

# Amorphous 1-propanol in interstellar ices – crystallization revisited

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## ABSTRACT

A recent publication described laboratory measurements of infrared spectra of solid 1-propanol, a likely interstellar ice component. The authors concluded that amorphous 1-propanol does not produce crystalline 1-propanol on warming and that 1-propanol remains as a solid far above its melting point. New laboratory results presented here show that both conclusions are false. A spectrum of crystalline 1-propanol is presented along with the first band strengths for two infrared features in both the amorphous and crystalline forms of the compound. Extensions and astrochemical applications are described.

**Key words:** astrochemistry – molecular data – methods: laboratory: molecular – methods: laboratory: solid state – ISM: molecules.

## 1 INTRODUCTION

The only alcohols reported as solids in the interstellar medium (ISM) are methanol (CH<sub>3</sub>OH), for which firm identifications have been published, and ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), for which only suggestive identifications have been reported (Allamandola et al. 1992; Boudin et al. 1998; McClure et al. 2023; Rocha et al. 2024). Given the ease with which methanol and ethanol can be made in low-temperature ices (e.g. Moore & Hudson 1998), it is reasonable to expect that 1-propanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH) and other straight-chain aliphatic alcohols might also be part of interstellar ice mantles. Gas-phase 1-propanol has been identified in the ISM by two different groups (Belloche et al. 2022; Jiménez-Serra et al. 2022).

A study of solid 1-propanol recently appeared in this journal and included infrared (IR) spectra of 1-propanol, vacuum-UV (VUV) spectra of the compound, and molecular dynamics simulations of the IR spectra and structure of 1-propanol ices (Ramachandran et al. 2024). The authors' results led them to draw two interesting conclusions. First, it was stated that amorphous 1-propanol can be heated under vacuum to sublimation without ever crystallizing. Secondly, the authors reported that 1-propanol remains in the solid form beyond its melting temperature. These two conclusions are sufficiently counterintuitive and contrary to expectations based on previous laboratory work that they deserve closer examination. Therefore, new laboratory results are presented here for solid amorphous 1-propanol as studied by IR spectroscopy, new work that contradicts both of the qualitative conclusions of Ramachandran and 15 co-authors (Ramachandran et al. 2024).

## 2 EXPERIMENTAL METHODS

The methods and procedures used were as described in our group's previous papers in this journal (e.g. Hudson & Gerakines 2019; Gerakines et al. 2023). In short, 1-propanol (Sigma Aldrich, Extra

Dry) was vapour-phase deposited onto a pre-cooled CsI substrate in a vacuum chamber ( $\sim 1 \times 10^{-8}$  Torr) interfaced to an IR spectrometer. Conventional transmission IR spectra were recorded as 200-scan accumulations at a resolution of 1 cm<sup>-1</sup>, with the IR beam perpendicular to the ice and substrate. Growth rates of ice thickness varied from about 1 to 5 μm h<sup>-1</sup> as determined by laser interferometry. The refractive index of amorphous 1-propanol ice at 10 K was taken as  $n = 1.288$  (670 nm) and the density as  $\rho = 0.652$  g cm<sup>-3</sup>, both as reported previously (Hudson et al. 2020). See also Hudson et al. (2017) for more details.

The 1-propanol used was degassed with liquid nitrogen and several freeze-pump-thaw cycles. The liquid was clear and colourless at room temperature and when frozen at 77 K. At no time during the thaw step was there any indication of crystallization, such as cracks, cloudiness, or the formation of small crystallites.

## 3 RESULTS

### 3.1 Infrared spectra – phase changes

Three things helped guide this investigation into the possibility that amorphous 1-propanol does not crystallize under vacuum. First, our research group has examined amorphous forms of dozens of compounds composed of small molecules (less than about 15 atoms), such as alcohols, aldehydes, esters, nitriles, and amines, usually the simplest of their type in a specific chemical family. In every case, the amorphous solid form of the compound was found to crystallize on warming. Secondly, it was known that amorphous ethanol, the next-smaller alcohol to 1-propanol, will crystallize on warming (Hudson 2017) as will 1-butanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), the next larger one (Crowder & Townsend 1977). Finally, it was known that a rich literature exists related to amorphous and crystalline 1-propanol, going back nearly a century (Parks & Huffman 1926). Calorimetric and diffraction studies have shown that 1-propanol will crystallize when an amorphous sample is held between the compound's glass-transition temperature,  $\sim 99$  K (e.g. van Miltenburg and van den Berg 2004) and its melting point,  $\sim 149$  K (Takahara et al. 1994).

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Several papers (e.g. Talón et al. 2002; Ramos et al. 2013) have used a temperature near 130 K for crystallization, and so 130 K was used for this study.

The bottom trace of Fig. 1 is an IR spectrum of an amorphous 1-propanol ice made at 10 K with a thickness of about 2  $\mu\text{m}$ . The spectrum is essentially identical to one already published here (Hudson & Gerakines 2019). The other spectra in the figure show the result of warming the 10-K ice to the temperatures indicated. These spectra agree qualitatively with those of Ramachandran et al. (2024), but a quantitative comparison between Fig. 1 and the IR spectra of Ramachandran et al. (2024) is impossible as those authors did not state an ice thickness and none of their spectra have a vertical axis with numbers and tick marks with which to compare absorbance values. Some other differences worth noting are that the spectra in Fig. 1 are at a slightly higher resolution (1  $\text{cm}^{-1}$  versus 4  $\text{cm}^{-1}$ ) and that a 100-K spectrum is shown. The changes seen at 100 K near 3300–3200  $\text{cm}^{-1}$  are not shown in the paper of Ramachandran et al. (2024), but could be significant given that the glass transition temperature of 1-propanol is around that temperature. Also, by recooling an ice that had been warmed it was found that the changes seen in Fig. 1 were irreversible. For example, the IR spectrum of an ice that was warmed from 10 to 125 K did not revert to the appearance of the initial spectrum of the 10-K sample when the ice was re-cooled to that temperature.

Few changes were seen after the 1-propanol ice of Fig. 1 was held for about 16 h at 125 K. The ice then was warmed from 125 to 130 K over about 5 min and then was held at 130 K for another 16 h. The resulting band splittings, shifts in peak positions, and intensity changes can be seen by comparing spectra (a) and (b) of Fig. 2. Such differences are characteristic of the changes observed when an amorphous ice crystallizes. Therefore, the middle spectrum in Fig. 2 is assigned to crystalline 1-propanol at 130 K. Recooling the sample to 10 K gave few additional changes, mainly the sharpening of some lines. A subsequent rewarming to 130 K gave the same spectrum as before at 130 K.

Warming this same crystalline 1-propanol ice from 130 K to 147 K at a few degrees per minute hardly changed the spectrum, but holding a few minutes at 148 K caused the crystalline-ice features to weaken substantially. Warming to 149 K and then 150 K completely removed them and gave the IR spectrum (c) at the top of Fig. 2. The melting point of 1-propanol is given by Takahara et al. (1994) as 148.81 K at 1 bar, and since it will scarcely be different in a vacuum system, the top spectrum in Fig. 2 is assigned to liquid 1-propanol. Warming any sample above 150 K gave a slow decrease in all spectral features, as expected, and they were completely gone after a few minutes at 175 K. As a check, 1-propanol vapour was condensed onto the CsI substrate pre-cooled to 160 K. The resulting IR spectrum matched the one at the top of Fig. 2, as expected for the liquid compound. No interference fringes, typical of solids, were observed during 1-propanol condensation at 160 K. That liquid 1-propanol was present under vacuum is attributed to a low vapour pressure of the compound.

In a separate experiment, another amorphous 1-propanol ice was prepared at 10 K and then warmed to 160 K at several degrees per minute, as in Ramachandran et al. (2024), not holding at either 125 K or 130 K for 16 h. The IR spectrum evolved from (a) at the bottom of Fig. 2 to (c) at the top, with no pronounced spectral changes and no crystalline-ice IR features observed. In yet another experiment, 1-propanol was condensed at 55 K, as opposed to 10 K. Warming to and then holding at 130 K gave spectral changes resembling those already shown in Fig. 2.

### 3.2 Infrared spectra – peak positions, band strengths

So few IR spectra of solid 1-propanol have been published that here we present expansions for both the amorphous and crystalline forms. High and low wavenumber regions are seen for 1-propanol at 10 K and 125 K in Figs 3 and 4, taken from the lower- and uppermost traces of Fig. 1. Of the IR features seen in the 10-K spectrum of Fig. 4, the two near 1019 and 968  $\text{cm}^{-1}$ , marked with asterisks, are reasonably strong and well-separated from other absorbances. The areas of those two bands were plotted as a function of thickness for six ices in the usual way (i.e. Beer's Law plots) and from the slopes of the resulting regression lines (correlation coefficients > 0.993), IR band strengths were calculated – see Gerakines et al. (2023) for more details of the calculation or Hollenberg & Dows (1961) for the original description of the method – the apparent band strengths ( $A'$ ) of these features at 10 K were  $A'(1019 \text{ cm}^{-1}) = 2.55 \times 10^{-18} \text{ cm molecule}^{-1}$  and  $A'(968 \text{ cm}^{-1}) = 5.99 \times 10^{-18} \text{ cm molecule}^{-1}$ , with an uncertainty of about 5 per cent in each case. Table 1 lists these two  $A'$  values. With these band strengths it is possible to quantify laboratory spectra of amorphous 1-propanol ices near 10 K. It is also possible to use these two band strengths to find those of other mid-IR features of 1-propanol by forming ratios of band areas, and even to extend such work into the near- and far-IR regions (Gerakines et al. 2005; Giuliano et al. 2014).

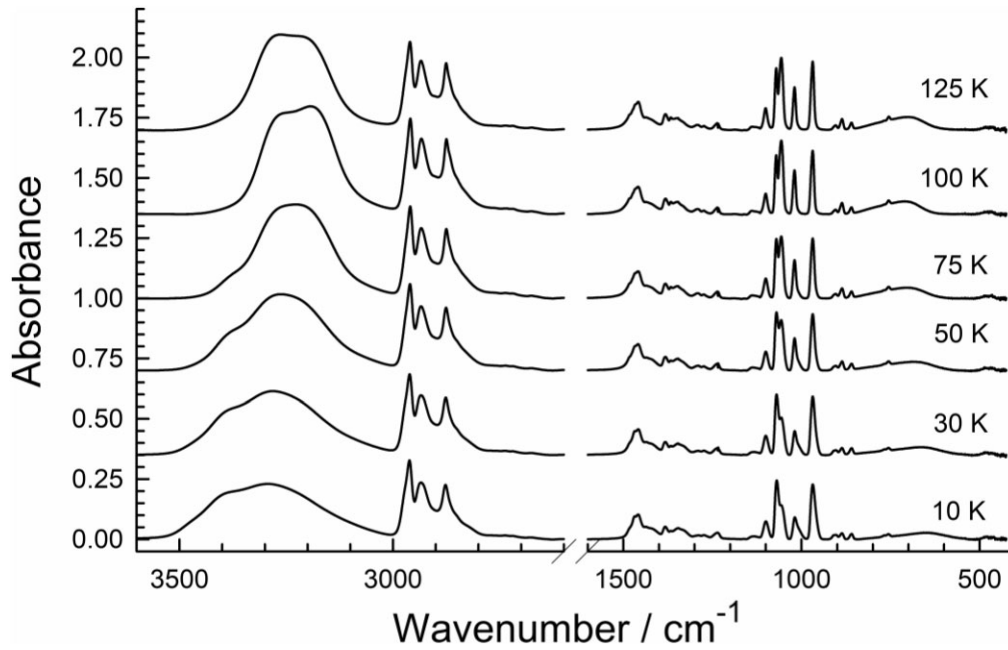
Enlargements of the high- and low-wavenumber regions of the IR spectrum of crystalline 1-propanol are shown in Figs 5 and 6. The ice for these figures was made by depositing 1-propanol at 10 K and then warming to 130 K to crystallize it, as already described, and then recooling to 10 K. No attempt has been made to assign the IR peaks in the crystalline ice, and no literature spectrum has been found for comparison. Two IR band strengths ( $A'$ ) were measured by comparing band areas before and after crystallization. Using the two amorphous-ice band strengths already given,  $A'(1019 \text{ cm}^{-1}) = 2.62 \times 10^{-18} \text{ cm molecule}^{-1}$  and  $A'(970 \text{ cm}^{-1}) = 3.00 \times 10^{-18} \text{ cm molecule}^{-1}$  were found for crystalline 1-propanol at 130 K, again with an uncertainty of about 5 per cent in each case. Table 1 also lists these  $A'$  values. The calculation assumes that there was no change in column density on crystallization.

The  $\sim 5$  per cent uncertainties in  $A'$  values were calculated using both a least-squares routine and a propagation-of-error approach, taking into consideration uncertainties in both  $x$  and  $y$  quantities in the slopes of the Beer's law plots (Hudson & Yarnall 2022).

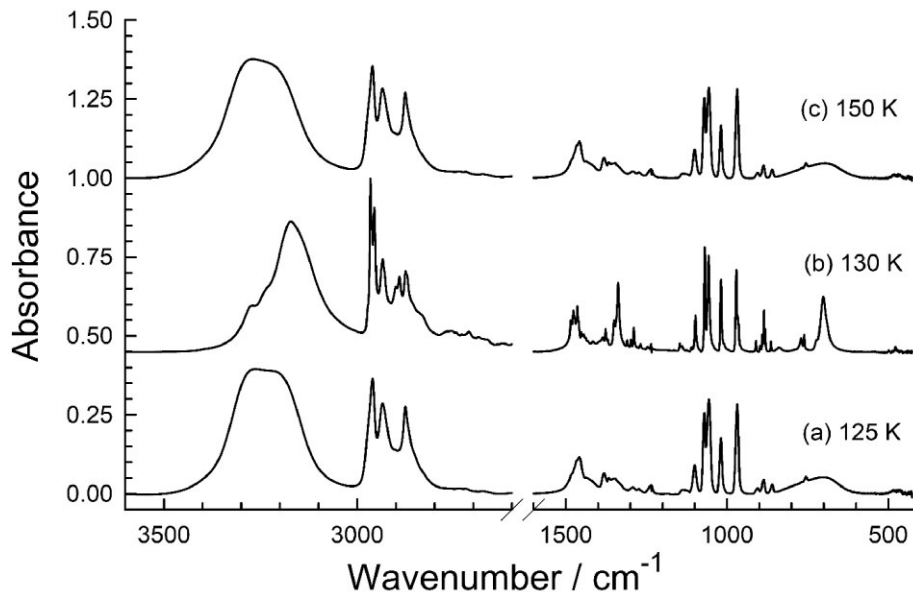
### 3.3 Vapour pressure of 1-propanol

In Section 3.1, 1-propanol's stability above its melting point under vacuum was attributed to the liquid compound's low vapour pressure. Khanna et al. (1990) have described how IR spectra can be used to determine an ice's vapour pressure, and their method was adopted here. A crystalline 1-propanol ice was prepared at 130 K as already described, and then warmed to 160 K to melt it. The resulting liquid sample was held at that temperature for  $\sim 3.5$  h, during which time the IR bands of 1-propanol at 1019 and 968  $\text{cm}^{-1}$  were recorded and integrated as the liquid slowly evaporated. The decreases in column density derived from those areas gave the average flux ( $F$ ) of vapourizing 1-propanol molecules as  $9.3 \times 10^{13} \text{ molecules cm}^{-2} \text{ s}^{-1}$  from which, using equation (1) below, a vapour pressure of  $2.6 \times 10^{-7} \text{ Torr}$  at 160 K was calculated. The  $m$  in (1) is the mass of a 1-propanol molecule. See Khanna et al. (1990) for details of the calculation.

$$p = F \sqrt{2 \pi m k T} \quad (1)$$



**Figure 1.** Infrared spectra of amorphous 1-propanol made and recorded at 10 K and then warmed to the temperatures indicated. The ice’s initial thickness was approximately 2  $\mu\text{m}$ . Spectra have been offset vertically for clarity.



**Figure 2.** Infrared spectra of 1-propanol made at 10 K and then warmed and held for 16 h at 125 K to give spectrum (a), then warmed and held 16 h at 130 K to give (b), and then warmed to 150 K to give (c). As before, the ice’s initial thickness was  $\sim 2 \mu\text{m}$  and spectra have been offset vertically for clarity.

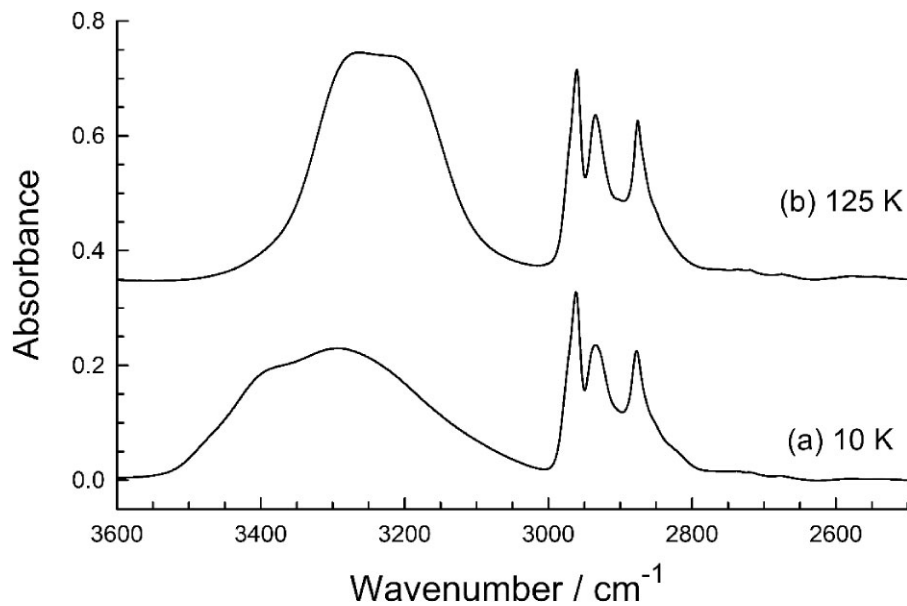
## 4 DISCUSSION

### 4.1 Infrared spectra and phase changes

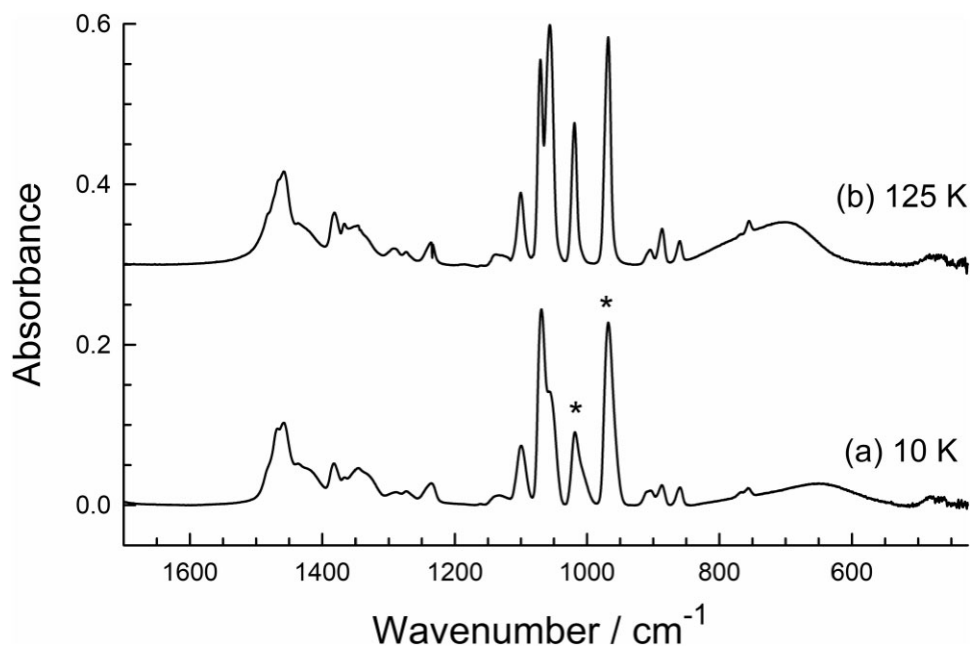
The spectra in Fig. 2 show that crystalline 1-propanol can indeed be made by warming the amorphous compound under vacuum and that crystalline 1-propanol will liquefy when warmed past its melting point. The key factors in producing crystalline 1-propanol were ice formation at a low temperature followed by slow warming and a pause for crystallization. Examination of the literature on 1-propanol clearly shows that hours to days have been needed for crystallization

(Takahara et al. 1994; van Miltenburg and van den Berg 2004; Konstantinov et al. 2017). Given the resemblance of the IR spectra of amorphous and liquid 1-propanol, it should be emphasized that warming an amorphous sample quickly with an insufficient pause for crystallization can give the false impression of an ice that does not melt when warmed past its melting point.

The spectra of 1-propanol in Fig. 1, and particularly the spectrum for 125 K, strongly resemble that of liquid 1-propanol, for which IR peak assignments were given by Fukushima & Zwolinski (1968), Max et al. (2002), and Michniewicz et al. (2008), and which are summarized in Table 2. A change in the relative peak heights for



**Figure 3.** Infrared spectra of amorphous 1-propanol made at 10 K and then warmed to 125 K. The upper spectrum has been offset vertically by 0.35 for clarity.



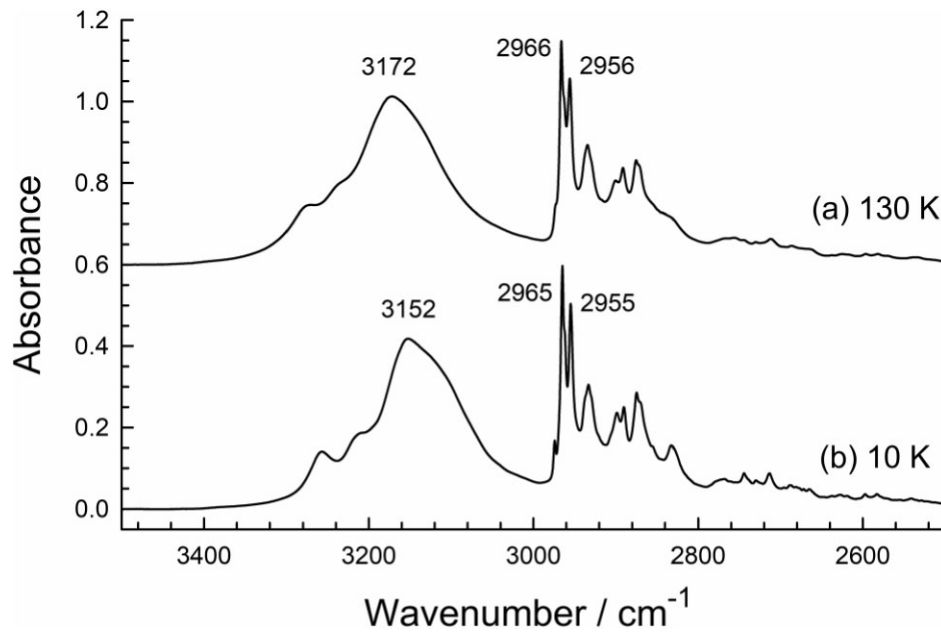
**Figure 4.** Infrared spectra of amorphous 1-propanol made at 10 K and then warmed to 125 K. The upper spectrum has been offset vertically by 0.30 for clarity. Asterisks mark two features for band-strength measurements.

**Table 1.** IR band strengths for 1-propanol.<sup>a</sup>

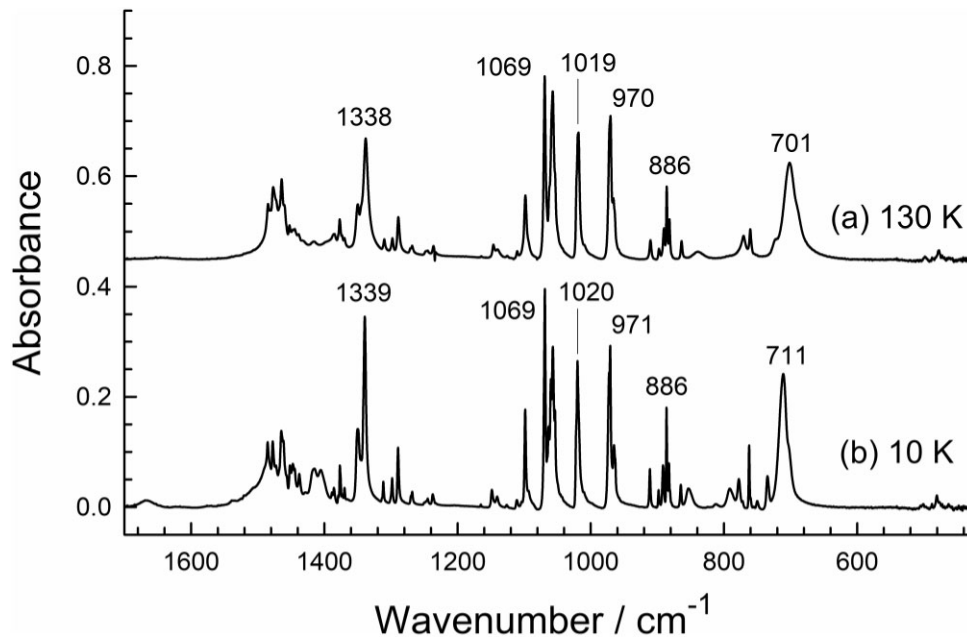
State of ice	T/K	Position <sup>b</sup> /cm <sup>-1</sup>	Integration Range/cm <sup>-1</sup>	$A'/10^{-18}$ cm molecule <sup>-1</sup>
amorphous	10	1018	1033–986	2.55
amorphous	10	968	986–936	5.99
crystalline	130	1019	1027–986	2.62
crystalline	130	970	986–936	3.00

<sup>a</sup>Uncertainties in  $A'$  are about 5 per cent.

<sup>b</sup>Positions rounded to the nearest 1 cm<sup>-1</sup>.



**Figure 5.** Infrared spectra of crystalline 1-propanol at 130 K and then cooled to 10 K. The upper spectrum has been offset vertically by 0.6 for clarity. Positions of three peaks are given, each to the nearest  $1\text{ cm}^{-1}$ .



**Figure 6.** Infrared spectra of crystalline 1-propanol made 130 K and then cooled to 10 K. The upper spectrum has been offset vertically by 0.45 for clarity. Positions of four peaks are given, each to the nearest  $1\text{ cm}^{-1}$ .

features near  $1069$  and  $1056\text{ cm}^{-1}$  with temperature was seen as the temperature was raised above 10 K, the absorbance at  $1056\text{ cm}^{-1}$  growing while that near  $1069\text{ cm}^{-1}$  remained about the same. As five different conformational isomers of 1-propanol are known (e.g. Jiménez-Serra et al. 2022), it is tempting to attribute the changes observed near  $1069$  and  $1056\text{ cm}^{-1}$  with temperature to the conversion of one isomer into another. However, more work is needed to support or refute this suggestion as the differences in IR spectra among these isomers seem to be small (Michniewicz et al. 2008). See our study of amorphous cyclopropanecarboxaldehyde for

an example of a low-temperature conformational change in an ice (Hudson & Coleman 2019).

The two IR band strengths reported here for amorphous 1-propanol appear to be the first published, so comparison possibilities are limited. However, our group has measured band strengths for the C-O stretch of both methanol and ethanol. The comparison is  $A'$  ( $\text{CH}_3\text{OH}$ ,  $1028\text{ cm}^{-1}$ ) =  $16.2 \times 10^{-18}$ ,  $A'$  ( $\text{CH}_3\text{CH}_2\text{OH}$ ,  $1050\text{ cm}^{-1}$ ) =  $14.1 \times 10^{-18}$ ,  $A'$  ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ,  $968\text{ cm}^{-1}$ ) =  $5.99 \times 10^{-18}\text{ cm molecule}^{-1}$ . The value for  $\text{CH}_3\text{OH}$  is from Hudson et al. (2024), while that for  $\text{CH}_3\text{CH}_2\text{OH}$  is from Hudson (2017). All are for



**Table 2.** IR positions and assignment for 1-propanol.

Amorphous ice <sup>a</sup>	Liquid <sup>b</sup>	Assignment <sup>b</sup>
3292.8	3333.3	OH stretch (associated)
2961.5	2963.4	CH <sub>3</sub> asymm stretch
2934.5	2936.7	CH <sub>2</sub> asymm stretch
2877.1	2878.2	CH <sub>2</sub> (1) symm stretch
1458.2	1457.4	CH <sub>3</sub> asymm distortion
1382.3	1383.1	CH <sub>3</sub> symm distortion
1346.3	1346.3	CH <sub>2</sub> (1) wag
1235.8	1235.2	CH <sub>2</sub> (1) twist
1133.6	1132.4	CH <sub>2</sub> (1) rock
1099.6	1099.9	CH <sub>3</sub> rock
1069.0	1069.4	CH <sub>3</sub> -CH <sub>3</sub> , C-O stretches
1018.4	1017.5	CH <sub>3</sub> -CH <sub>2</sub> , CH <sub>2</sub> -O torsions
968.1	968.9	CH <sub>2</sub> -O stretch, O-H distortion
886.9	887.4	OH and CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> distortion
859.4	858.4	OH and CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> distortion
756.4	754.1	CH <sub>2</sub> and CH <sub>3</sub> rock
649.6	648.9	C-OH out-of-plan bend
476.6	479.3	O-CH <sub>2</sub> -CH <sub>2</sub> scissor

<sup>a</sup>This work, 10 K amorphous ice.

<sup>b</sup>From Michniewicz et al. (2008), 298 K liquid. Similar assignments are in Fukushima & Zwolinski (1968) and Max et al. (2002).

amorphous ices near 10 K and are of a similar order of magnitude, as expected.

Before leaving this section, it should be said that the phases and phase transitions of the smaller alcohols, such as 1-propanol, are much more complex than described here. A large number of investigations have been conducted on the glassy, amorphous forms of these compounds and the formation of a supercooled liquid or a plastically crystalline solid near the glass-transition temperature of each alcohol (Ramos et al. 2013). The IR methods used here appear to be incapable of unequivocally identifying such changes and their astrochemical relevance is uncertain. Therefore, the results in this paper have been described simply in terms of crystalline and non-crystalline solids and subsequent changes involving sublimation or melting.

#### 4.2 Vapour pressure of 1-propanol

The lowest temperatures we have found for vapour pressures of 1-propanol are from Kemme & Kreps (1969) who studied liquid 1-propanol from 370.5 to 292.4 K. It is dangerous to extrapolate from that range to the ice at 160 K studied here, but no other literature results seem available. Using the Kemme & Kreps data, a standard Clapeyron plot gave an extrapolated vapour pressure of  $2.6 \times 10^{-6}$  Torr at 160 K. Using those authors' constants for the Antoine equation gave an extrapolated vapor pressure of  $3.8 \times 10^{-8}$  Torr at 160 K. Our result,  $2.6 \times 10^{-7}$  Torr at 160 K, sits comfortably between the calculated values, but little else can be said. Since only one ice was studied, with two IR bands being followed, there is ample room for extension and improvement. Vapour pressure measurements with a quartz-crystal microbalance would be useful.

#### 4.3 Connections to other compounds

Knowing that amorphous forms of other relatively small alcohols crystallize on warming it was expected that 1-propanol would do the same, and the results presented here show that to be the case. The changes with temperature of IR spectra of 1-propanol in Figs 1 and 2 are reminiscent of previous work on solid ethanol (Hudson 2017),

a study that was used to reinterpret earlier results on ethanethiol, CH<sub>3</sub>CH<sub>2</sub>SH, from Pavithraa et al. (2017).

Concerning liquefaction, two other compounds that our group has seen liquefy under vacuum are propane (CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>) and propylene (CH<sub>2</sub>CHCH<sub>3</sub>), as reported in Hudson et al. (2021). We now suggest that 1-propanol can be added to ethanol, ethanethiol, propane, and propylene as compounds that can melt in a vacuum system and persist long enough for an IR spectrum to be recorded. These compounds could be useful as calibration standards for checking temperatures of cold substrates under vacuum. See, for example, Grundy et al. (2024). Of course the time that the resulting liquid will persist before evaporation will certainly depend on the size (thickness) of the sample and the background pressure. A sufficiently thin amorphous 1-propanol ice might even undergo sublimation before crystallization, as in the case of ethanol (Burke et al. 2008).

#### 4.4 Interstellar ices and 1-propanol

The gas-phase ethanol-to-1-propanol ratio in the ISM has been reported to be on the order of 10 by Belloche et al. (2022) and Jiménez-Serra et al. (2022). Assuming this reflects the relative abundances of those alcohols in interstellar ice mantles, then the chances of an IR identification of solid 1-propanol are small as the more abundant solid ethanol has not yet been definitively identified. Put another way, the expected abundance of 1-propanol in an interstellar grain mantle is simply too low for an identification with contemporary IR technology even ignoring possible problems due to overlapping IR bands of different solid-phase compounds. The expected low abundance also suggests that 1-propanol will have a negligible influence on the physical properties of extraterrestrial ices, whether the compound is in the amorphous solid, crystalline, or liquid form.

Perhaps 1-propanol's greatest astrochemical relevance is that it can lead to other organic molecules than might be identified in meteorites, cometary ices, and asteroid samples or, on ejection into the gas phase of the ISM, be identified there spectroscopically. This alcohol might also be an indicator of the corresponding aldehyde, propanal (CH<sub>3</sub>CH<sub>2</sub>C(O)H), as alcohol-to-aldehyde oxidation has been shown

to occur in ices exposed to ionizing radiation (Hudson & Moore 2018), although the conversion has yet to be quantified. In fact, no firm reaction yields have been published for an alcohol-to-aldehyde oxidation in an extraterrestrial ice analogue.

#### 4.5 Other comments on a recent paper

This paper has focused on IR spectra related to the work of Ramachandran et al. (2024). For additional comments on the results found there, see the Appendix of this paper.

### 5 SUMMARY AND CONCLUSIONS

New laboratory experiments have now shown that warming amorphous 1-propanol under vacuum will produce crystalline 1-propanol, which then melts on further warming, just as expected. The crystallization is slow compared to that of methanol and ethanol, but can be brought about with sufficient time, which typically is present in abundance in extraterrestrial environments. Two IR band strengths are reported for the first time, as is the mid-IR spectrum of crystalline 1-propanol, to aid in future work. All things considered, it seems doubtful that 1-propanol will have a pronounced influence on the physical properties of interstellar ices.

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### DATA AVAILABILITY

The data underlying this article will be shared on reasonable request to the corresponding author. Spectra of crystalline 1-propanol are posted at <https://science.gsfc.nasa.gov/691/cosmicice/spectra.html> on the author's website.

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### APPENDIX – COMMENTS ON A RECENT PAPER ON 1-PROPANOL

It appears that some important literature results were missed by the authors of the recent study of amorphous 1-propanol (Ramachandran et al. 2024). Specifically, it was stated that ‘the crystal structure of 1-propanol is not yet experimentally known,’ but Talón et al. (2002) published one. A gas-phase VUV spectrum is available in Salahub & Sandorfy (1971) for comparison to the authors’ solid-phase work as is an earlier spectrum of amorphous 1-propanol (Hudson & Gerakines 2019), neither of which was referenced. None of the multiple calorimetric papers on crystalline 1-propanol were cited (e.g. Takahara et al. 1994; Konstantinov et al. 2017). Also, although the results of Ramachandran et al. (2024) echo those of Hudson (2017) on solid ethanol, warming an ice under vacuum past its melting point, that connection was not mentioned.

The IR simulations and crystal-structure predictions of Ramachandran et al. (2024) were presented to supplement solid-state laboratory results. However, the authors’ calculated structure differs from the one reported by Talón et al. (2002) based on diffraction measurements, a disagreement not acknowledged. Also, the results of the molecular-dynamics calculations of Ramachandran et al. (2024) were not supported by an example showing spectroscopic and structural results from the authors’ method to be in good agreement for a related compound with known IR spectra and crystal structure such as 2-propanol, for which X-ray diffraction results have been reported by Ridout & Probert (2014).

Vacuum-UV spectra of propanol also were presented in Ramachandran et al. (2024). A featureless slope rising from 200 to 120 nm at 10 K evolved into a weak peak near 142 nm at 120 to 147 K, followed by a decrease to the baseline at higher temperatures as the compound’s melting point, ~149 K, was passed. No detailed analysis was provided, and the eleven VUV spectra reported were

presented as eleven overlapping traces, hindering close inspection of each.

The VUV work just described cannot be reproduced as no thickness was provided for the authors' 1-propanol ice sample. Moreover, the vertical axis of the figure showing VUV spectra lacks numbers to indicate absorbance values, which would help to reproduce the work in other laboratories. [The vertical axis is labelled 'Absorbance (arb. units)', but absorbance is dimensionless.] A close comparison between the VUV and IR results of those same authors requires that ice thicknesses, warming rates, and annealing times be known for both types of measurement.

An alternative interpretation of those same VUV results is that the initial relatively featureless spectrum changes to show a peak at 142 nm when the ice crystallized or perhaps melted. As the melting point was passed, the spectrum reverted to its original featureless form with ice sublimation or liquid evaporation slowly removing the sample and bringing the absorbance down to the baseline. This is in reasonable agreement with the IR changes we observed for 1-propanol.

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