpatrick, 1960). The latter, in particular, are important because they show that solid $\text{CH}_3\text{CH}_2\text{CN}$ has two crystalline phases, with a transition between them occurring near 180 K, and for which there is little mention in the planetary-sciences literature. This lack of attention to propionitrile's two crystalline phases leads to uncertainty over just which ice phase has, or phases have, been studied by earlier workers and just which spectra are available, suitable, and most relevant for comparison to IR observations by spacecraft and for laboratory investigation.

Problems and uncertainties involving propionitrile ices likely are due to difficulties in preparing and identifying the various nitrile crystalline solids, which in turn can be traced to a lack of reference data. Here reference IR spectra of propionitrile's crystalline phases are presented along with values for two physical properties needed for quantitative studies. The approach used differs from earlier work in several ways. First, propionitrile's smaller congener, acetonitrile (CH_3CN , methyl cyanide), is used as a key to understanding the behavior of propionitrile itself. Second, use is made of the earlier thermodynamic results that show that each of these nitriles has two crystalline phases. Third, we use a previous IR study of CH_3SH and earlier powder diffraction work on CH_3CN to recognize the importance of Ostwald's step rule during crystallization (Hudson, 2016).

This approach and our new data complement the older studies and reconcile some inconsistencies in the literature. We first present new measurements of the refractive index (n) and density (ρ) of two solid forms of CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$, and then turn to the preparation and IR-spectral characterization of solid forms of CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$. Mid-IR spectra of the two crystalline polymorphs of the former do not appear to have been studied together for about 50 years, and we have not found any IR

identification of the low-temperature crystalline phase of propionitrile. For these two organic compounds, we have examined both the high- and low-temperature crystalline phases of each ice.

Before presenting these new results, it should be pointed out that this paper is quite different from the previous one on nitriles from this laboratory (Moore et al., 2010). The goal of that work was the measurement and extensive tabulation of nitrile optical constants, with almost no consideration of molecular structure or spectral interpretation. Here we are seeking insight, not numbers, by placing the focus on the ice sample itself, its identification, and its IR characterization. Once an ice is so examined and understood, the generation of numerical data can follow with greater confidence.

2. Laboratory Procedures

The equipment used and the procedures followed were the same as in recent papers from this laboratory (e.g., Hudson et al., 2017). Acetonitrile and propionitrile were purchased from Sigma Aldrich and used as received except for routine freeze-pump-thaw degassing, the use of desiccants, and vacuum-line distillation. For the preparation and purification of HCN see Gerakines et al. (2004).

The key variables in making our crystalline nitrile ices were deposition time, deposition temperature, and the closely related quantities of deposition rate and ice thickness. In the past, our lab's deposition rates usually were chosen so that an ice sample's thickness increased by no more than about 1 μm in 15 minutes, and the rate sometimes was considerably slower. However, for the present work we often deposited much faster, with a change in ice thickness closer to about 7 μm in 15 minutes. This was sufficient to generate nitrile ices at the higher temperatures (120 - 155 K) in the desired high- or low-temperature crystalline phase before sublimation. In some cases, ice samples were grown at a slower rate near 10 K and warmed to crystallize the resulting amorphous solid. Once the conditions of time, temperature, and rate were understood for making the various types of solids, few differences were seen in the final crystalline-ice spectra resulting from different preparation methods. Lab-to-lab variations, such as a cryostat's cooling capacity or a substrate's thermal contact with a cold finger, probably will necessitate variations on our conditions. See also the discussion of Tizek et al. (2004) on laboratory variables involved in making the crystalline phases of CH_3CN .

Infrared transmission spectra were recorded with resolutions from 2 up to 0.5 cm^{-1} from 4000 to 400 cm^{-1} , but the focus was almost entirely on the 3600 - 600 cm^{-1} region. A quartz crystal microbalance was used to measure densities, and two-laser interferometry was used to measure refractive indices at $\lambda = 670 \text{ nm}$ (Tempelmeier and Mills, 1968) in a UHV chamber. New density and refractive index values reported are the averages of three determinations, with standard errors in n and ρ on the order of ± 0.005 and $\pm 0.005 \text{ g cm}^{-3}$, respectively. Again, see Hudson et al. (2017) for details concerning ice preparation, the equipment used, and the data-analysis methods to

derive ice densities and refractive indices. For measurements of ice thicknesses and IR intensities, see our earlier papers and references therein (e.g., Hudson et al., 2014a; Hudson et al., 2014b).

Overall, there is little, if anything, that can be claimed as novel or unusual about the equipment used for this work. What is perhaps somewhat atypical was the method employed to prepare, identify, and characterize two elusive organic ices under vacuum, a method that involved much more rapid depositions than in some of our previous work. For another example, see Hudson (2016).

3. Results

3.1. Refractive indices and densities

Refractive index (n) and density (ρ) values were made in the course of this work, and will be needed for future studies. We measured n at 670 nm for HCN, CH₃CN, and CH₃CH₂CN near 15 K for amorphous ices and at higher temperatures for crystalline ones. Densities were measured only for amorphous nitriles as ρ for crystalline ices are available from published X-ray diffraction studies. See **Table 1** for the n and ρ values we used. Density differences for the two forms of each crystalline compound are expected to amount to only a few percent (e.g., CH₃CN: Enjalbert and Galy, 2002; CH₃OH: Torrie et al., 2002; CH₄: Bol'shutkin et al., 1971; H₂O, I_c and I_h: Loerting et al. 2011).

Table 1
Refractive Indices and Densities of Three Nitrile Ices

Compound	Amorphous Ice ^a		Crystalline Ice	
	n	$\rho / \text{g cm}^{-3}$	n	$\rho / \text{g cm}^{-3}$
HCN	1.325 (15 K)	0.808 (15 K)	1.39 (120 K) ^b	1.032 (153 K) ^c
CH ₃ CN	1.334 (15 K)	0.778 (15 K)	1.459 (140 K) ^a	1.058 (206 K) ^d
CH ₃ CH ₂ CN	1.311 (15 K)	0.703 (15 K)	1.463 (140 K) ^a	1.013 (100 K) ^e

^a This work; n and ρ are averages of three measurements

^b Moore et al. (2010)

^c Dulmage and Lipscomb (1951), low-temperature form

^d Enjalbert and Galy (2002), high-temperature form

^e Ennis et al. (2018), low-temperature form

3.2. CH_3CN , acetonitrile

Considerable time was spent studying solid CH_3CN , for which there exists X-ray and IR spectral data for its crystalline phases, to prepare for an examination of $\text{CH}_3\text{CH}_2\text{CN}$, for which much less structural data was available. Our CH_3CN experiments were designed to be of the "proof of concept" type, paving the way for work on $\text{CH}_3\text{CH}_2\text{CN}$, and not as an end unto themselves. First efforts were directed toward making both crystalline phases of CH_3CN and reproducing what little IR results were available for the low-temperature polymorph.

Condensation of acetonitrile vapor near 15 K produced an amorphous solid that could be warmed to crystallization near 100 K and which sublimed in a few minutes at 160 K (e.g., Hudson and Moore, 2004). Our IR spectra of amorphous CH_3CN ice at 15 K resembled those already in print (e.g., d'Hendecourt and Allamandola, 1986; Abdulgalil et al., 2013), and so are not shown here. Optical constants are in Moore et al. (2010).

Several conventions for designating nitrile crystalline ices are found in the literature, including the use of Greek letters (α , β) and Roman numerals (I, II). However, just which phase is denoted by which symbol does not seem to be agreed upon (e.g., see Abramczyk and Paradowska-Moszkowska, 2001). Therefore, following Knözinger and co-workers, we use simply LT and HT to refer to the low- and high-temperature forms, respectively, of crystalline nitriles (e.g., Tizek, 2004).

Calorimetric studies have shown that CH_3CN has two crystalline forms at low pressure, the transition temperature between them being 217 K (Putnam et al., 1965). Cooling liquid CH_3CN produces first the high-temperature (HT) form at 229 K, which can be retained at lower temperatures by rapidly cooling the sample. However, if the HT ice is held just below the transition temperature then it slowly converts into the low-temperature (LT) crystalline phase. We emphasize that this LT-HT transition temperature of 217 K is well above that at which our CH_3CN ices rapidly sublimed, making it impossible to prepare both crystalline forms of CH_3CN in our vacuum system by the conventional method of slowly warming an amorphous ice.

Several earlier studies helped us prepare both phases of crystalline CH_3CN . First, Pace and Noe (1968) recorded IR spectra of CH_3CN in closed cells and published enlargements of several spectral regions. Their spectra were invaluable in our attempts to identify the crystalline forms of our ices. Second, diffraction studies of Tizek et al. (2004) showed that warming amorphous CH_3CN can produce the high-temperature crystalline ice phase before the low-temperature one, a counter-intuitive result that can be justified on the basis of the Ostwald step rule (Ostwald, 1897). This suggested that warming our own amorphous CH_3CN samples also would produce the HT form of the compound. – The Ostwald Step Rule is simply a statement that crystallization follows a path leading first to a kinetically favored product, not a thermodynamically favored one.

– Finally, our recent work with CH₃SH, methanethiol, showed that in some cases it is possible to make the high-temperature phase of an ice well below its LT-HT transition temperature by using a carefully chosen set of temperature and deposition conditions (Hudson, 2016). This same work showed that warming amorphous CH₃SH gave a mixture of its LT and HT crystalline phases.

In the present study, warming amorphous CH₃CN ice at 1 - 2 K min⁻¹, and stopping to record IR spectra at selected temperatures, inevitably produced the HT phase of crystalline CH₃CN by ~100 K, the same phase made and described by, for example, Milligan and Jacox (1962) and later by Dello Russo and Khanna (1996) and Abdulgalil et al. (2013). Depositions at 100 - 120 K and higher also gave the HT form of acetonitrile. This formation of the HT phase of solid CH₃CN roughly 100 K below the compound's LT-HT transition temperature (i.e., 217 K) is of intrinsic interest, but the long timescales in astronomical settings would seem to favor conversions of ices to their most thermodynamically stable phase, in this case the LT polymorph.

We found it impossible to prepare the LT phase of CH₃CN in our vacuum systems when our usual rates of deposition and warming were employed, success being met only by using either faster deposition rates or faster warming rates. In one experiment, we deposited CH₃CN at 155 K about 10 times faster than usual for ~15 minutes. Spectra recorded immediately at that temperature matched those for the desired LT phase published by Pace and Noe (1968). The ice could then be cooled to record spectra at other temperatures. No changes were seen after the CH₃CN ice was left at 120 K overnight, and certainly none were expected as the sample was far below its LT → HT transition temperature of 217 K. Ices prepared in this same way at 150 K, but for shorter times and smaller thicknesses were in the HT crystalline form, but then converted to the LT one over several minutes. In a different experiment, amorphous CH₃CN was made as usual near 10 K, but then warmed rapidly (~7 K min⁻¹) to 165 K without stopping, held there about 1 minute, and then cooled to 120 K. Again, comparisons to the spectra of Pace and Noe (1968) showed that our ice was of the LT modification. Note that all amorphous-to-crystalline and crystalline-to-crystalline changes reported in this paper were irreversible in the vacuum systems used.

To our knowledge, these experiments are the first to give spectra of the LT phase of CH₃CN prepared by vapor-phase deposition in a high-vacuum chamber and characterized by mid-IR spectroscopy. **Figures 1 and 2** show survey spectra and expansions of two regions for our CH₃CN ices, and **Tables 2 - 4** give positions of selected IR peaks, conservatively rounded to the nearest 1 cm⁻¹. Results are included from other laboratories for comparison, in all cases the data being from transmission measurements. The only other data available for the LT phase is that, yet again, of Pace and Noe (1968). Peak positions are listed at two temperatures, one matching the lowest that those authors used. We emphasize that their spectra were of a crystalline solid made by slowly cooling a liquid, whereas ours were for an ice made either by rapid warming of an amorphous solid or rapid condensation of a vapor. All three methods gave the same IR spectrum, that of the LT phase in our **Figures 1 and 2**.

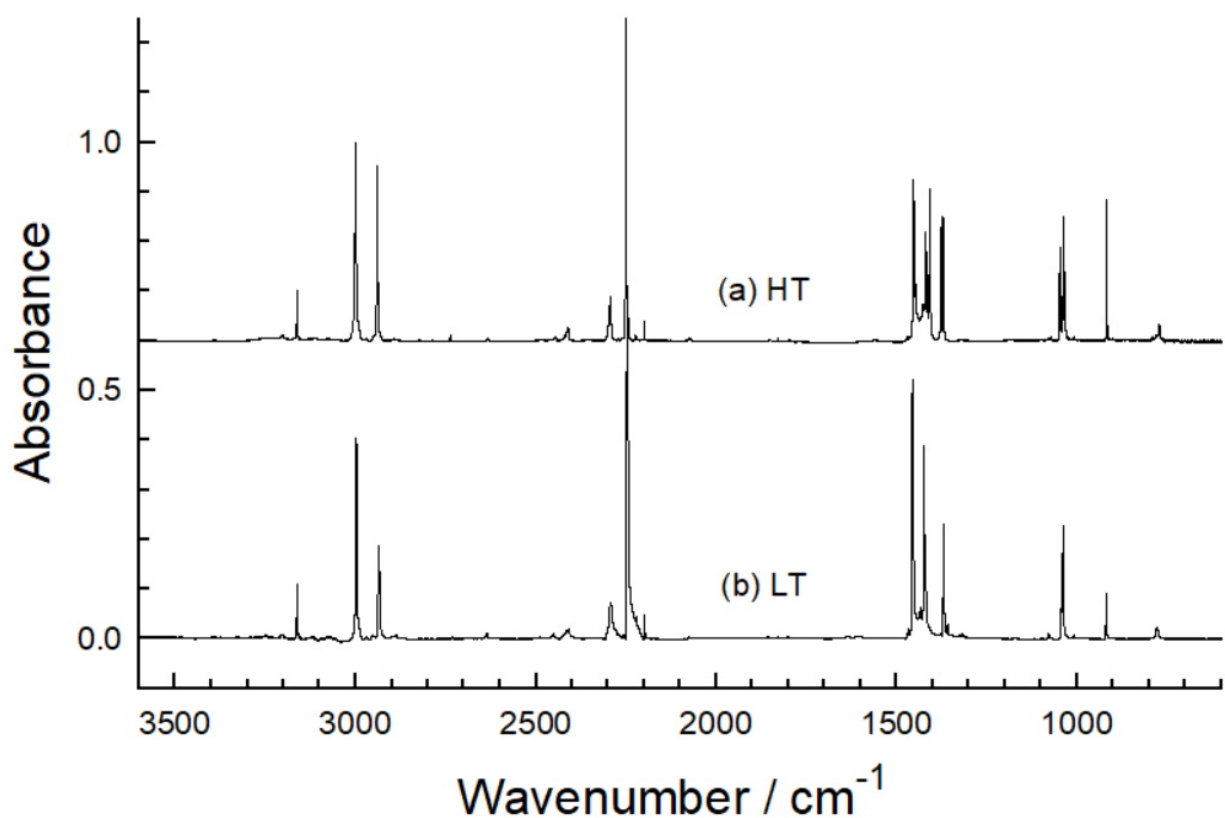


Fig. 1. Survey spectra of two crystalline forms of CH₃CN at 120 K. (a) The sample was deposited at 120 K, warmed to 150 K, and cooled to 120 K to give the high-temperature (HT) crystalline phase. (b) The sample was deposited at 10 K, warmed to 165 K, and cooled to 120 K to give the low-temperature (LT) crystalline phase. Spectra have been offset for clarity. Note that the peak near 2245 cm⁻¹ is off-scale in each spectrum, so as to show the weaker features. The spectral resolution was 0.5 cm⁻¹.

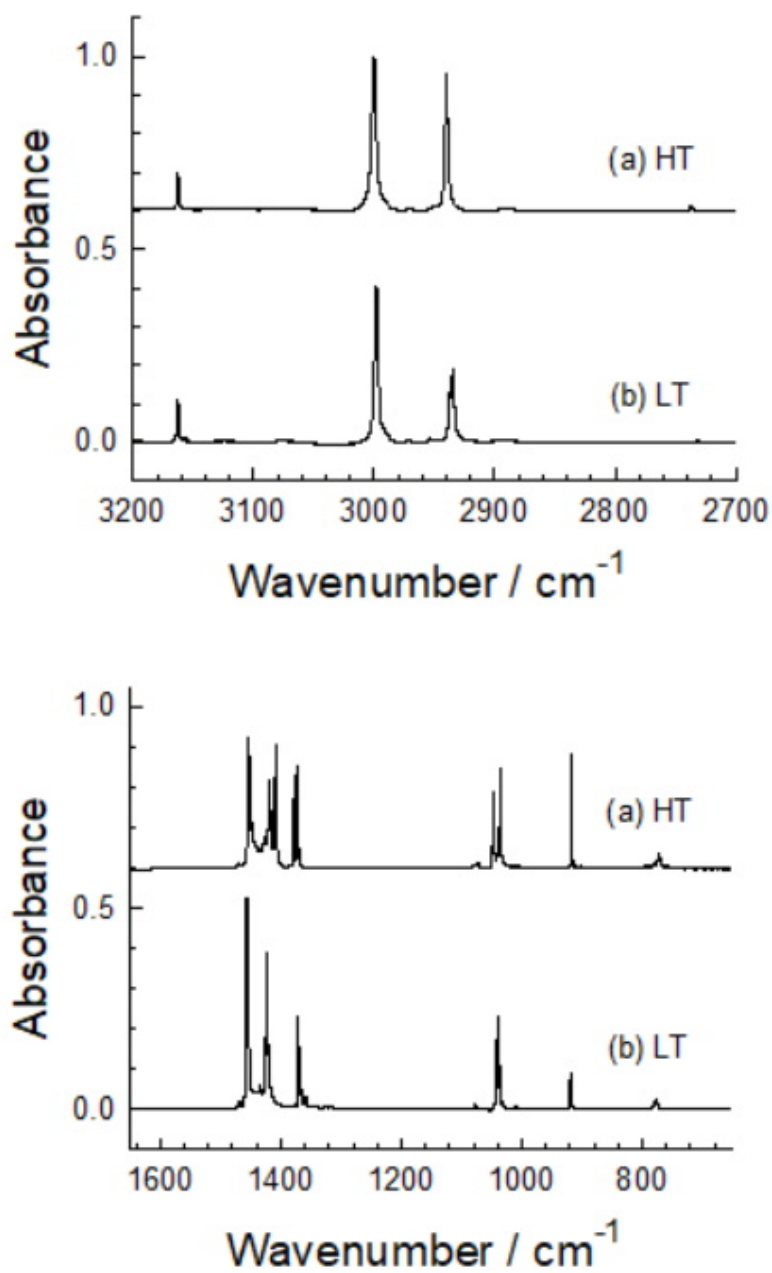


Fig. 2. Expansions of IR spectra of CH_3CN . See the caption of Figure 1 for details.

Table 2
Positions of Selected IR Peaks of Solid Amorphous and Liquid CH₃CN ^a

Approximate description ^a	Amorphous Ice, 9 K ^b	Amorphous Ice, 10 K ^c	Liquid 238 K ^d
C-H asymm stretch	3000	3001	3001
C-H symm stretch	2940	2941	2942
C≡N stretch	2252	2251	2252
combination bands	1447	1447	1443
CH ₃ asymm deformation	1410	1409	1415
CH ₃ symm deformation	1373	1373	1374
CH ₃ rock	1039	1038	1039
C-C stretch	919	917	919
overtone	784, 761	---	753

^a Positions in cm⁻¹; assignments from Pace and Noe (1968)

^b This work

^c d'Hendecourt and Allamandola (1988); no peak listed near 760 cm⁻¹

^d Pace and Noe (1968)

Table 3
Positions of Selected IR Peaks of High-Temperature Crystalline CH₃CN ^a

Approximate description ^a	This work 81 K ^b	Literature 77 K ^c	Literature 95 K ^d	Literature 223 K ^e
C-H asymm stretch	3000	3002	3000 2989	3000.7
C-H symm stretch	2940	2940	2939	2941.0
C≡N stretch	2251	2252	2251 2247	2252.0
combination bands	1454 1451 1448	1456.0 1453.0 1449.5	1455 1452 1449 1445	1447.9
CH ₃ asymm deformation	1420 1416 1408	1421.5 1417.8 1409.5	1421 1417 1408	1415.3
CH ₃ symm deformation	1378 1372	1379.0 1372.7	1379 1372 1369	1376.2 1370.7
CH ₃ rock	1049 1040 1036	1048.0 1039.2 1035.0	1049 1040 1036 1032	1044.8 1040
C-C stretch	918	917.8	918, 915	917.8
overtone	793, 775	---	786, 776	753

^a Positions in cm⁻¹; assignments from Milligan and Jacox (1962), Pace and Noe (1968), Dello Russo and Khanna (1995), and references therein.

^b This work

^c Milligan and Jacox (1962); prepared by vapor-phase deposition

^d Dello Russo and Khanna (1995); prepared by vapor-phase deposition

^e Pace and Noe (1968); prepared by cooling liquid CH₃CN

Table 4
Positions of Selected IR Peaks of Low-Temperature Crystalline CH₃CN ^a

Approximate description ^a	This work 120 K ^b	This work 81 K ^b	Literature 81 K ^c
C-H asymm stretch	2996	2996	2995.7
C-H symm stretch	2937 2934	2936 2934	2933.2
C≡N stretch	2247	2247	2247.3
combination bands	1457 1453	1458 1454	1457 1456.2 1452.1
CH ₃ asymm deformation	1424 1420	1425 1420	1436.1 1425.4 1421.4 1419.4
CH ₃ symm deformation	1371 1368 1366	1370 1368 1366	1370.1 1367.9 1365.9
CH ₃ rock	1044 1039 1038	1043 1039 1038	1043.3 1039.4 1034.2
C-C stretch	920 918	920 918	920.5, 919.0, 915.4
overtone	778	779	779.3, 777

^a Positions in cm⁻¹; assignments from Pace and Noe (1968)

^b This work

^c Pace and Noe (1968); prepared by cooling liquid CH₃CN

3.3. $\text{CH}_3\text{CH}_2\text{CN}$, propionitrile

Propionitrile has two crystalline phases under low-pressure conditions, with a melting point of 180 K and a solid-solid transition temperature of 177 K between the two crystalline forms (Weber and Kilpatrick, 1962). With just a 3-K interval of stability for the HT phase of propionitrile, it is not surprising that only the LT crystalline phase has had its structure determined by X-ray methods (Ennis et al., 2018).

We began our propionitrile work with the amorphous form of the ice, measuring n from about 15 to 150 K. Refractive indices for this compound were reported recently (Nna-Mvondo et al., 2019), and in **Figure 3** we compare those values with our new results. The reasons for the differences between the two sets of data are unknown.

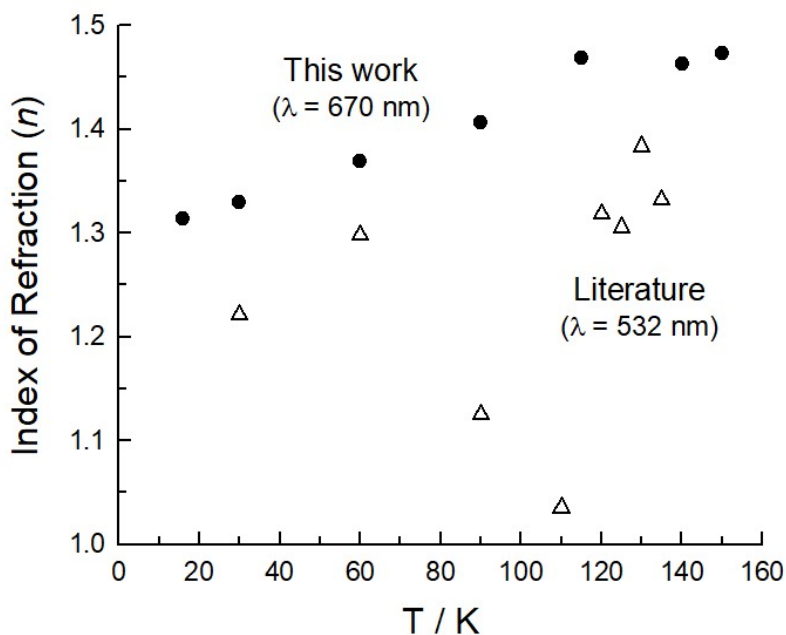


Fig. 3. Index of refraction of propionitrile ices. The literature values are from Nna-Mvondo et al. (2019).

Although mid-IR transmission spectra of solid amorphous propionitrile have been published, enlargements of spectral regions can be hard to find. In **Figure 4** we show a survey spectrum, and **Figure 5** shows expansions of several regions. For comparison, we also include a spectrum of liquid $\text{CH}_3\text{CH}_2\text{CN}$ recorded at room temperature between NaCl plates. As expected, the two spectra are quite similar. Older liquid-phase spectra can be found in Heise et al. (1991) and even in Coblentz (1905).

More significant are our results for crystalline propionitrile. Having made both crystalline forms of CH_3CN after a judicious choice of experimental conditions, we reasoned that we also could make the two forms of crystalline $\text{CH}_3\text{CH}_2\text{CN}$ by similar approaches, and such was the case. **Figures 4 and 5** also show IR spectra of crystalline propionitrile ices made at 150 K by vapor-phase deposition, trace (d) in each case being for an ice either grown quickly (increase in ice's thickness of $\sim 25 \mu\text{m hour}^{-1}$) or by allowing the ice of spectrum (c) to stand at 150 K for 5 - 10 minutes. This dependence of the ice's IR spectrum on deposition temperature and rate was reminiscent of our experience with CH_3CN and also the diffraction work of Tizek et al. (2004). Therefore, in analogy with the behavior of CH_3CN , the IR spectrum of the final, evolved form of solid propionitrile is assigned to the compound's low-temperature phase. **Table 5** summarizes peak positions for both crystalline phases of propionitrile. During the HT $\rightarrow$ LT conversion, isosbestic points were seen near 2991, 2949, 1462, 1265, 1074, and 1011 cm^{-1} , consistent with the interpretation that the spectra were from just two absorbers, the two crystalline phases of propionitrile.

Propionitrile IR spectra other than those shown here were observed during crystallization and during the HT $\rightarrow$ LT conversion, presumably from conformational changes, but have not been studied. We emphasize that regardless of the method of sample preparation and treatment, the resulting IR spectrum either resembled one of the two seen at the bottom of **Figure 4** or it evolved into one of them.

Our n_{670} values in **Table 1** can be used to determine ice thicknesses by interferometry (i.e., interference fringes), but it is often convenient to have a direct measure of ice thickness from a spectrum itself. For this reason, we calculated the apparent absorption coefficient (α') of three IR peaks of crystalline propionitrile. For the HT phase we found $\alpha'(1467 \text{ cm}^{-1}) = 2300 \text{ cm}^{-1}$ and for the LT phase we obtained $\alpha'(1458 \text{ cm}^{-1}) = 2980 \text{ cm}^{-1}$, both at 150 K. The IR peak near 780 cm^{-1} underwent little change as the HT phase converted into the LT one. For it we measured $\alpha'(780 \text{ cm}^{-1}) = 1580 \text{ cm}^{-1}$. Ice thicknesses can be calculated from $2.303 \times (\text{peak's absorbance}) / \alpha'$. These values of α' are for a spectral resolution of 2 cm^{-1} .

3.4. Far-IR spectra

No new far-IR work was done for this paper, but the archival far-IR spectra from Moore et al. (2010) were examined. It was found that amorphous propionitrile ices made at 50 K and warmed to 140 K had peaks near 547, 387, and 226 cm^{-1} , but that they shifted to 546, 392, and 221 cm^{-1} over several hours at 140 K. A different sample prepared by vapor-phase deposition at 140 K had peaks near 546, 392, and 221 cm^{-1} that did not change position. Dello Russo and Khanna (1996) and Khanna (2005) reported far-IR peaks within 1 cm^{-1} of those given here. An attractive interpretation for these results is that the first three peaks listed are for propionitrile's HT crystalline phase and the second set are for the LT phase, but more work is needed to test this interpretation.

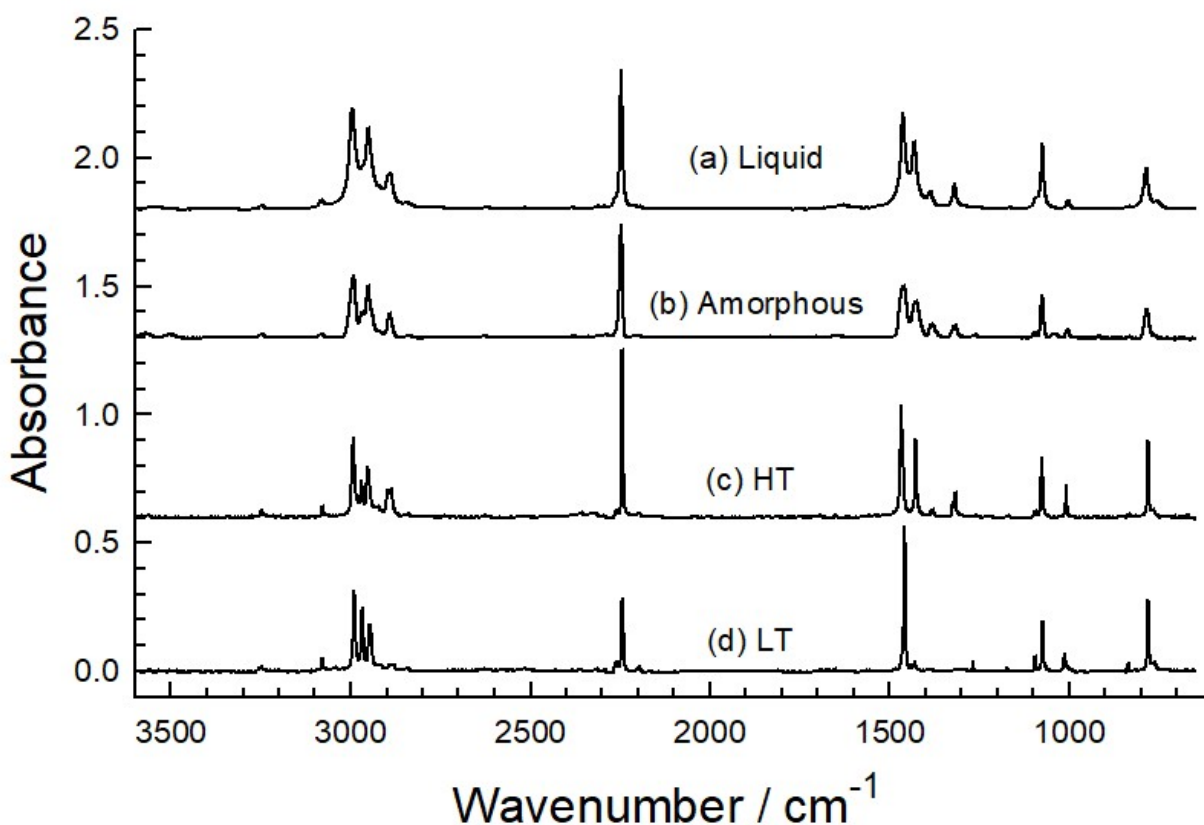


Fig. 4. Four IR survey spectra of $\text{CH}_3\text{CH}_2\text{CN}$. Spectrum (a) is of a liquid sample near 290 K, spectrum (b) is of an amorphous ice at 9 K, and spectrum (c) is for a high-temperature crystalline sample made by deposition at 150 K. Thicknesses were not measured for (a) and (b), and the two spectra have simply been scaled vertically to roughly match. The thickness of the ice sample in (c) was $\sim 4 \mu\text{m}$. Spectrum (d) was of the same sample from (c), but recorded at 150 K about 5 minutes after standing at that temperature. Spectra have been offset vertically for clarity. The spectral resolution was 2 cm^{-1} .

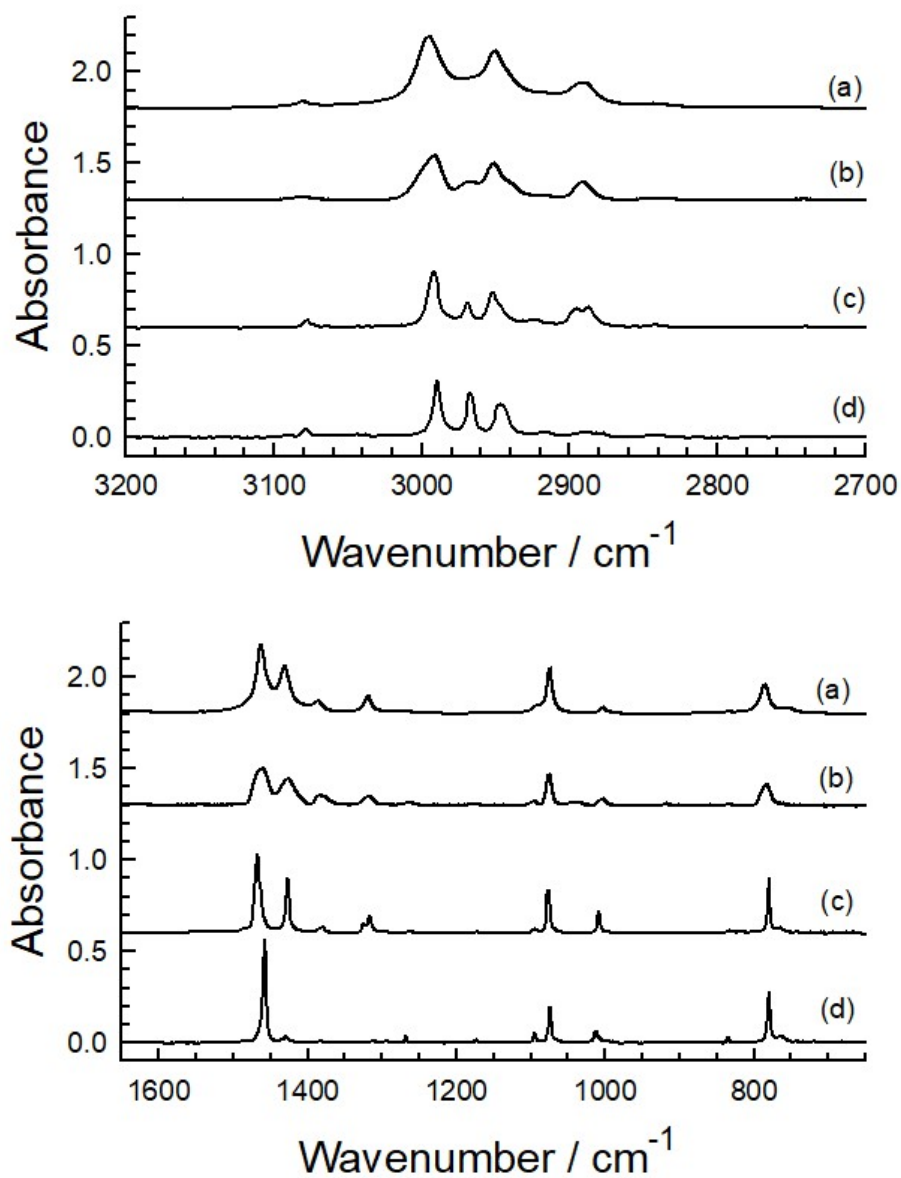


Fig. 5. Expansions of IR spectra of $\text{CH}_3\text{CH}_2\text{CN}$. See the caption of Figure 4 for details.

Table 5
Positions of Selected IR Peaks of Crystalline CH₃CH₂CN ^a

Approximate description ^b	High- temperature phase, 150 K	Low- temperature phase, 150 K ^c
CH ₃ asymm stretch	2992	2990
CH ₂ asymm stretch	2969	2967
CH ₃ symm stretch	2952	2947
CH ₂ symm stretch	2896 2887	
C≡N stretch	2244	2244
CH ₃ asymm bend	1467	
CH ₂ bend	1427	1458
CH ₃ symm bend	1382	
CH ₂ wag	1325 1317	
CH ₂ twist	1263	1268
CH ₂ rock + CH ₃ rock + CH ₂ twist	1095	1095
CH ₃ rock + CC stretch	1076	1074
CH ₃ wag + CC stretch	1008	1013
CH ₃ rock + CC stretch + CCN bend	835	835
CH ₃ rock + CH ₂ rock	780	780

^a Positions in cm⁻¹

^b For assignments, see Heise et al. (1981), Crowder (1986), and Dello Russo and Khanna (1996).

^c Missing positions correspond to peaks that were substantially broadened to the point of almost no intensity.

4. Discussion

4.1. Density and refractive index results

The consistency of our density and refractive index measurements can be tested by calculating the molar refraction (R_M) of each compound using equation (1), where M is the compound's molar mass in g mol^{-1} .

$$R_M = \left(\frac{M}{\rho}\right) \left(\frac{n^2 - 1}{n^2 + 2}\right) \quad (1)$$

Since contributions of individual chemical bonds to R_M are roughly constant for each bond type (e.g., Denbigh, 1940), and since HCN, CH_3CN , and $\text{CH}_3\text{CH}_2\text{CN}$ differ by increments of CH_2 , then a linear relation is expected between R_M and the number of carbon atoms in each compound. **Figure 6** shows that this expectation was met for our amorphous and crystalline nitriles. See Hudson and Coleman (2019) for a recent example of the use of R_M to check data on ices.

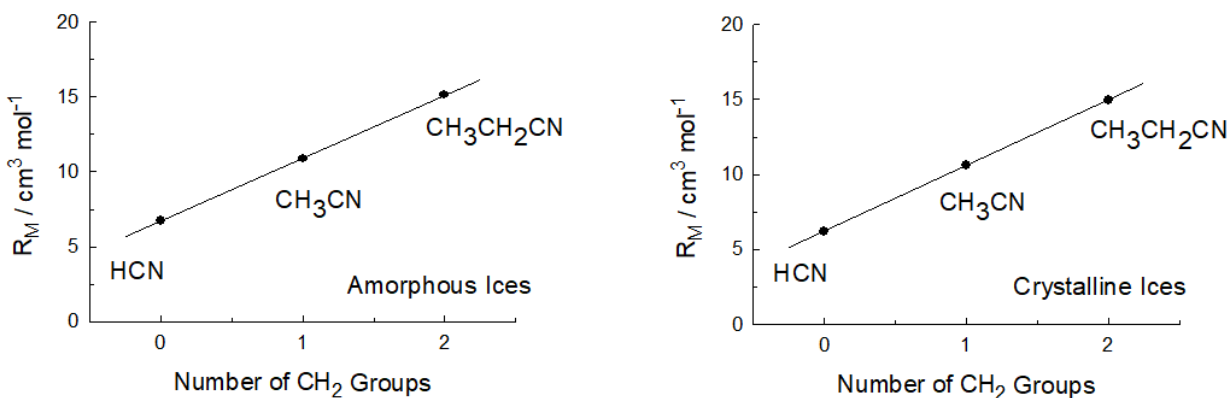


Fig. 6. Molar refractions of three organic compounds. The left-hand plot is for amorphous ices and the right-hand plot is for crystalline ices. See Table 1 for the n and ρ values used to calculate R_M .

Figure 3 shows a substantial discrepancy between our n values for propionitrile and those recently published (Nna-Mvondo et al., 2019). The range in n for the latter seems quite large, and the $n(110\text{ K}) = 1.035$ seems unusually small ($n_{\text{air}} \sim 1$). In our acetylene (C_2H_2) work, we saw an unexpected drop in n with temperature in the region of a crystallization (Hudson et al., 2014a). Difficulties in measuring n in the temperature region of phase changes or crystallizations are suspected.

4.2. Relation to previous work - CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$

Quantitative comparisons to published spectra often are hindered by no thickness being stated for an ice sample, no numerical scale included for transmission or absorbance, and differences in temperature and the way the spectra were recorded (e.g., reflection mode). Even qualitative comparisons for the presence or absence of IR peaks, peak positions, and the shapes of IR bands can be difficult. Further, as of this writing (November 2019) the nitrile results of Moore et al. (2010) appear to be the only ones that are freely and readily available in electronic form. Nevertheless, it is possible to make a few qualitative statements about previous spectroscopic work and its relation to what is presented here.

For CH_3CN , our **Tables 2 - 4** show good agreement between our IR spectral positions for the amorphous and crystalline solids and those found in the literature. Such comparisons confirm that the crystalline ices studied by Milligan and Jacox (1962), Dello Russo and Khanna (1996), Moore et al. (2010), and apparently all others doing similar work were indeed for the high-temperature phase of acetonitrile. The same applies to the CH_3CN work of Ennis et al. (2017), as those authors clearly noted. The paper of Pace and Noe (1968) reported data for the low-temperature phase of CH_3CN , prepared by cooling a room-temperature liquid. The close agreement between their IR spectra and ours shows that the LT phase can also be made, with care, by vapor-phase deposition.

For $\text{CH}_3\text{CH}_2\text{CN}$, the spectra in our **Figures 4 and 5** show differences for the compound's two crystalline forms, differences that can be used to help identify the phases of $\text{CH}_3\text{CH}_2\text{CN}$ in previous work. There are dramatic differences in the 1500 to 1400 cm^{-1} region and in the relative intensities for the peaks at 3000 to 2900 cm^{-1} . Perhaps more significant is that the compound's HT phase has distinct IR features near 2891, 1382, 1321 cm^{-1} that are lacking, or at least considerably weakened, in the LT phase.

The oldest work on icy $\text{CH}_3\text{CH}_2\text{CN}$ we have examined is that of Wurrey et al. (1977). No solid-phase IR spectra were shown, but the authors did present an extensive table of peak positions. Peaks observed at 2897, 1381, and 1323 cm^{-1} suggest that the ice made at 83 K and then annealed (details not given) had at least some of the HT crystalline phase in it. The peak listed at 1457 cm^{-1} could be for the LT phase, but without a spectrum it is impossible to tell.

Dello Russo and Khanna (1996) published a careful, extensive spectroscopic study of eight nitriles including $\text{CH}_3\text{CH}_2\text{CN}$ that was heated to 140 K following deposition at 15 K (Khanna et al., 2005). Propionitrile peaks near 1380 and 1310 cm^{-1} , found in the authors' Figure 2 and Table III, show that the ice sample contained at least some of the HT phase, but no enlargements were shown from which to draw a more definitive conclusion.

The paper of Khanna (2005) is particularly interesting. The author's Figure 2 shows IR spectra for a propionitrile ice made at 60 K, warmed to 120 K, and then cooled and warmed to other temperatures for recording spectra. At 15 K, peaks are found near 2890, 1380, 1320 cm^{-1} , indicative of the HT form of propionitrile, along with what appear to be that phase's two sharp peaks near 1468 and 1427 cm^{-1} . As the ice's temperature was raised to 150 K, those two peaks changed to just one near 1458 cm^{-1} and the aforementioned three were lost, all signs that the ice was converting into the LT phase. This is the earliest IR observation we have found suggesting the HT $\rightarrow$ LT conversion by warming a propionitrile ice. Unfortunately, several spectral regions were obscured by the cryo-deposition of H_2O -ice onto the author's sample, the H_2O coming from the author's vacuum system.

Figures 12 and 13 in Moore et al. (2010) show a mid-IR survey spectrum for propionitrile at 95 K. Enlargements in Figure 10 compare spectra of ices made by (trace b) warming an amorphous sample from 50 to 140 K and (trace c) by depositing $\text{CH}_3\text{CH}_2\text{CN}$ at 140 K. Using the present paper's **Figures 4 and 5** we now can identify both of those earlier samples as being HT crystalline propionitrile, with perhaps some amount of LT mixed in. Had each ice been held longer at 140 K, or warmed slightly, we now know that either sublimation or a conversion to the LT spectrum of our **Figures 4 and 5** would have resulted.

The paper of Couturier-Tanburelli et al. (2017) presents a different difficulty as their spectra were not recorded by transmission, but rather in a reflection mode, which can alter observed band intensities (e.g., Maeda and Schatz, 1961; Pacansky and England, 1986). Those same authors mentioned the similarity of their propionitrile spectra to those in our earlier paper (Moore et al., 2010), and we agree as concerns peak positions, but the relative intensities of some of the IR features listed are slightly different from ours. As for their ice's phase, IR peaks near 2900, 1375, and 1313 cm^{-1} show that it was either partially or wholly in the HT crystalline phase when warmed from 20 to 125 K. We have observed similar spectra which, on additional warming, appear to give rise solely to the LT phase of propionitrile. Despite a few differences between our spectra and those of Couturier-Tamburelli et al. (2017), their work agrees with ours for an ice that has not quite reached a stage of conformational equilibrium. We do not expect those author's photochemical results, an important part of their paper, to change because of the new spectra presented here.

The recent paper of Nna-Mvondo et al. (2019) has an extensive set of far-IR data, but the few mid-IR spectra presented are on a small scale, hindering firm comparisons to previous work and efforts to identify the phase of the authors' crystalline sample. Those authors' Table 3 gives peak positions for propionitrile at 135 K, with three intense features listed for the 1470 to 1430 cm^{-1} region, along with IR peaks at 2893, 1383, and 1311 cm^{-1} . From our preceding comments on other papers, and from comparisons to our **Figures 4 and 5**, we conclude that the $\text{CH}_3\text{CH}_2\text{CN}$ ice of Nna-Mvondo et al. (2019) at 135 K was a mixture of the LT and HT crystalline phases of the compound, or perhaps wholly the HT phase. No spectra were shown to illustrate how the authors' ices changed on warming, no recognition was made of the two crystalline

propionitrile phases found by calorimetry (Weber and Kilpatrick, 1962), and no comparisons were made between the spectroscopic behaviors of propionitrile and its smaller homolog, CH₃CN.

The astrochemical publications that most directly address the formation, IR spectra, and structure of crystalline nitriles are those of Ennis and colleagues (Ennis et al., 2017, 2018). Their CH₃CN and CH₃CH₂CN ices were made in a collisional cooling cell, IR spectra of solid CH₃CN and CH₃CH₂CN at 110 K were presented, and peak positions at 95 K were tabulated. From comparisons to the work of Dello Russo and Khanna (1996) the HT crystalline phase of CH₃CN was identified, but the authors explicitly noted that an identification of the propionitrile phase was impossible due to the "insufficient literature" on CH₃CH₂CN. The two lower traces of our **Figures 4 and 5**, and the peak positions in our tables, show that the ice of Ennis et al. (2017) was dominated by the HT crystalline phase, for reasons similar to those already mentioned for the ices of Nna-Mvondo et al. (2019) and others. In fact, the agreement between the CH₃CH₂CN spectra of Ennis et al. (2017) and our own HT ice appears to be excellent.

To summarize this examination of published mid-IR spectra of crystalline propionitrile, nearly all work to date appears to have produced ices that were somewhere between partially and entirely in the HT phase, in agreement with expectations from CH₃CN. It is perhaps ironic that the poor vacuum system of Khanna (2005) allowed him to warm his CH₃CH₂CN ice to a temperature high enough to initiate the HT-LT phase change without sublimation, although the H₂O-ice that cryo-deposited from that same vacuum system also obscured several spectral regions.

Having compared our crystalline propionitrile spectra to those already published, we end this section with a comparison between our results and those for the liquid and gas phases, starting with propionitrile's C≡N stretching band near 2250 cm⁻¹. The spectra of Duncan and Janz (1955) show that the relative intensity of this feature increases considerably on going from the gas phase to the liquid, a change that also can be seen by comparing the gas-phase spectrum of Wurrey et al. (1977) to the liquid-phase spectrum of Heise et al. (1981). This relative increase in intensity for the C≡N stretch resembles the change in our **Figure 4** in the C≡N peak height on going from the monomer-based LT crystalline phase to the dimer-based HT phase, a change from a phase dominated by isolated molecules to one of dimeric, or at least interacting, species (*vide infra*). Also in **Figure 4**, the simplification in the 1500 - 1400 cm⁻¹ region on going from the HT form (two strong peaks) to the LT form (one strong peak) is similar to the simplification found with propionitrile on going from the liquid phase (two strong peaks) to the gas phase (one strong peak). See also the compilation of Pouchert (1997) for room-temperature spectra.

4.3. Formation of crystalline phases

Our results and the preceding discussion show that the formation and IR identification of molecular ice phases can be considerably more complex than is

apparent *a priori*. Variations in lab-to-lab procedures and equipment, such as the cooling capacities of cryostats, can alter the rates and temperatures of crystallization. Also, Jacox (1962) noted that the "appreciable heat" released on gas-phase deposition can mean that an ice's temperature differs from that registered by a temperature-reading device, such as a thermocouple or diode, comments echoed by Mizuno et al. (2016) in their work on amorphous CO₂. Moreover, simply warming an amorphous ice does not, as perhaps intuitively expected, always lead to the most thermodynamically stable crystalline solid, but rather to the most kinetically favored one. For more on this point, see the discussion of Tizek et al. (2004). In short, lab-to-lab variations do not necessarily prove the "non-reproducibility" of a preparation, warming, or annealing method (Nna-Mvondo et al., 2019), but rather the difficulties one can encounter, often unrecognized without further investigation and appreciation of chemical complexities.

We should add here that of the nitrile IR spectra we have examined (Moore et al., 2010) those of propionitrile are the most complicated, and for that reason we have made no attempt to document and assign every small feature observed in each phase, such as the numerous overtone and combination bands present (Heise et al., 1981). Sufficient information has been included here for others to prepare CH₃CH₂CN ices and to determine their phases.

In analogy with acetonitrile, one expects the HT phase of propionitrile to be characterized by centrosymmetric anti-parallel dimers, meaning that the dipole moments of the members of a nitrile pair point in opposite directions (Ford and Glasser, 2001). In contrast, the molecules of the LT phase of propionitrile are expected to have dipole moments in the same direction in parallel chains (Torrie and Powell, 1992). As anti-parallel dimers are expected for the amorphous solid, the kinetically favored product (Ostwald step rule) on crystallization is the HT phase. Formation of the more-stable LT phase below ~180 K is achieved on laboratory timescales by using the heat released on rapid condensation to overcome the energy barrier to the crystalline-crystalline phase change. Again, see Tizek et al. (2004) for structural details, including their observations of how the deposition rate and temperature for ice formation influence the phase of the ice that results on warming. Our IR results for both CH₃CN and CH₃CH₂CN agree with those authors' diffraction studies, and verify the prediction of a similar behavior for the two nitriles. Those same authors also found that experimental conditions can alter the temperature at which an amorphous solid crystallizes (Tizek et al., 2004). In short, both the temperature and the product of a crystallization can depend on the sample's preparation and history.

4.4. Astrochemical applications and future work

One motivation for the decades-long study of solid CH₃CH₂CN by planetary scientists has been the observation by both the Voyager and Cassini missions of an emission feature near 221 cm⁻¹ in the far-IR spectra of Titan (e.g., Kunde et al., 1981; Coustenis et al., 1999; Jennings et al., 2012). Our results show that the laboratory measurements of propionitrile used to interpret such spacecraft data have been based

on ices that are, in nearly every case, of an unknown or uncertain solid phase and perhaps even of questionable relevance. Specifically, Titan's atmosphere is much below propionitrile's LT-HT transition temperature, yet much of previous laboratory work has involved the HT crystalline phase, although in some cases the phase cannot be identified. In this paper we have provided sufficient information so that ambiguities in ice-phase identification, regardless of the spectral region studied, should be considerably less if not removed entirely.

Future work on propionitrile, and also acetonitrile, will benefit from the spectra and n and ρ data presented here, such as for studying how these nitriles and their reaction products might contribute to Titan's atmosphere. Investigations of ice mixtures involving our nitriles can use our results for calibrations of each component's abundance. Other suggestions for future investigation include the following:

- X-ray diffraction results are needed for both crystalline forms of propionitrile.
- An analysis of the IR spectra of both crystalline phases of $\text{CH}_3\text{CH}_2\text{CN}$ is needed, making use of diffraction results.
- Higher-resolution IR spectra are needed for both crystalline phases of propionitrile, particularly in the $1500 - 1400 \text{ cm}^{-1}$ region.
- A reassessment of IR intensities, such as absorption coefficients and band strengths, is needed for crystalline propionitrile.
- Band strengths for each propionitrile phase can be used to measure solid-phase vapor pressures for the compound (Khanna et al., 1990).
- Extensions to the near- and far-IR regions are needed, the latter being particularly important for Titan work. For example, from the work of Dello Russo and Khanna (1996) and Khanna (2005), it appears that a far-IR peak of HT crystalline propionitrile near 226 cm^{-1} shifts to about 221 cm^{-1} for the LT temperature phase, which is near the aforementioned IR feature in Titan's atmosphere.
- Studies by differential scanning calorimetry of the exo-/endothermic changes accompanying the crystallizations and phases changes of the nitriles we examined.
- Computational studies of the crystalline forms of propionitrile are needed, with a start already found in Ennis et al. (2018).
- Knowing that the two simplest alkyl nitriles behave in similar ways, it would be useful to know if other members of the $\text{H}(\text{CH}_2)_n\text{CN}$ series, such as butyronitrile ($n = 3$), do the same.

Finally, we suggest that the methods and equipment we have used for studying crystalline nitriles, involving vacuum systems and closed-cycle cryostats, may not always be necessary or even desirable. Closed cells cooled with liquid nitrogen may be preferable in some cases, preventing sublimation.

5. Summary

Two nitrile ices have been examined in this paper, those made from CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$. Both the high- and low-temperature crystalline forms of CH_3CN were prepared by vapor phase deposition, the low-temperature form for perhaps the first time with this method. Lessons learned from acetonitrile were combined with a knowledge of the relevant thermodynamic and spectroscopic literature to isolate two crystalline phases of propionitrile, one identified and characterized here spectroscopically for the first time. These new results were used to reexamine seemingly disparate studies from the past 40+ years, including multiple publications of propionitrile IR spectra related to Titan from the Voyager and Cassini missions. Propionitrile's low-temperature crystalline phases have now been made and characterized by infrared spectroscopy, and the results should be useful as the other problems we have listed are addressed.

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