



Cite this: *Phys. Chem. Chem. Phys.*,
2018, 20, 1838

Propane and propane–water interactions: a study at cryogenic temperatures†

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The phase transition of solid propane and a propane–water mixture under ultrahigh vacuum has been investigated using reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption mass spectrometry (TPD-MS). Here, the investigation is divided into two sections: the phase transition of pure propane and the interaction of propane with water. RAIR spectra of pure propane reveal an unknown crystalline phase at 50 K (phase I), which gradually converts to a known crystalline phase (phase II) at higher temperature. This conversion is associated with certain kinetics. Co-deposition of water and propane restricts the amorphous to crystalline phase transition, while sequential deposition ($\text{H}_2\text{O}@C_3\text{H}_8$; propane over predeposited water) does not hinder it. For an alternative sequential deposition ($C_3\text{H}_8@H_2O$; water over predeposited propane), the phase transition is hindered due to diffusional mixing within the given experimental time, which is attributed to the reason behind the restricted phase transition.

Received 21st September 2017,
Accepted 12th December 2017

DOI: 10.1039/c7cp06467e

rsc.li/pccp

Introduction

The interaction of water-ice with different molecules in the solid state is significant due to its relevance in the chemistry of the interstellar medium and planetary science.^{1–3} Low temperature vapour deposition on metal surfaces generally results in amorphous molecular solids, which have random molecular orientations in their structure. Such amorphous molecular solids, being metastable, upon heating to higher temperatures transform to their more stable forms, namely crystalline solids.^{1,4–6} The amorphous to crystalline phase transition is an irreversible process, with only a few exceptions reported so far.⁷ Studies of such phase transitions of molecular solids have been receiving tremendous interest due to their relevance to diverse phenomena ranging from biological science to environmental engineering and even the interstellar medium.^{2,3,8} Molecular solids with different phases provide unique physical and chemical environments, which need to be studied and analysed.^{9–11} As a result, phase transitions of many different molecular solids have been investigated over the years, thus creating a vast area of research.

Propane, a component of natural gas, is an important molecule in terms of research and applications. However, there are limited studies on the phase transitions of solid propane. The phase behaviour of propane aerosols was studied under conditions relevant to Titan's atmosphere.¹² The glass transition and crystallization of propane have been studied using calorimetry¹³ and time-of-flight secondary ion mass spectrometry (TOF SIMS).¹⁴ TOF SIMS study revealed that crystalline propane undergoes mixing with amorphous solid water (ASW) because a liquid like phase occurs as a result of pre-melting.¹⁴ The Cassini–Huygens and Voyager 1 expeditions have shown that propane is present, albeit in the gas phase, in Saturn's atmosphere¹⁵ and in its largest satellite, Titan.¹⁶ It has been reported that photochemical reactions of methane in Titan synthesize propane.^{16–19} Many laboratory studies have been focusing on the chemistry of solid propane due to its relevance to Titan. These include the irradiation of propane ice and the chemical reactions of propane with radicals such as the ethynyl radical (C_2H) or the butadiynyl radical (C_4H), which are abundant in many astrophysical environments.^{20–22} These discoveries have led to an accelerated research on the behaviour of propane.

Infrared spectroscopy has been used to study the phase behaviour of solid propane. An IR spectroscopic study reveals that propane forms a crystalline solid at ~ 77 K.²³ The reported IR bands in the $700\text{--}1400\text{ cm}^{-1}$ range of crystalline propane²³ are very similar to crystalline phase II of the present study. Lang and co-workers¹² identified the phase behaviour of propane and *n*-pentane aerosols with relevance to Titan's atmosphere. However, to the best of our knowledge, no IR spectroscopic

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cp06467e

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studies on the phase transitions of pure propane at cryogenic temperatures under ultrahigh vacuum (UHV) conditions exist. A study of this molecule is significant in the context of the formation of clathrate-hydrates. Propane clathrate hydrates are one among the well-studied systems in the literature owing to their application in the energy sector.²⁴ Low temperature is one of the conditions required for propane to form a clathrate hydrate at a suitable pressure. The interactions of naturally occurring gaseous propane with water differ depending on the local conditions.

Water-ice is omnipresent and is one of the most abundant condensed phase molecular species in the universe. Water-ice is known to exist in many structural forms.^{25,26} Among them, the crystalline and amorphous forms can be generated through vapour deposition at a suitable temperature under UHV conditions. Amorphous solid water (ASW) is the most common form at ≤ 130 K.²⁷ The porosity of water-ice (ASW) governs elementary processes like diffusion,^{28,29} adsorption of gaseous species,^{28–30} rapid desorption of trapped gases (termed a molecular volcano),³¹ phase transition,³² tunneling reactions,²⁹ *etc.* Several different experimental techniques can be carried out to study these phenomena. Infrared spectroscopy and temperature-programmed desorption mass spectrometry are two such tools used in the investigation reported here.

Here, in this study, we report two investigations. Firstly, we studied the phase transition of pure propane in the 10–80 K temperature range. We observed that solid propane undergoes multiple phase transitions between 50 K and 70 K. Multiple phase transitions of propane are related to the conversion from the amorphous state to crystalline phase I and the subsequent transition from phase I to crystalline phase II at a higher temperature. It is noteworthy that until now there has been no concrete evidence for the existence of phase I of propane which is crystalline in nature and stable in the 50–55 K temperature range. Secondly, the phase behaviour of propane in the presence of ASW in the same temperature range was investigated. Propane upon mixing with water resisted phase transitions to a great extent. In the presence of ASW, diffusion of propane takes place, which might be the reason behind the restricted phase transitions in such systems.

Experimental

Generally, ice layers were grown in a UHV chamber through direct deposition of vapour (or a vapour mixture) on a cryo-cooled substrate. The substrate can be constructed from various materials, and the choice depends on the purpose of the experiment.³³ Here, a Ru(0001) single crystal was chosen and used as the substrate because it has no effect on the phase transition or the interactions between molecular solids. In a typical experiment, the substrate was cooled to ~ 10 K prior to deposition, a temperature achieved through a combination of a helium cryostat, comprehensive heat-shielding of the sample, and excellent thermal contact between the substrate holder and the cryofinger. Once the substrate was cooled, the sample

vapour was guided to the chamber through a thin gas line. The angle at which the gas or vapour was directed, the rate of deposition and substrate temperature together determine the resulting ice morphology.³³

The present experiment was carried out in a custom-built instrument to study the interaction or chemical reactions in molecular solids of interstellar relevance. Details of the instrument are given elsewhere.³⁴ This instrument consists of a UHV chamber made of stainless steel. The pressure inside the chamber was maintained in the order of 10^{-10} mbar. The vacuum was achieved using several turbo molecular pumps.³⁴ In this instrument, various spectroscopic components such as a low energy ion scattering-mass spectrometer (LEIS-MS), an alkali ion based secondary ion mass spectrometer (SIMS), a temperature programmed desorption-mass spectrometer (TPD-MS) using a residual gas analyzer and also a reflection absorption infrared (RAIR) spectrometer are present. The substrate was mounted on a copper holder, which in turn was attached at the tip of a closed cycle helium cryostat.³⁴ The substrate can attain any temperature between 10 and 1000 K. The temperature was measured by employing a thermocouple sensor attached to the substrate. Repeated heating at higher temperatures prior to vapour deposition ensured surface cleanliness. The temperature ramping was controlled and monitored using a temperature controller (Lakeshore 336). In the present study, we have used a temperature window of 10–180 K to investigate the interaction of propane and propane-water-ice systems.⁹

Millipore water (H_2O of 18.2 M Ω resistivity), taken in a test tube, connected to the sample line through a glass-to-metal seal, was used for the experiment. The water sample line was connected through an all metal leak valve to the experimental chamber. The Millipore water was further purified through several freeze–pump–thaw cycles before introducing into the UHV chamber. A propane gas canister (purity: $\sim 99.95\%$), purchased from Rana Industrial Gases & Products, was directly connected through a needle valve to the sample line. During the experiment, samples were vapour deposited using separate leak valves for propane and water at a constant pressure onto the cold Ru(0001) single crystal. Sample inlet tubes were kept very close to the single crystal to achieve uniform growth of the molecular solids. The deposition of molecular solids was controlled through leak valves, and the monolayer (ML) coverage was evaluated assuming that 1.33×10^{-6} mbar s = 1 ML, which has been estimated to contain $\sim 1.1 \times 10^{15}$ molecules per cm^2 .³⁵ Before beginning the experiment, the chamber pressure was maintained at $\sim 8 \times 10^{-10}$ mbar to collect the RAIRS background and blank spectra. The inlet pressure during the sample deposition was decided based on the coverage desired at the time of the experiment. Here, for the deposition of 150 MLs of propane, the chamber was backfilled at $\sim 5 \times 10^{-7}$ mbar of propane and was exposed to the surface for 5 minutes.

RAIR spectra were recorded using a Bruker FT-IR spectrometer, Vertex 70 model. The IR beam was taken out of the infrared spectrometer and was focused onto the substrate using gold-plated mirrors and re-focused out using another gold-plated mirror to an external MCT detector. The vacuum chamber

was fitted with ZnSe flanges which are transparent to the IR beam. The IR beam was passed through this ZnSe window into the vacuum chamber. The spectra were collected in the 4000–550 cm^{-1} range with 2 cm^{-1} resolution. Each spectrum was averaged to 512 scans to get a better signal to noise ratio.

For the temperature programmed desorption-mass spectrometry (TPD-MS) analysis, the surface was moved to a fixed position using the sample manipulator in order to ensure that the surface is very close to the mass spectrometer inlet. During TPD-MS measurements, the surface was heated at a constant ramp rate (30 K min^{-1}). A suitable mass of the desorbed species was selected using a linear quadrupole mass spectrometer analyser, and the intensity of the desorbed species was plotted as a function of temperature. Mass spectrometers were supplied by Extrel CMS, USA.

Results and discussion

Phase transition of propane

In this work, the phase transition of propane was characterized by surface sensitive reflection absorption infrared spectroscopy (RAIRS). We found an unknown crystalline phase (phase I) of propane at 50 K, which gradually transforms to the known crystalline phase II. To start with, 150 MLs of propane were prepared by the condensation of gaseous propane on a Ru(0001) substrate at 10 K. Under these low temperature conditions, the propane ice is in the amorphous state. Previous reports have suggested that the vapour deposited molecular solid forms an amorphous structure at low temperature.¹⁰ Soon after deposition, the system was allowed to equilibrate and a RAIR spectrum was taken at 10 K. Different vibrational modes of amorphous propane observed in the 10 K spectrum are shown in Fig. S1 (ESI†). The amorphous propane ice was annealed at a ramp rate of 2 K min^{-1} to induce crystallization. RAIR spectra were collected at specific temperatures upon warming, and a time delay of 2 minutes was given for each temperature for the solid to get equilibrated with the substrate temperature.

Fig. 1a and b depict the change in the RAIR spectra of 150 MLs of propane in the $-\text{CH}_3$ deformation and $-\text{C}-\text{H}$ stretching regions, respectively, at different temperatures. The absorption bands of pure propane-ice were identified, and the corresponding fundamental vibrational modes were assigned. Table S1 (ESI†) provides a list of the same with other references. In Fig. 1, the RAIR spectrum at 10 K shows different primary vibrational modes of propane positioned at $\sim 2962 \text{ cm}^{-1}$ ($-\text{CH}_3$ symmetric stretching), $\sim 2935 \text{ cm}^{-1}$ ($-\text{CH}_2$ antisymmetric stretching), $\sim 2872 \text{ cm}^{-1}$ ($-\text{CH}_2$ symmetric stretching), $\sim 1471 \text{ cm}^{-1}$ ($-\text{CH}_3$ d-deformation), $\sim 1386 \text{ cm}^{-1}$ and $\sim 1369 \text{ cm}^{-1}$ ($-\text{CH}_3$ s-deformation). The $-\text{CH}_3$ d-deformation mode of propane was analysed in great detail as it exhibited a profound change during the temperature variation. Again various reports^{12,23,36,37} have suggested that the $-\text{CH}_3$ d-deformation region around ~ 1430 to 1500 cm^{-1} is the most sensitive spectral range for discriminating between phases of solid propane. Upon heating the system from 10 to 40 K, no spectral change was observed in any of the vibrational modes as compared to that at 10 K. Annealing to 50 K brought a significant spectral change in Fig. 1b. A new peak appeared at $\sim 2949 \text{ cm}^{-1}$, positioned near the $-\text{C}-\text{H}$ stretching region shown. Upon heating further from 50 to 60 K, the peak at $\sim 2962 \text{ cm}^{-1}$ split into two peaks positioned at ~ 2966 and $\sim 2960 \text{ cm}^{-1}$. The other vibrational peaks starting from 2850 to 3000 cm^{-1} remained the same as before. From Fig. 1a, it is evident that a broad peak at $\sim 1471 \text{ cm}^{-1}$ in the 10 K spectrum has split into three peaks at $\sim 1477 \text{ cm}^{-1}$, $\sim 1461 \text{ cm}^{-1}$, and $\sim 1443 \text{ cm}^{-1}$ upon heating to 50 K. For better understanding, these three new peaks are termed peak 1, peak 2 and peak 3, respectively. This splitting of broad peaks into multiple narrow peaks indicates the phase transition from the amorphous state to the crystalline state of propane.¹⁰ This phase transition has been termed the “first phase transition” as another phase transition was observed upon further annealing. The first phase transition leads to the formation of an unknown crystalline phase, which we have termed “phase I”. As the temperature of the system was increased from 50 to 60 K, a new peak appeared at $\sim 1472 \text{ cm}^{-1}$ (represented as peak 4) along with the other

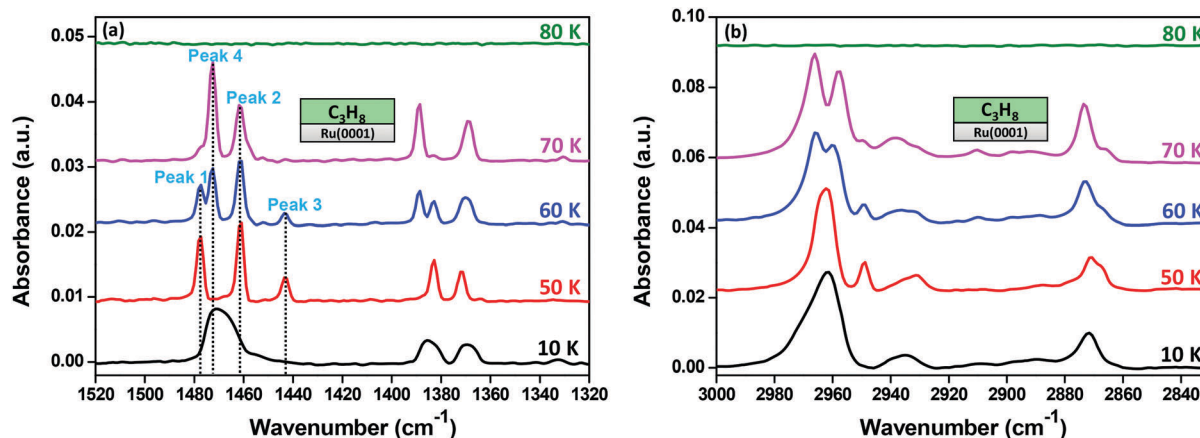


Fig. 1 Temperature-dependent RAIR spectra of 150 MLs of solid propane deposited at 10 K on Ru(0001). Spectra corresponding to the (a) $-\text{CH}_3$ deformation region and (b) $-\text{C}-\text{H}$ stretching region, at different temperatures. Each spectrum is distinctly different.

peaks (peaks 1, 2 and 3). Upon further annealing to 70 K, a significant change was noticed in Fig. 1a; that is, peaks 2 and 4 remained as such, while peaks 1 and 3 disappeared. The spectral changes suggest that there exists a second phase transition which involves the conversion of phase I to another crystalline phase II. There have been several reports on the phase transition of different molecular solids based on infrared spectroscopic observations. The phase transition is generally associated with the splitting of the peak in the IR spectra of the corresponding molecules. For example, crystallization of water-ice involves the splitting of the broad O–H peak of amorphous ice.^{4,5}

Pavese and Besley³⁸ measured the triple-point temperatures of the two solid phases of propane, namely a metastable $s(\alpha)$ phase and another stable $s(\beta)$ phase. The triple-point temperatures of $s(\alpha)$ and $s(\beta)$ were found to be 81.226 ± 0.003 K and 85.520 ± 0.003 K, respectively. The transition between these two solid phases occurred in the 79.6 to 81.2 K temperature range. Our experiments were performed by the vapour deposition of propane under UHV conditions, and the amorphous to crystalline phase I transition was observed at 50 K. Although there are some similarities between Pavese and Besley's work and our experimental observations, we found an important difference between these two studies. In Pavese and Besley's work, when the metastable $s(\alpha)$ phase was left overnight, it converted into the more stable $s(\beta)$ phase. However, in our experiments, we observed that crystalline phase I was stable over 12 hours at 50 K as shown in Fig. S2 (ESI†).

The phase transition at a lower temperature (50 K) as compared to the phase transition temperature in an earlier report³⁸ may be attributed to the UHV conditions. Pavese and Besley³⁸ suggested that the $s(\alpha)$ phase was metastable and unpredictable in behaviour, but our crystalline phase I was stable (as shown in Fig. S2, ESI†) and only converted to phase II upon annealing to a higher temperature (55 K). This phase transition occurred at 55 K reproducibly. The difference in the stability of the phases, reproducible phase transition temperature, and experimental conditions of our work support our claim of the existence of an "unknown crystalline phase" in our system.

A phase transition involving the transformation from an amorphous to a crystalline state is known as an irreversible process,^{10,39} because the latter is thermodynamically more stable due to its highly ordered structure. Here, both phases I and II are crystalline. The reversibility of both the first and second phase transitions was checked by depositing 150 MLs of propane at 10 K and heating to 50 K to form phase I, following which the system was cooled back to 10 K. As the IR spectra remained unaltered after this (as shown in Fig. S3, ESI†), it was confirmed that the phase transition to phase I was irreversible. A similar experiment was carried out for phase II at 70 K and IR spectra are shown in Fig. S4 (ESI†). Once again, the phase transition was found to be irreversible.

In order to confirm the presence of multiple phase transitions between 50 K and 70 K, experiments were performed with different surface coverages of propane to examine how surface coverage influences the phase transition of propane.

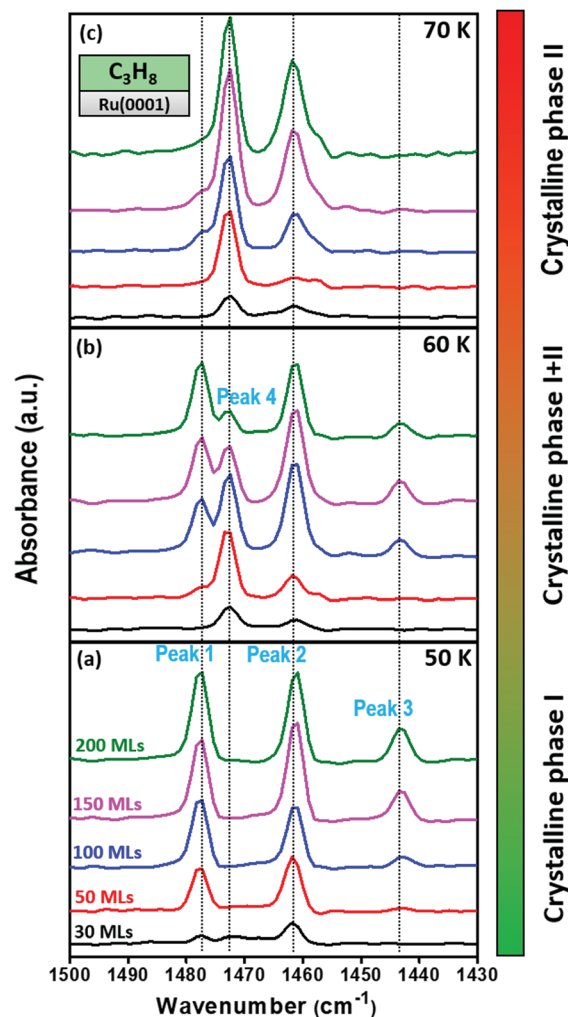


Fig. 2 RAIR spectra in the $-\text{CH}_3$ d-deformation region of propane at different surface coverages starting from 30 to 200 MLs at (a) 50 K, (b) 60 K and (c) 70 K. Various coverages of propane were initially deposited at 10 K on a Ru(0001) substrate and subsequently heated to higher temperatures, and spectra were collected.

Fig. 2 illustrates the RAIR spectra of propane at different surface coverages starting from 30 to 200 MLs at three different temperatures. Fig. 2a shows the $-\text{CH}_3$ d-deformation region of propane at 50 K, where peaks 1, 2 and 3 are present. At 50 K, these peaks are attributed to phase I of propane as shown earlier in Fig. 1a. The positions of all three peaks remain intact at this temperature despite an increase in the surface coverage of propane. The increase in the number of monolayers only resulted in enhanced intensities of all the peaks, thereby suggesting a linear relationship between the number of molecules on the surface and the intensities of the infrared peaks. However, the intensities of peak 3 for 30 and 50 MLs are much lower as shown in Fig. 2a, owing to the lower number of propane molecules on the surfaces of these coverages. Although RAIRS is a surface sensitive technique, it can measure the bulk of a sample up to a few hundred MLs. Therefore, this phenomenon is well expected.⁵

Fig. 2b shows at 60 K the presence of both phase I and phase II at different surface coverages of propane. However, it is

evident that for lower surface coverages (30 and 50 MLs), only peaks 2 and 4 exist, indicating the complete conversion of phase I to phase II. In other words, this temperature is sufficient enough to provide the thermal energy for the completion of the second phase transition within the experimental time scale. It is also noticeable that at 60 K itself, for slightly higher coverages of propane (100, 150 and 200 MLs), all the split IR peaks (peak 1 to peak 4) are present but at different intensities, implying that phase I did not convert completely to the other stable phase II. The number of monolayers plays a crucial role in the case of the second phase transition, particularly in our experimental time scale. In Fig. 2b, the gradual decrease in the intensity of peak 4 for 100, 150 and 200 MLs of propane is related to the lesser extent of conversion to phase II at these coverages. As the number of propane molecules is more for higher coverages, there is only a partial second phase transition at 60 K. In our experimental time scale, at relatively higher coverages (100 MLs or more), this temperature is not sufficient to provide the required thermal energy. The second phase transition requires a higher thermal energy to form phase II. The experimental data from Fig. 2a suggest that the conversion of phase I to phase II is associated with certain kinetics as will be explained later. Fig. 2c shows the presence of only peak 2 and peak 4 at 70 K, leading to the conclusion that, at this temperature, phase I is converted completely to the more stable phase II irrespective of the coverage.

In this work, the formation of phase II from phase I is associated with temperature- and time-dependent kinetics. Fig. 3a and b show the changes in the RAIR spectra of propane in the $-\text{CH}_3$ d-deformation region and the $-\text{C}-\text{H}$ stretching region, respectively. A 150 MLs propane film prepared at 10 K followed by heating to 50 K leads to the formation of crystalline phase I. This crystalline phase I is stable at 50 K for over 12 hours as shown in Fig. S2 (ESI[†]), and the IR spectra remained unaltered even after 12 hours. However, upon heating the system to 55 K and maintaining there for a stipulated amount of time, a significant spectral change was observed as depicted in Fig. 3.

No spectral change was observed at 50–55 K until 1 hour of maintaining the system at 55 K. In Fig. 3a, at 55 K with increasing time, the intensities of peaks 1 and 3 decreased and the intensity of peak 4 increased, but peak 2 remained unaltered with only just a little broadening in the peak width. The data collected and the behaviour observed strongly support the existence of phase I of propane at 50 to 55 K. Moreover, in Fig. 3a, the 3 hour IR spectrum corresponding to 55 K resembles the 60 K spectrum, which in turn is the same spectrum obtained at 70 K upon continuous heating (Fig. 2c). Fig. 3b also shows a similar observation. Here, as time progresses, the peak at $\sim 2962\text{ cm}^{-1}$ splits into two other peaks which are positioned at $\sim 2966\text{ cm}^{-1}$ and $\sim 2959\text{ cm}^{-1}$. It is also noticeable that the intensity of the peak at $\sim 2949\text{ cm}^{-1}$ reduces as time increases. We have performed the same time dependent experiments at the two temperatures (60 and 65 K), and the results acquired show a similar behaviour, except for the variation in the experimental time scale. This observation suggests that crystalline phase I of propane readily converts to the more stable crystalline phase II either upon warming or keeping it at a particular temperature (above 55 K) for sufficient time. However, to the best of our knowledge, no reports exist describing propane's phase I, which is crystalline in nature, and that this phase readily converts to crystalline phase II at a temperature higher than 55 K with associated kinetics.

As we see, the phase I to phase II conversion has a temperature effect, which indicates not only a thermodynamic influence but also a rather crucial kinetic one. To study the kinetic behaviour of the process, we performed experiments at three different temperatures (55, 60 and 65 K) and monitored the evolution of different peaks due to the conversion of phase I to phase II at different time intervals. As mentioned before, the intensities of peak 1 and peak 4 have a significant effect in the conversion process; therefore, two peaks have been analysed to obtain the necessary kinetic information. The intensity of peak 4 is characteristic of phase II, whereas the intensity of peak 1 is characteristic of phase I, which means that an increase in the

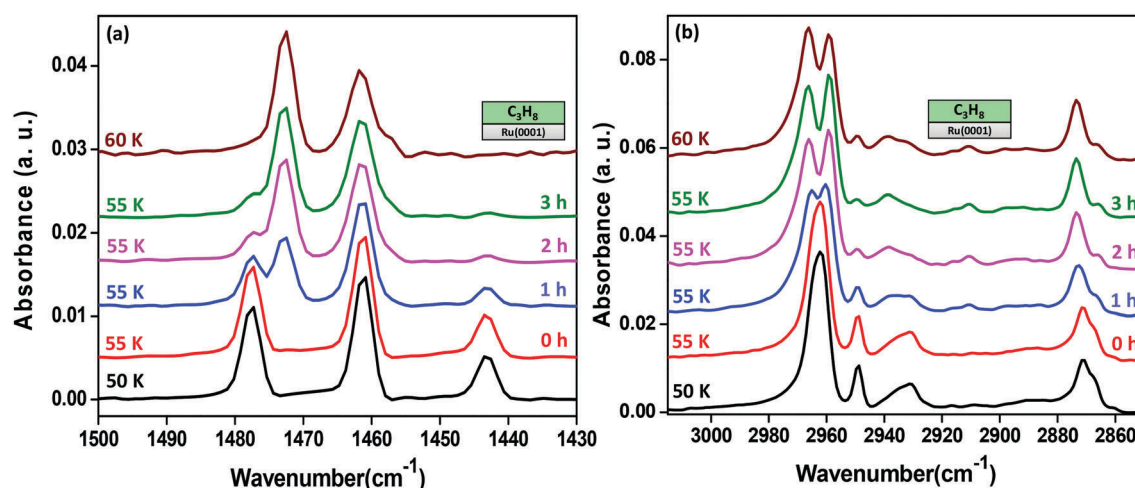


Fig. 3 Time-dependent RAIR spectra of 150 MLs of propane at 55 K. RAIR spectra in the (a) $-\text{CH}_3$ d-deformation region and (b) $-\text{C}-\text{H}$ stretching region at different temperatures: 50 K (black), 55 K (at different time intervals) and 60 K (brown).

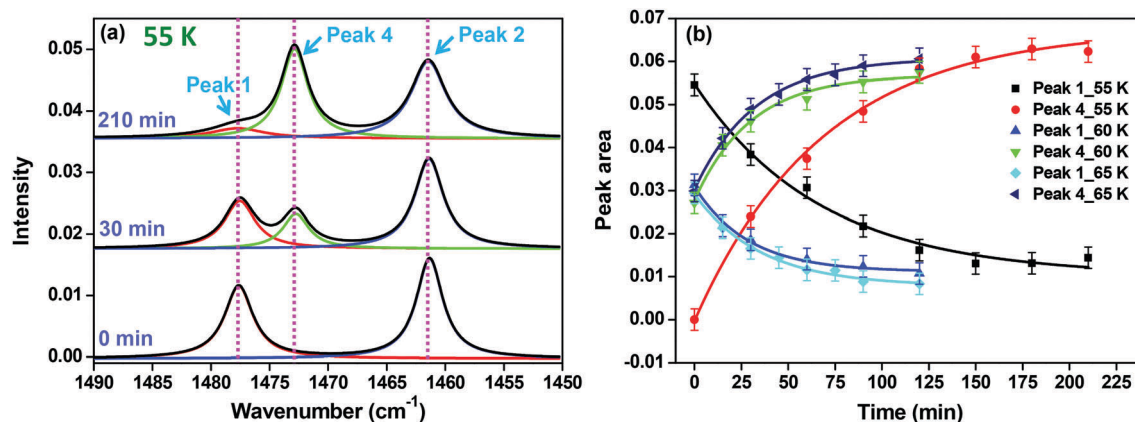


Fig. 4 (a) Lorentzian fits of the spectra of 150 MLs of propane at 55 K at different time intervals. (b) First order exponential fits of the areas of peak 1 and peak 4 at three different temperatures (55, 60, and 65 K) at different time intervals.

intensity of peak 4 or a reduction in the intensity of peak 1 is due to the increase in the concentration of phase II and reduction in the concentration of phase I, respectively, and the presence of both peaks hints at the co-existence of both phases. To perform the kinetic study, first, the spectra were subjected to a Lorentzian fit and then the components were analysed. Fig. 4a represents one such Lorentzian fit at 55 K for 150 MLs of propane at different time intervals. Here, the peaks are fitted with either two or three components, which correspond to peaks 1 and 2, or peaks 1, 4 and 2, respectively. We could notice from the fitted spectra that at time $t = 0$ min there are only two components, namely, peak 1 and peak 2, and gradually peak 1 splits into two components with time. One component remains at the same position (peak 1), whereas another component appears in the lower wavenumber region, which is termed peak 4. As peak 4 starts appearing, the intensity of peak 1 starts reducing, which indicates the transformation of phase I to phase II, and as time increases, most of the phase I converts to phase II. In Fig. 4b, we plotted the integrated peak area of both the components (peak 1 and peak 4) against time at three different temperatures. The plots are suitably fitted with first order exponential fits, which

indicate that the conversion follows first order kinetics. Based on this assumption, the rate coefficients at different temperatures were calculated and subsequently the activation energies of the conversion processes were also determined. To calculate the rate coefficient, it was assumed that the peak area of each component is proportional to the concentrations of the respective phases. Peak 1 was considered to calculate the rate coefficient, and the peak area at $t = 0$ was considered as the initial concentration (A_0) of phase I and A_t as the concentration at time t .

Fig. 5a depicts the first order kinetic plots where $\ln(A_0/A_t)$ vs. t were plotted at three different temperatures and were fitted to the straight lines, and again the slopes of the straight lines provide the rate coefficient at each temperature. The rate coefficients calculated using this method are presented in the Arrhenius plot in Fig. 5b. The plots of $\ln k$ vs. $1/T$ for 150 MLs of propane at three different temperatures show a good straight-line fit. From the slope ($-E_a/R$) of the straight line, the conversion activation energy of phase I to phase II was calculated to be $1.095 \text{ kJ mol}^{-1}$. Although the calculated activation energy had a lot of uncertainty due to assumptions and approximations considered in the calculation, it gives an indication of the energy

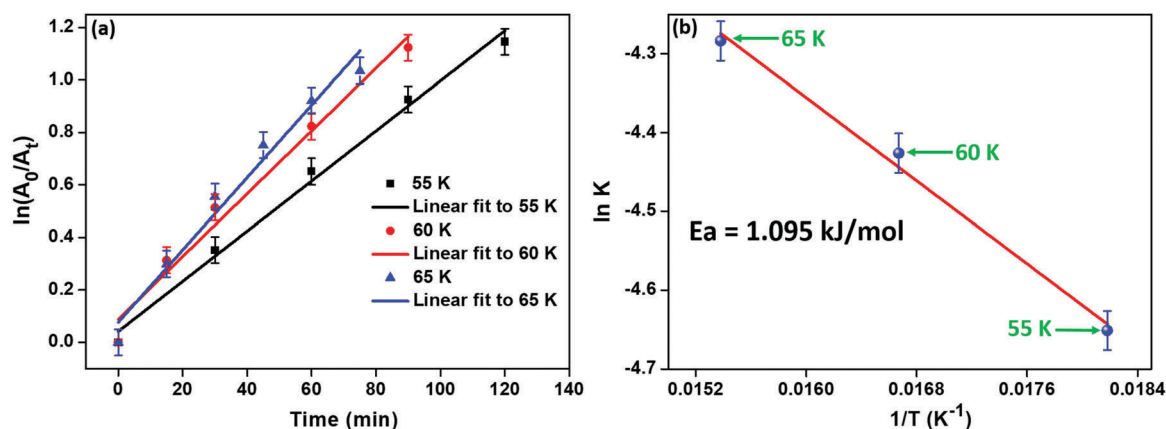


Fig. 5 (a) First order kinetic plots of 150 MLs of propane at three different temperatures (55, 60, and 65 K). Slopes of the linear fits give the rate coefficients of the conversion of phase I to phase II at respective temperatures. (b) Arrhenius plots of rate coefficients at three different temperatures (55, 60, and 65 K).

involved in the conversion process of phase I to phase II in this temperature range. From the calculated activation energy, it is thus comprehensible why the transition of phase I to phase II is possible only at a temperature higher than 55 K.

Phase transition study of propane in the presence of water

In this section, a phase transition study of propane in the presence of water is discussed. Here, different systems were chosen depending on the method of molecular vapour deposition on the Ru(0001) substrate, such as sequential deposition and co-deposition techniques of propane and water at 10 K. The sequential deposition was carried out in two ways, *viz.*, a propane layer over a H₂O layer and a H₂O layer over a propane layer, and they are referred to as H₂O@C₃H₈ and C₃H₈@H₂O, respectively, and C₃H₈ + H₂O is used to refer to the co-deposited system.

Fig. 6a shows the temperature-dependent RAIR spectra of the H₂O@C₃H₈ system in the –CH₃ d-deformation region. The experiment was carried out with a constant amount of water and propane (150 MLs each). Upon heating the system at a constant ramping rate, the broad infrared peak at 50 K splits to give peaks 1, 2 and 3, which were attributed to the formation of phase I. Upon further annealing to 70 K, peak 4 appeared and peak 2 remained constant with the disappearance of peaks 1 and 3, suggesting the formation of phase II. The experimental observations lead to the conclusion that the H₂O@C₃H₈ system behaves the same as a pure propane system, as all the RAIR peaks are identical to the latter with the variation of temperature. It can be concluded from here that when water is below the propane layer for the H₂O@C₃H₈ system it is incapable of influencing the phase transitions of propane.

On the other hand, Fig. 6b shows the temperature-dependent RAIR spectra of C₃H₈ + H₂O, the co-deposited system. Between Fig. 6a and b, there is a marked difference; while in the former there are clear indications of phase transitions occurring in propane, there are no such signs of the same in the latter. Here, two major shoulders were observed at ~1471 and ~1466 cm^{−1}

and remained constant irrespective of the increase in temperature. This characteristic behaviour has led to the inference that when propane is thoroughly mixed with water (C₃H₈ + H₂O system) it results in the restriction of the phase transition, and subsequently, crystallization does not occur. As a result, propane remains in the disordered or the so-called amorphous state. Recent studies on the formation of propane aerosol particles under conditions relevant to Titan's atmosphere¹² revealed that propane aerosols remain in a disordered state. The IR spectra reported for the propane aerosol are broad and less structured¹² and match exactly with the IR spectra as shown here in Fig. 6b. The likely explanation for this behaviour is the formation of viscous liquid propane droplets.¹² This reported explanation is most likely because, as observed in Fig. 6b, the broad feature of the IR spectra is due to the amorphous nature of propane. The spectral features in Fig. 6b suggest that the disordered structure of propane is due to the presence of water molecules, which hinders the molecular rearrangement of propane making it crystalline. This restriction of the phase transition of propane in the presence of water can be explained using the crystal structure of propane.^{40–42} Crystalline propane (space group *P*2₁/*n*, *Z* = 4) is known to have a layered structure. In this, each propane molecule is described as an irregular pentagon where its carbon skeleton acts as the plane.⁴¹ In the layered structure of propane, the packing of pentagon motifs is such that it leaves a little space or gaps in between. There are two types of gaps in the layered structure of propane leading to the ineffective packing compared to other alkanes (ethane or *n*-butane). Each propane molecule is surrounded by six gaps.⁴¹ For the crystallization of propane, the packing of pentagons with the appropriate gap is essential. When propane was co-deposited with water, the gaps are filled by the water molecules, and propane thus cannot undergo crystallization. As a result, propane exhibits only the amorphous or disordered structure in the C₃H₈ + H₂O system.

In the next set of experiments, water was condensed on a propane ice film to investigate its role in the crystallization

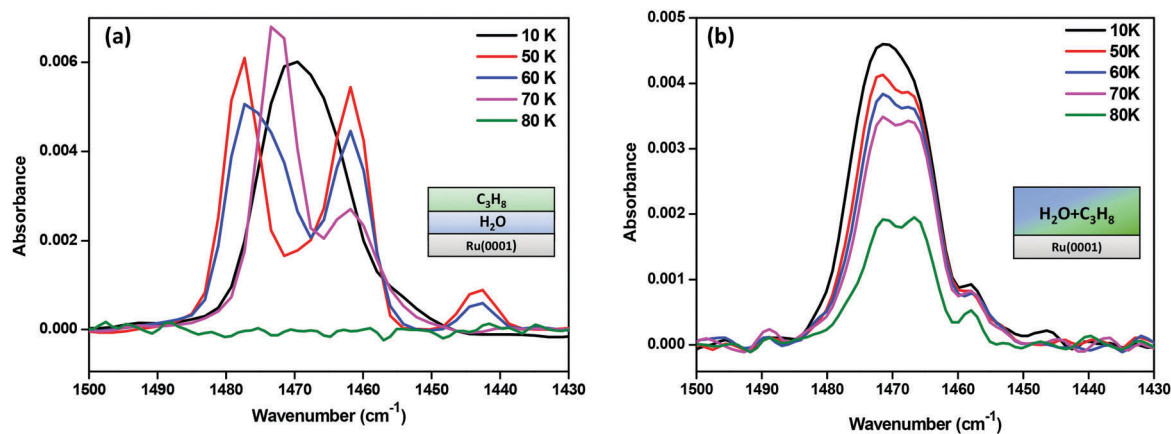


Fig. 6 (a) Temperature-dependent RAIR spectra in the –CH₃ d-deformation region for 150 MLs of propane deposited on 150 MLs of ASW, and (b) temperature-dependent RAIR spectra in the –CH₃ d-deformation region for 300 MLs of propane and H₂O co-deposited at a 1:1 ratio on Ru(0001) at 10 K.

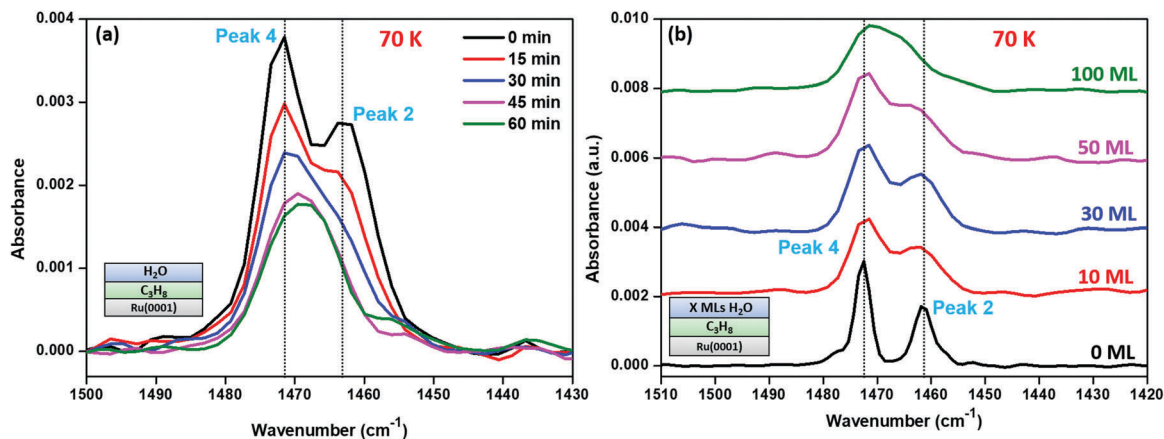


Fig. 7 (a) Time-dependent RAIR spectra of 300 MLs of sequentially deposited ASW on propane (1 : 1) at 70 K, and (b) changes in the $-\text{CH}_3$ d-deformation region in the RAIR spectra of a 50 MLs propane film when the overlayer coverage of ASW was varied from (0 to 100 MLs at 70 K). The insets show the schematics of the surfaces and film thicknesses. Both propane and H_2O were deposited at 10 K on a $\text{Ru}(0001)$ surface and heated to 70 K.

process of the underlying propane layers. Temperature-dependent RAIR spectra of the $\text{C}_3\text{H}_8/\text{H}_2\text{O}$ system in the $-\text{CH}_3$ d-deformation region are shown in Fig. S5 (ESI[†]), where a similar trend to that observed in the case of the $\text{H}_2\text{O}/\text{C}_3\text{H}_8$ system is seen (propane undergoes crystallization). The experimental data from Fig. 6a and Fig. S4 (ESI[†]) suggest that temperature has no role to play in the $\text{H}_2\text{O}/\text{C}_3\text{H}_8$ system for the diffusional mixing of propane and water to inhibit crystallization. In contrast, the experimental time influences the diffusional mixing for the $\text{C}_3\text{H}_8/\text{H}_2\text{O}$ system as shown in Fig. 7a. Time-dependent RAIR spectra of 300 MLs of the $\text{C}_3\text{H}_8/\text{H}_2\text{O}$ system (1 : 1) at 70 K are shown in Fig. 7a. After the sequential deposition at 10 K, the system was heated at a constant ramping rate of 2 K min^{-1} to 70 K. At 70 K, RAIR spectra were taken at each 15 minute interval. As time progresses, the split peaks (peak 2 and peak 4) merges together to give a single broad peak with a subsequent loss of intensity. At 70 K, which is very near to the propane desorption temperature, the propane molecules get enough mobility on the surface to trigger diffusion through the water overlayer. Thus propane undergoes a transformation from the crystalline structure to an amorphous structure. Given enough time at 70 K, the $\text{C}_3\text{H}_8/\text{H}_2\text{O}$ system becomes completely amorphous due to the diffusional mixing of propane and water. During the experiment, some amount of propane molecules desorbed from the surface, leading to the loss of intensity with time.

In order to study the effect of water on the phase transitions of the underlying propane film, at first 50 MLs of propane were deposited and then different coverages of water (starting from 0 to 100 MLs) were deposited on top of propane at 10 K. These $\text{C}_3\text{H}_8/\text{H}_2\text{O}$ systems of different ratios were annealed to 70 K and RAIR spectra were taken. Fig. 7b shows the results. Here, as the overlayer coverage of water was increased, peaks 2 and 4 became broader, and finally, it became a nearly single band. Diffusional mixing of propane molecules into the pores of the water overlayer leads to an amorphous state for the $\text{C}_3\text{H}_8/\text{H}_2\text{O}$ system. From Fig. 7b, it is evident that the diffusion of propane molecules is directly proportional to water overlayer coverage.

For 100 MLs of water, as the number of water pores is higher, the diffusion is complete to give the completely disordered structure of propane, showing that it is similar to amorphous propane.

Fig. 8 displays the temperature-programmed desorption (TPD) spectra for 150 MLs of pure propane, 300 MLs of $\text{C}_3\text{H}_8 + \text{H}_2\text{O}$ and 300 MLs of the $\text{C}_3\text{H}_8/\text{H}_2\text{O}$ system. All the mentioned systems were heated at a rate of 30 K min^{-1} to get the TPD spectra. The TPD spectrum of propane shows that it desorbs at $\sim 76 \text{ K}$; however, when co-deposited with water, propane remains trapped under the film until crystallization of water at 145 K. Although most of the propane desorbs at $\sim 76 \text{ K}$. This kind of release of trapped gases from the water-ice is well known in the literature and termed a “molecular volcano”.^{5,31,43} The reason behind the occurrence of the molecular volcano is the formation of a release pathway for the trapped gases. This pathway can be formed by the formation of cracks, fissures, or grain boundaries that accompany the crystallization kinetics of amorphous water-ice.⁵ The TPD trace for the $\text{C}_3\text{H}_8/\text{H}_2\text{O}$ system also shows similar features which contain a “propane volcano” at $\sim 145 \text{ K}$ where ASW undergoes crystallization.

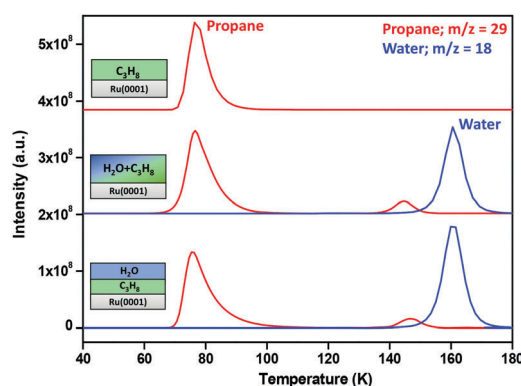


Fig. 8 TPD-MS spectra for different propane and water-ice systems, where the ramping rate was 30 K min^{-1} . The films prepared are schematically represented in the insets.

Conclusions

In this paper, we have studied the phase transitions of propane both alone and in the presence of ASW. Studies carried out using a combination of RAIRS and TPD-MS techniques have provided significant insights into the phase behaviour of solid propane. A temperature dependent RAIRS study of pure propane showed that it underwent multiple phase transitions between 50 and 70 K. A coverage dependent RAIRS study of propane not only confirmed the multiple-phase transitions theory but also gave valuable insights into an unknown crystalline phase (phase I) observed around 50–55 K. A time-dependent RAIRS study of propane ice revealed the kinetics associated with the conversion of phase I to phase II. These two phases of propane, namely crystalline phase I and phase II, were studied and it was clear that the latter is a more ordered structure, thus requiring more time or energy for its achievement. The phase transitions were all observed as abrupt shifts in the RAIRS peaks or occurrences of new peaks at the respective temperatures, viz., 50 K, 60 K and 70 K.

In order to extend our understanding, a study of interactions between propane and ASW was also carried out. Sequentially and co-deposited systems of propane and water-ice were studied. It was seen that propane when deposited on top of water-ice underwent phase transitions in a manner exactly the same as pure propane in the absence of water. However, when it was under a layer of water ($\text{C}_3\text{H}_8@(\text{H}_2\text{O})$), phase transitions were time dependent. The co-deposited ($\text{C}_3\text{H}_8 + \text{H}_2\text{O}$) system did not show phase transitions as those observed in pure propane. TPD-MS of the systems proved the same, with propane desorption peaks, for both $\text{H}_2\text{O}@(\text{C}_3\text{H}_8)$ and $\text{C}_3\text{H}_8 + \text{H}_2\text{O}$ systems, appearing at 76 K and 145 K; the latter peak being the delayed desorption of propane molecules trapped within the water matrix.

Overall, we conclude that propane undergoes multiple phase transitions that are severely hindered in the presence of water-ice. The restricted phase transitions are attributed to the fact that propane is capable of diffusing into the water matrix when it is co-deposited with water and when it is below water. This behaviour of propane is indicative of propane's capacity to enter and lodge into small cages of water, namely clathrates. While no such clathrate hydrates with propane as guest molecules under UHV conditions have been reported so far, the propane–water interactions positively reinforce the hypothesis of such clathrates being formed. Further kinetic and thermodynamic studies of the system could possibly give insights into the right conditions under which such UHV clathrate hydrates may be formed. Propane being an important abundant species in Titan's atmosphere, the phase transition and crystallization behaviour may be important there. This work addresses several important fundamental aspects to understand the structure of solid propane.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

T. P. acknowledges the Science and Engineering Research Board (SERB), the Department of Science and Technology (DST), Government of India, for research funding. J. G. thanks the University Grants Commission (UGC) for a research fellowship. A. K. H. thanks Stella Maris College, Chennai, for her summer internship.

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