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### Key Points:

- Rapid formation of clathrate hydrates from interaction between liquid ethane and water ice at 1 bar is demonstrated for the first time
- Kinetics data at 150–173 K yield an activation energy of 14.8 kJ/mol, implying a diffusion-controlled mechanism for clathrate formation
- Extrapolation to Titan's conditions suggests that ethane-clathrate caps can form on seasonal time scales, which may explain polar depressions

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## Rapid Formation of Clathrate Hydrate From Liquid Ethane and Water Ice on Titan

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**Abstract** Liquid ethane is present in the lakes and seas observed on Titan's surface by the *Cassini-Huygens* mission. While interaction between liquid hydrocarbons and water ice is expected to result in the formation of clathrate hydrates, such reaction (and its kinetics) has not yet been demonstrated for cryogenic liquids under relevant planetary conditions. In this paper, we report the first experimental evidence for rapid formation of clathrates upon direct contact of liquid ethane with water ice at 1 bar using micro-Raman spectroscopy. Kinetics experiments conducted in the temperature range 150–173 K yield an activation energy of  $14.8 \pm 2.2$  kJ/mol, which is suggestive of a diffusion-controlled mechanism for clathrate formation. This implies that a clathrate reservoir can form within seasonal time scales on Titan if liquid ethane comes into contact with a pre-existing icy bedrock, which may hold important implications for the structure and dynamics of Titan's crust and its global evolution.

**Plain Language Summary** Saturn's moon Titan has a dense atmosphere and liquid lakes (of methane and ethane) on its surface. These organic compounds are the main constituents of natural gas on Earth. Water is completely frozen and comprises most of Titan's bedrock materials. Under the right conditions, it is common for water ice to form new solids that trap natural gas in their structures, called clathrate hydrates. On Earth, clathrate hydrates are often found in the permafrost and deep ocean. However, Titan is so much colder that these natural gases exist as liquids. We do not yet know if clathrates can form under such conditions, and if so, how quickly. In this study, we prepared small grains of water ice, bathed them in liquid ethane, and monitored the rate at which clathrate hydrates appear. Our data confirm that clathrates would indeed form on Titan from an ethane lake or rain event onto water ice, and they would do so very quickly (in just a few Earth years). This suggests that clathrate hydrates can be an important material on Titan that may be encountered by future missions there.

## 1. Introduction

Titan is the only body in the Solar System aside from Earth that maintains a substantial nitrogen-dominated atmosphere and stable bodies of liquid on its surface. Owing to the low surface temperatures (92–94 K), the liquid phase is comprised primarily of methane and ethane. These hydrocarbons take part in active geological processes analogous to Earth's hydrological cycle, including cloud formation in the atmosphere and rain-fall onto the surface to pool in lakes (mostly in the polar regions). Ethane clouds have been detected at Titan's North Pole by the Visual and Infrared Mapping Spectrometer (VIMS) onboard the *Cassini* spacecraft (Griffith et al., 2006). They form as a result of stratospheric collapse during the winter. These ethane rains can explain the presence of ~12% in volume of ethane in the northern seas (Hayes et al., 2018).

Coincidentally, Titan's temperature and pressure conditions also permit the existence of stable clathrate hydrate phases both on the surface and in its interior (Choukroun et al., 2013). Clathrate hydrates are a type of inclusion compounds whereby small guest molecules are trapped inside symmetric water cages. The types of structure that form depend largely on the size of the guest species: small hydrocarbons such as methane and ethane induce formation of structure I (sI), while larger molecules such as propane and isobutane result in structure II (sII). The presence of clathrates has long been suggested in Titan's interior (Lewis, 1971; Lunine & Stevenson, 1987), and they are believed to play a significant role in its hydrocarbon cycle (Choukroun & Sotin, 2012). In order to better assess the contribution of clathrates to outgassing and exchange processes over geological time scales, it is essential to have a good estimate of the amount of

clathrates that can be stabilized in the ice crust. This in turn would require knowledge of the formation kinetics of clathrates under Titan-like pressure and temperature conditions. Despite a long history of clathrate investigation, the kinetic aspect has, however, remained poorly constrained in the literature (Mousis et al., 2014). As such, new experimental data are needed to fully characterize clathrate hydrate formation along the liquid hydrocarbon-water ice equilibrium.

In general, comprehensive kinetics data on clathrate formation are scarce and often acquired under conditions not relevant to planetary bodies. Due to the low solubility of hydrocarbons in liquid water, previous studies on clathrate formation kinetics (e.g., Al-Otaibi et al., 2010; Gainey & Elwood Madden, 2012; Wang et al., 2002) primarily involved ice-gas interaction at high pressures (tens of bars) and high temperatures (near the freezing point of water). In this work, formation of clathrate is performed by mixing liquid ethane and water ice under Titan-like atmospheric pressure of 1 bar. To the best of our knowledge, this is the first demonstration of ethane clathrate being formed under such conditions. The only other experimental work to date that has investigated clathrate formation at low pressure is that of Falabella and Vanpee (1974), in which ice crystals were shaken in the presence of 0.08–0.98 bar of gaseous ethane for about 12 hr until 5–10% of the ice were converted into clathrates. Subsequent pressure-temperature equilibration and extrapolation of the data gave a value of 240.8 K for the dissociation temperature at 1 bar. As such, Titan's surface conditions are well within the stability zone of ethane clathrate. Its potential presence can have a significant impact on the humidity of ethane in the atmosphere, an aspect that has yet to be incorporated in current Titan's climate models (e.g., Mitchell & Lora, 2016).

In this study, Raman spectroscopy is employed to investigate formation and growth of clathrates, owing to its fast time scales and sensitivity toward different chemical environments of the guest species. Characteristic vibrational signatures of ethane clathrate have been well-established (Sloan & Koh, 2008; Subramanian & Sloan, 2002), where trapped ethane molecules are known to exhibit a  $\nu_3$  symmetric C–C stretching mode at  $1,001\text{ cm}^{-1}$  when in the large  $5^{12}6^2$  cages and at  $1,020\text{ cm}^{-1}$  in the small  $5^{12}$  cages of sI near 274 K. In the C–H region, large-cage ethane molecules display diagnostic doublet bands at 2,891 and  $2,946\text{ cm}^{-1}$  due to the  $\nu_1 + 2\nu_{11}$  Fermi resonance. Note that the large-cage  $\nu_3$  mode is blue-shifted from its respective gas-phase frequency by  $\sim 7\text{ cm}^{-1}$  while the Fermi modes are red-shifted by  $\sim 10\text{ cm}^{-1}$ . As a result, these vibrational signatures can be used to definitively identify the formation as well as monitor the growth of clathrates in our samples.

## 2. Materials and Methods

In the Raman experiments, a fine powder of water ice ( $\sim 100\text{-}\mu\text{m}$  grain size) was used as the starting material for clathrate formation. This texture was chosen in order to maximize the surface area for reaction with liquid ethane. Powdered ice was obtained by grinding frozen droplets of deionized water under liquid nitrogen, followed by transferring it onto a microscope slide precooled at 140 K inside a Linkam LTS350 cryostage. A small aliquot ( $\sim 1\text{ mL}$ ) of liquid ethane, produced from direct condensation of gaseous ethane (Matheson Tri-Gas, ultrahigh purity 99.95%), was deposited directly on top of the powdered ice. The sample was subsequently warmed to a specific temperature (150, 155, 163, 168, or 173 K) and clathrate formation monitored by acquiring sequential Raman spectra using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR) that is equipped with an external Nd:YAG laser (frequency-doubled 532 nm, 50 mW) as the excitation source. Spectra were obtained with an 1,800 grooves/mm grating, providing a resolution of  $0.5\text{ cm}^{-1}$  per detector pixel. A silicon chip was used for frequency calibration by virtue of its sharp, well-defined peak at  $520.7\text{ cm}^{-1}$ . Deconvolution of experimental spectra was carried out using Lorentzian peak profiles via the multipeak fitting tool of Igor Pro (v6.12, Wavemetrics, Inc.).

Thermal stability studies were performed after each experimental run to determine the dissociation temperature  $T_d$  at 1 bar. Complementary to the previous work by Falabella and Vanpee (1974) which relied on extrapolation to get the dissociation temperature at 1 bar (240.8 K), we conducted direct measurement of  $T_d$  spectrally and also found a dissociation temperature of 240 K. This agreement both verifies the dissociation temperature extrapolated from the low-pressure study and confirms the clathrate nature of the species being formed.

### 3. Results

Figure 1 shows representative Raman spectra acquired upon exposure of water ice to liquid ethane at 163 K over the course of an hour. The initial spectrum obtained after 1 min of contact (blue trace) shows essentially identical features to that of liquid ethane in both the C–C (peak at  $992\text{ cm}^{-1}$ ) and C–H (peaks at  $2,883$  and  $2,940\text{ cm}^{-1}$ ) regions (Vu et al., 2014). After half an hour (red trace), a slight shoulder begins to emerge at  $1,000\text{ cm}^{-1}$ , which is indicative of ethane trapped in the large  $5^{12}6^2$  cages of sI clathrate. This peak becomes more prominent over time as the clathrate continues to grow, in conjunction with a decrease in intensity of the liquid ethane peak at  $992\text{ cm}^{-1}$  (green trace). Additional confirmation of clathrate formation can be seen in the C–H stretching modes of ethane, where the  $\nu_1 + 2\nu_{11}$  Fermi doublet bands in the liquid phase have been blue shifted to  $2,886$  and  $2,942\text{ cm}^{-1}$  upon emergence of the  $1,000\text{-cm}^{-1}$  clathrate feature. Together, these spectral signatures unambiguously establish that clathrate formation can occur readily under laboratory time scales upon interaction of liquid ethane and water ice at 1 bar. Microscopic images obtained at this stage (not shown) also reveal evidence for recrystallization of the sample upon incorporation of ethane into the water ice lattice.

As the  $\nu_3$  stretch at  $1,000\text{ cm}^{-1}$  is the most intense and diagnostic feature for enclathrated ethane, its temporal evolution can be used to monitor the growth of clathrate. In order to account for the small variation in the amount of ice probed across our experiments, we have measured the area of this peak against the sum of all the water ice modes in the  $3,100\text{--}3,500\text{-cm}^{-1}$  region. This ratio is subsequently normalized to the highest clathrate fraction at each temperature. Figure 2 displays a typical data set acquired from the formation kinetics experiments, where clathrate growth is observed to follow an exponential curve (orange trace). Each of these kinetics curves provides a characteristic time constant  $\tau$ , defined to be the time for the reaction to reach  $1 - 1/e \approx 63\%$  completion. The clathrate fraction,  $x$ , as a function of time can then be expressed as

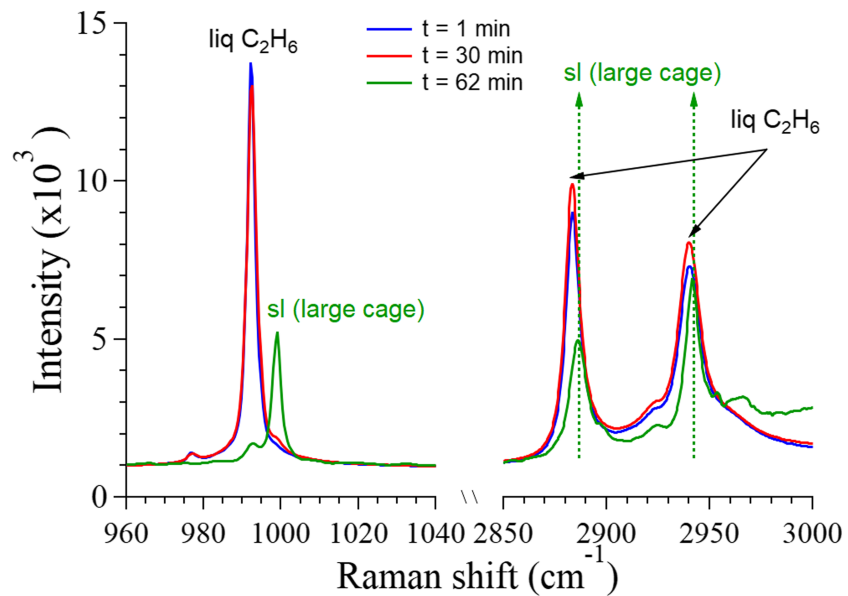
$$x = 1 - e^{-k(t-t_0)} = 1 - e^{-(t-t_0)/\tau} \quad (1)$$

where  $k$  is the reaction rate constant ( $k = 1/\tau$ ) and  $t_0$  is the induction time for the reaction. Note that the obtained value of  $\tau$  is independent of the peak normalization method as it depends only on the curvature of the exponential growth and not on the absolute clathrate fraction. Table 1 lists the average characteristic time constants and rate constants measured in this work, along with their uncertainties, for five different temperatures between 150 and 173 K (experiments were repeated 3–5 times at each temperature). Within the limits of our experimental precision, the reaction rate is found to be slower with decreasing temperatures, as one may expect.

From the obtained reaction rate constants, an activation energy  $E_a$  for the reaction can be derived via a standard Arrhenius relationship where  $k = Ae^{-E_a/RT}$ . A plot of  $\ln k$  versus  $1/T$  of the obtained experimental data (Figure 2, inset) yields an activation energy of  $14.8 \pm 2.2\text{ kJ/mol}$ , which is comparable to that for the diffusion of small hydrocarbons in water ( $12.1\text{ kJ/mol}$ ; Witherspoon & Saraf, 1965). Such relatively low activation energy (as compared to the typical hydrogen bonding energy of  $13\text{--}32\text{ kJ/mol}$  in water ice (Chaplin, 2010)) thus suggests a diffusion-controlled mechanism for clathrate formation and is consistent with the immiscibility of liquid ethane and water ice. Since diffusion can be seen as a “random-walk” process wherein the molecules undergo a series of displacements that are small compared to interatomic spacing (Witherspoon & Saraf, 1965), it does not necessarily require the breaking of hydrogen bonds in water ice. As a result, supersaturation of water ice by the guest molecules from contact with the liquid phase (and subsequent rearrangement of the lattice) is likely the main driving force behind this clathrate formation reaction.

### 4. Discussion

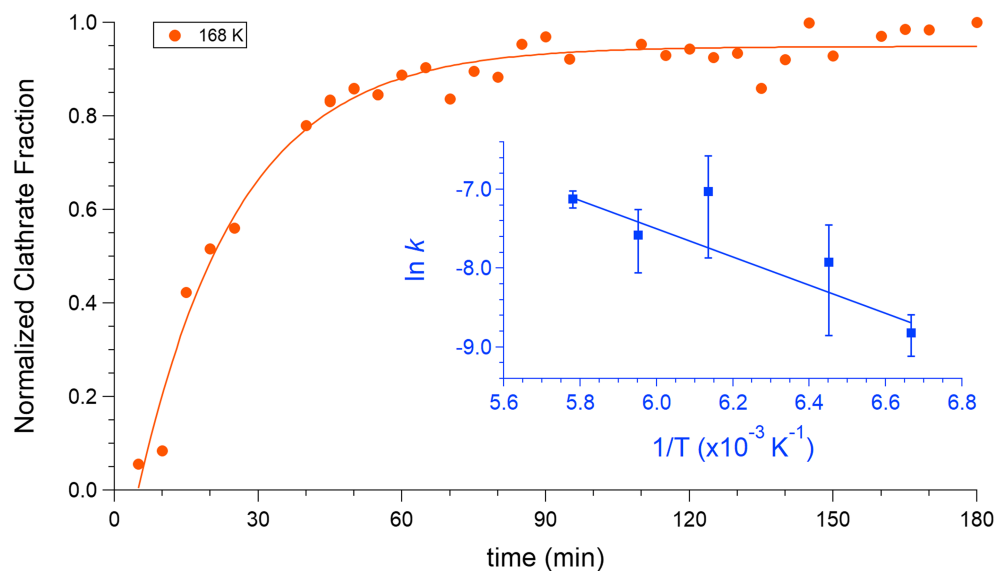
The ease of clathrate formation at the liquid ethane-ice interface under Titan-like conditions holds important implications for its geology. The renowned thermodynamic stability of clathrate hydrates under Titan's surface conditions strongly suggests their ability to act as a reservoir of volatiles on this icy moon (Choukroun et al., 2013; Grasset & Pargamin, 2005; Lunine & Stevenson, 1987; Osegovic & Max, 2005). However, *Cassini-Huygens* was not equipped to formally detect the presence of clathrate hydrates, which



**Figure 1.** Raman spectra of ethane clathrate formed from a liquid ethane-ice mixture at 163 K. Note the growth of the features at 1,000, 2,886, and 2,942  $\text{cm}^{-1}$  (green dashes), which are characteristic of ethane trapped in the large cages of sl clathrate, over time. Liquid ethane peaks are marked by black arrows and labels.

may in turn raise questions on whether they can actually exist on the surface. The experimental results obtained here show that clathrate hydrates can indeed form, and rather readily, via reaction of liquid-state clathrate formers with water ice under Titan's surface conditions.

The fairly modest activation energy as derived from our data set for the case of liquid ethane implies that a clathrate reservoir may form quickly (compared to geologic time scales) if rain and/or lake fluids come into contact with a preexisting icy mantle. In Figure 3a, we have extrapolated the time that would be required for clathrate to form at 90 K (the lowest possible temperature on Titan where liquid ethane



**Figure 2.** Representative growth curve of ethane clathrate from interaction between liquid ethane and water ice (e.g., at 168 K). Fit of the data is made using equation (1). Inset shows an Arrhenius plot of the experimental rate constants (Table 1), which yields an activation energy of  $14.8 \pm 2.2$  kJ/mol for clathrate formation.

**Table 1**

Characteristic Time Constant  $\tau$  (in min) and Rate Constant  $k$  (in  $s^{-1}$ ) for Formation of Ethane Clathrate as Measured in This Work

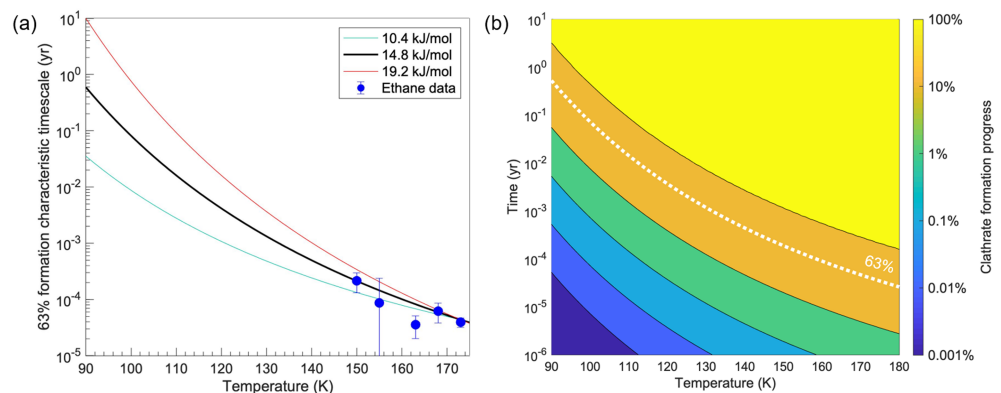
Temperature (K)	No. of experiments	Average $\tau$ (min)	Average $k$ ( $\times 10^{-4} s^{-1}$ )	$\ln$ (average $k$ )	Errors $\ln k$ (max/min)
150	3	152 $\pm$ 43.8	1.482	-8.817	0.229/-0.297
155	4	97.5 $\pm$ 79.7	3.629	-7.922	0.474/-0.932
163	5	39.0 $\pm$ 8.1	8.903	-7.024	0.451/-0.842
168	5	46.7 $\pm$ 12.7	5.102	-7.581	0.321/-0.476
173	4	23.0 $\pm$ 3.8	8.062	-7.123	0.103/-0.115

Note. The last column indicates the maximum and minimum (minus sign) uncertainties of  $\ln k$ .

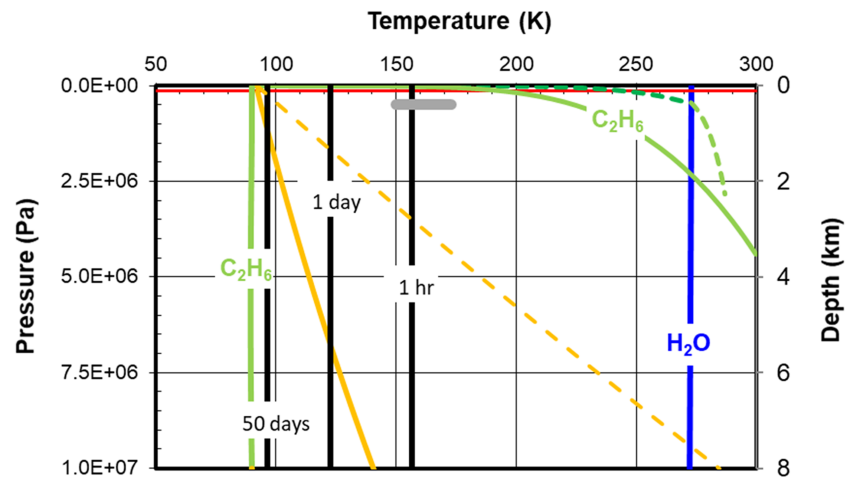
can come into contact with water ice) using the obtained  $E_a$  value of 14.8 kJ/mol. The result indicates that reaction at 90 K would take less than one Earth year to reach  $(1 - 1/e) \approx 63\%$  completion (black trace). Even if one considers the  $2\sigma$  upper bound of the activation energy (i.e., the upper end of the 95% confidence interval from our data set) of 19.2 kJ/mol, it would still only require about 10 Earth years to reach 63% clathrate formation (red trace), an extremely short time compared to the geological age of Titan.

Figure 3b displays the calculated time that would take for the clathrate formation reaction to reach various completion levels, from 0.001% to 100%, assuming the nominal value of 14.8 kJ/mol for the activation energy. The result shows that at 90 K, clathrate formation is expected to reach full completion in approximately 4 Earth years, which is on the order of a Titan season (one Titan year  $\approx 29$  Earth years). Note, however, that the extrapolation of our experimental results likely reflects the most favorable conditions for clathrate formation, where small grains of water ice (on the order of a few hundred microns) are bathed in liquid ethane. In more realistic situations for Titan, such as an ethane rain event onto a thick water ice slab, the time scale can potentially be longer. Nevertheless, it is reasonable to expect that clathrates will still form very quickly over the first few layers of the ice substrate.

As liquid ethane percolates deeper into Titan's crust, the kinetics will likely be faster owing to an increase in temperature. Additionally, since the thermal conductivity of clathrates is about an order of magnitude lower than that of water ice (Ross & Andersson, 1982; Waite et al., 2007), the formation of clathrates would provide a larger thermal gradient for the same heat flux, leading to even faster kinetics at depth. This increase in the temperature gradient is illustrated in Figure 4 for a heat flux of 10 mW/m<sup>2</sup>, which is typical of the heat power produced by the decay of long-lived radioactive elements and tidal dissipation (e.g., Chen et al., 2014). The two end-member models displayed correspond to a porous upper crust (8 km) made of either pure water ice



**Figure 3.** (a) Characteristic time scale for clathrate formation from liquid ethane + water ice at  $(1 - 1/e) \approx 63\%$  completion. Black trace is constructed using the nominal  $E_a$  value of 14.8 kJ/mol derived from experimental data (blue dots) while red and turquoise traces denote  $2\sigma$  deviations. (b) Time required for ethane clathrate formation at various levels of completion assuming  $E_a$  value of 14.8 kJ/mol. White dashed curve represents the 63% completion, and is identical to the black trace in (a).



**Figure 4.** The characteristic time of ethane clathrate formation (vertical black lines) at Titan's conditions is much shorter than geological time scales. The stability domain of liquid ethane is bounded by the green curves, while green dashes indicate the stability curve of ethane clathrates. The melting curve of water ice is shown in blue. Gray box denotes the range where experimental data reported in this work were acquired. The temperature profile for a 10-mW/m<sup>2</sup> heat flux is represented with (dashed orange line) and without (full orange line) clathrates, assuming a porous regolith filled with liquid ethane.

or ethane clathrates. The temperature profile for water ice takes into account the strong temperature dependence of thermal conductivity. The pores are filled with liquid hydrocarbons whose thermal conductivity is also temperature-dependent and lower than that of clathrates. Because the molecular volume of water ice is about 12% smaller than that of ethane clathrates (Erfan-Niya et al., 2011), the porosity is reduced by the transformation. The temperature profiles are calculated with 20% porosity for the water ice model (full orange curve) and 10% porosity of the ethane clathrate model (dashed orange curve). Unlike water ice whose thermal conductivity is strongly temperature-dependent, the thermal conductivity of ethane clathrates is constant. At 4-km depth, the temperature would be equal to 114 K for the water ice case and 185 K with the ethane clathrate.

Ethane is produced in Titan's upper atmosphere by the photolysis of methane followed by the recombination of two CH<sub>3</sub> radicals (Wilson & Atreya, 2004). The present production rate was estimated to be 170 kg/s based on Cassini observations (Lavvas et al., 2008). Ethane rains on the poles during winter when the downwelling circulation branch surrounding the pole causes ethane to descend from the stratosphere to the tropopause, where it condenses and precipitates to the surface (Griffith et al., 2006), such explaining the dearth of atmospheric ethane. Extrapolation of the present laboratory results indicates that at Titan's surface temperature of 92–94 K, ethane would react with porous water ice crust very rapidly, on seasonal time scales, to form polar caps of ethane clathrates (Figure 4). Owing to their larger density relative to water ice (and methane clathrates), the ethane-clathrate polar caps would subside, which can explain that the poles are topographic depressions about 300 m deep (Corlies et al., 2017). With Titan being very close to hydrostatic equilibrium (Durante et al., 2019), the depression can be explained by the presence of an ethane clathrate layer between 1.5 and 4.5 km depending on the porosity of Titan's crust and the extend of the polar cap (Choukroun & Sotin, 2012). The temperature at the base of the ethane clathrate polar caps would be equal to 130 and 200 K for thicknesses of 1.5 and 4.5 km, respectively (Figure 4). The present laboratory experiments support the model of ethane clathrate caps at the Titan's poles.

Methane clathrates may also form in Titan's crust through a similar process. Methane rains happen more widely on Titan's surface (Mitchell & Lora, 2016), which may lead to the presence of a global clathrate layer (Mousis & Schmitt, 2008). Given that methane and ethane both form structure I clathrates and the physical interaction governing them (van der Waals) are the same, it is plausible that the activation energy and characteristic time scale for methane clathrate formation would be fairly similar to those for ethane. Kinetics data for reaction rates between liquid methane and water ice, however, are currently lacking, and future studies are thus warranted.

## 5. Conclusions

We have reported for the first time the rapid formation of ethane clathrate hydrate from interaction between liquid ethane and water ice at 1 bar and derived its formation kinetics between the temperature range 150–173 K. Successful formation of ethane clathrate is confirmed spectrally via its characteristic Raman signatures at 1,000, 2,886, and 2,942  $\text{cm}^{-1}$ . These features could potentially be useful as identifiers of ethane clathrates for a Raman probe on future in situ missions. An inferred activation energy of 14.8 kJ/mol is relatively modest and consistent with a diffusion-controlled mechanism for clathrate formation. Extrapolation to 90 K indicates that this reaction can occur in less than  $\sim 10$  Earth years or one Titan season under its surface conditions, implying that clathrates could be the dominant product if liquid ethane comes into contact with a pre-existing ice-rich bedrock. Given recent detection of the latter across Titan's tropical region (Griffith et al., 2019), ethane clathrates could be among the likely surface materials that upcoming missions such as *Dragonfly* may encounter.

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