

AN INFRARED SPECTROSCOPIC STUDY OF AMORPHOUS AND CRYSTALLINE ICES OF VINYLACETYLENE AND IMPLICATIONS FOR SATURN'S SATELLITE TITAN

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ABSTRACT

Laboratory infrared spectra of amorphous and crystalline vinylacetylene ices were recorded in the range of 7000–400 cm^{-1} . The spectra showed several amorphous features in the ice deposited at 10 K, which were then utilized to monitor a phase transition between 93 ± 1 K to form the crystalline structure. Successive heating allows monitoring of the sublimation profile of the vinylacetylene sample in the range of 101–120 K. Considering Titan's surface temperature of 94 K, vinylacetylene ice is likely to be crystalline. Analogous studies on related planetary-bound molecules such as triacetylene and cyanoacetylene may be further warranted to gain better perspectives into the composition of the condensed phases in the Titan's atmosphere (aerosol particles) and of Titan's surface. Based on our studies, we recommend utilizing the ν_1 and $\nu_{16}/\nu_{11}/\nu_{17}$ fundamentals at about 3300 and 650 cm^{-1} to determine if solid vinylacetylene is crystalline or amorphous on Titan.

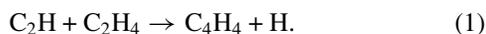
Key words: astrochemistry – infrared: solar system – methods: laboratory – planets and satellites: individual (Titan)

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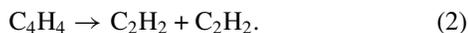
1. INTRODUCTION

During the last two decades, the chemical composition of Titan's atmosphere has been explored extensively (Liang et al. 2007). Today, it is well established that Titan's chemical inventory is the result of a rich, coupled photochemistry of two main atmospheric constituents: molecular nitrogen (N_2) and methane (CH_4). The stratospheric trace constituents have been firmly identified via infrared spectroscopy onboard the *Voyager* 1 and 2 spacecraft (Coustenis et al. 1989, 1991) and by the *Cassini*–*Huygens* mission (Coustenis et al. 2007). In the gas phase, these are the hydrocarbon molecules acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), methylacetylene (CH_3CCH), propane (C_3H_8), diacetylene (C_4H_2), and benzene (C_6H_6) (Coustenis et al. 2007; Hébrard et al. 2007), nitriles such as hydrogen cyanide (HCN), cyanoacetylene (HCCCN), and cyanogen (C_2N_2) (Coustenis et al. 2007; Hébrard et al. 2007), as well as oxygen-bearing molecules carbon dioxide (CO_2), carbon monoxide (CO), and water (H_2O). The emission lines of these molecules in the gas phase can also be utilized as valuable tracers to collect data on temperature profiles, on the potential existence of cold traps and freeze out zones, on molecular abundances in the stratosphere, and may also help understanding of the formation of the organic aerosol layers on Titan (Vinatier et al. 2007).

One of the likely hydrocarbons, but still lacking in spectroscopic evidence, is the vinylacetylene molecule (C_4H_4). This species can be formed via the bimolecular reaction of atmospheric ethynyl radicals (C_2H) with ethylene (C_2H_4) to yield vinylacetylene plus atomic hydrogen (Equation (1)) in the gas phase:



In line with current photochemical modeling of Titan's atmosphere (Wilson & Atreya 2004; Yung et al. 1984), it signifies the recent photochemical simulation (Stearns et al. 2006) that upon photolysis, stratospheric vinylacetylene may produce ultimately acetylene (C_2H_2) (Equation (2)), a critical constituent of Titan's atmosphere:



Relevant to radioastronomical searches, the rotational spectra of vinylacetylene have been extensively recorded in the laboratory (Thorwirth & Lichau 2003; Thorwirth et al. 2004), as well as to some extent gas phase spectra in the ultraviolet (Fahr & Nayak 1996) and infrared (Tørneng et al. 1980) regime of the electromagnetic spectrum. However, since Titan's surface is predicted to be “cold” (94 K) and lower temperatures of about 70 K are present in the upper atmosphere (50 km), vinylacetylene could also exist in its solid form as an ice—either amorphous or crystalline. Preliminary infrared spectra of crystalline vinylacetylene were recorded (Tørneng et al. 1980). However, to date no systematic comparison of infrared spectra of crystalline and amorphous vinylacetylene ices have been conducted. Likewise, the stability and transformation temperature of amorphous ice to a crystalline structure remains elusive. Therefore, temperature-dependent infrared spectra of crystalline and amorphous vinylacetylene ices shall be recorded in greater detail serving to guide future investigations of Titan via infrared spectroscopy. Encouraged by the contribution of Khanna and coworkers, condensed species such as cyanoacetylene (HCCCN), acetylene (C_2H_2), dicyanoacetylene (NCCCCN, C_4N_2), and possibly propionitrile ($\text{C}_2\text{H}_5\text{CN}$) were suggested to be condensable on Titan (Khanna 2005a, 2005b; Russo & Khanna 1996; Samuelson et al. 1997). Herein, we expand these studies and report temperature-dependent infrared spectra of amorphous and crystalline ices of vinylacetylene and aim to pin down the stability of crystalline versus amorphous vinylacetylene ices at distinct temperatures.

2. LABORATORY APPROACH

2.1. Vinylacetylene Synthesis

Vinylacetylene was synthesized following the literature procedures (Hennion et al. 1958; Stearns et al. 2006; Tørneng et al. 1980). Briefly, to the mixture of ethylene glycole (132 ml) and *n*-butyl cellulolve (26 ml), 1,4-dichlorobutene (40 g) was added dropwise at a temperature above 438 K. The evolving vinylacetylene was carried away in helium carrier gas, bubbled

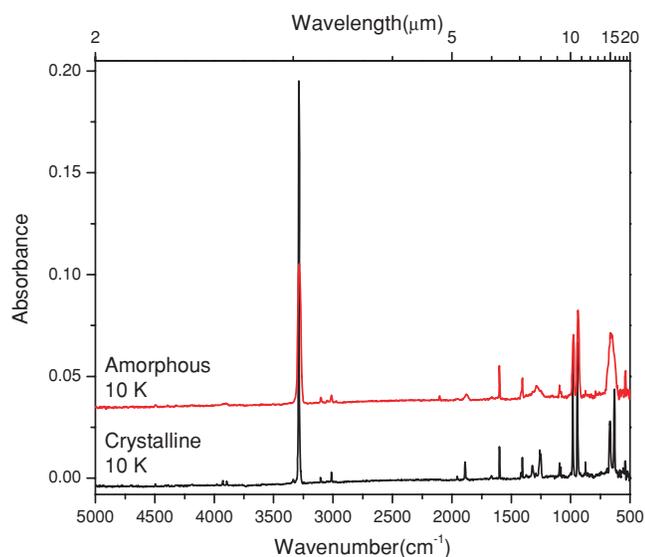


Figure 1 Mid-infrared spectra of amorphous and crystalline vinylacetylene ices recorded at 10 K.

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through an aqueous sodium hydroxide (NaOH) solution (13%), and trapped in liquid nitrogen. The crude vinylacetylene at this stage is about 95% pure. A trap-to-trap distillation ensued resulting in the purity of >99.5%. Gas mixtures of 5% vinylacetylene in helium (99.9999%; Gaspro) were prepared at room temperature with a total pressure of 2 atm. A minor side product (less than 0.5%) of the synthesis is assigned to *cis*-1-chloro-1,3-butadiene (Borg et al. 1980).

2.2. Experimental Setup

Amorphous vinylacetylene ices were prepared by condensing the helium–vinylacetylene gas mixtures onto a silver substrate held at 10 K (Zheng et al. 2006; Zheng & Kaiser 2007). Under these conditions, only vinylacetylene condenses. The deposition typically lasts 10 minutes at 1.6×10^{-7} Torr. The ice thickness was estimated to be about 44 ± 5 nm with a column density of about 4.1×10^{16} molecule cm^{-2} based on the computed infrared absorption coefficient (intrinsic band strength of 1.3×10^{-17} cm molecule $^{-1}$; Mebel et al. 2006) of the 3 μm band (ν_1) and a modified Lambert–Beer relationship (Bennett et al. 2004; Herrebout & Van der Veken 2002). The deposited ices were warmed with a temperature gradient of 0.5 K minute $^{-1}$; infrared spectra of the sample were taken *on line* and in situ monitoring the range of 7000–400 cm^{-1} with 4 cm^{-1} resolution (Nicolet 6700 FTIR). A quadrupole mass spectrometer (Balzers QMS420) was also tuned in to record the temperature-dependent ion-count profiles of vinylacetylene at $m/z = 52$ (C_4H_4^+) which sublimed during the heating process.

3. SPECTROSCOPIC AND PHYSICAL PROPERTIES OF SOLID VINYLACETYLENE

3.1. Amorphous Ices Formed at 10 K

Vinylacetylene is planar and considered a prolate near-symmetric top. From the total 18 vibrational fundamentals, the first 13 modes (ν_1 – ν_{13}) belong to a' symmetry, whereas the rest (ν_{14} – ν_{18}) hold the a'' symmetry. Except for ν_{13} and ν_{18} , all other fundamentals fall within the mid-infrared range of this study. Along with multiple overtones and combination bands,

Table 1
Vibrational Band Positions of Crystalline and Amorphous Vinylacetylene Ices

Amorphous (cm^{-1}) (10 K)	Crystalline (cm^{-1})		Gas Phase (cm^{-1}) Reference ^a	Assignment	Carrier	
	(10 K)	(100 K)	Reference ^a			
4495	4495	4495	
3912 (br) ^b	3928, 3894	3928, 3896	...	$\nu_1 + \nu_{11}/\nu_1 + \nu_{17}$	Combination	
3284	3288	3288	3287	ν_1	$\equiv\text{CH}$ str	
3102	3104	3105	3106	ν_2	$=\text{CH}_2$ asym str	
3049	3049	3049	3050	ν_3	$=\text{CH}$ str	
3014	3014	3014	3015	ν_4	$=\text{CH}_2$ sym str	
2973	2972	...	2973	2990–2985	Combination	
2103	2103	2103	2101	2111	ν_5	$\text{C}=\text{C}$ str
1954	1954	1954	1954	1975	$\nu_9 + \nu_{10}$	Combination
1877	1888	1887	1889	1868–1848	$2\nu_{15}$	Overtone
1663	1667	1667	1665	1660–1643	$\nu_9 + \nu_{11}$	Combination
1599	1599	1599	1599	1599	ν_6	$\text{C}=\text{C}$ str
1418 (sh) ^b , 1407	1419, 1407	1419, 1407	1408, 1405	1415	ν_7	$=\text{CH}_2$ scissors
1374	1373	1374	1370	1370	$\nu_{10} + \nu_{12}$	Combination
1289 (br) ^b	1323	1323	1319	1305–1282	$\nu_9 + \nu_{12}$	Combination
	1292	1292	1293	1312	ν_8	$\text{C}=\text{C}-\text{H}$ bend
	1259, 1252	1259, 1252	1260, 1251	1265–1230	$2\nu_{11}/2\nu_{17}/\nu_{11}+\nu_{17}$	Combination
1095, 1083	1095, 1083	1095, 1083	1094, 1082	1096	ν_9	$=\text{CH}_2$ rock
979	982	982	980	974	ν_{14}	$\text{C}=\text{C}-\text{H}$ bend
938	944	944	943	927	ν_{15}	$=\text{CH}_2$ wag
876	876	876	876	874	ν_{10}	$\text{C}-\text{C}$ str
655 (br) ^b	670	669	665	677	ν_{16}	$=\text{CH}_2$ twist
	632	632	636	625	ν_{11}	$\text{C}\equiv\text{C}-\text{H}$ bend
			628	618	ν_{17}	$\text{C}\equiv\text{C}-\text{H}$ bend
542	542	542	542	539	ν_{12}	$\text{C}=\text{C}-\text{C}$ bend

Notes.

^a Tørneng et al. 1980.

^b br: broad; sh: shoulder.

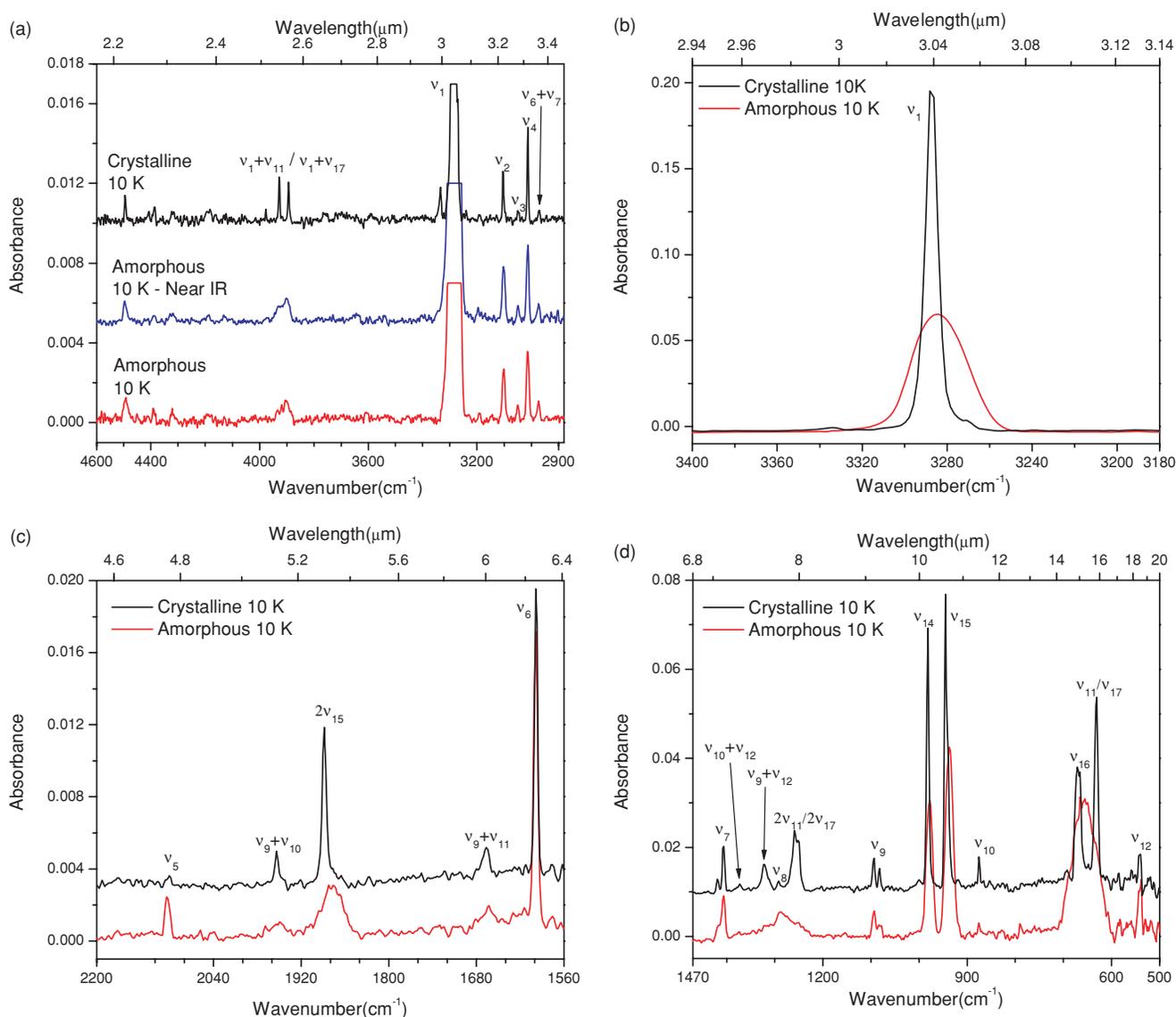


Figure 2 Infrared spectra of the vinylacetylene ices with vibrational assignments. Refer to Table 1 for band positions. The ν_1 band has been truncated to fit in the figure. The overview spectra from 5000 to 500 cm^{-1} is shown in Figure 1. Panel (b) presents an expanded view of the ν_1 region showing both the crystalline and the amorphous phase spectra. Panels (c) and (d) expand the 2200–1560 and 1470–500 cm^{-1} ranges of the overview spectra as depicted in Figure 1.

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infrared spectra of solid vinylacetylene were recorded in our laboratory (Figure 1, Table 1). Amorphous vinylacetylene ices were initially prepared at 10 K. Broad absorption characteristics of the amorphous structure appear to stand out near 650 and 1300 cm^{-1} , while the line broadening is also significant for the bands at 950, 1900, and 3300 cm^{-1} .

3.2. Annealing and Phase Transition to Crystalline Ice

The phase transition of solid vinylacetylene was closely monitored by annealing the amorphous ice to 100 K with a gradient of 0.5 K minute^{-1} . As evident from the change of the infrared spectra with increasing temperature (Figures 1–3), the amorphous ice crystallizes at 92–94 K. It is a coincidence that this temperature is close to Titan's surface temperature of 94 K. The annealing above 94 K does not promote further changes. The crystalline ice at 100 K was then recycled back to 10 K, during which the ice became invariant to the temperature drops. In Figure 1, overview spectra of both amorphous and crystalline

ices were recorded at 10 K in the mid-infrared range. Detailed band assignments are shown in Figure 2 and listed in Table 1. Given the spectral resolution of 4 cm^{-1} , our band assignments of the crystalline ice are in accord with those reported in the literature, except that both fundamentals of ν_{11} and ν_{17} in our measurement appear inseparable, lying at 632 cm^{-1} , a median of those literature values, 636 and 628 cm^{-1} , respectively (Tørmeng et al. 1980). Also, we found hitherto undiscovered absorptions in the near-infrared range at about 3900 cm^{-1} , assigned to $\nu_1 + \nu_{11}/\nu_1 + \nu_{17}$, and at 4500 cm^{-1} (Figure 2).

The amorphous ice of vinylacetylene vividly contrasts with the crystalline counterpart by the following signatures. First, there are three spectral regions at 655, 1289, and 3912 cm^{-1} , where the absorptions of amorphous ice are uncharacteristically broad and clumpy in nature, but upon crystallization transformed into structured and well-defined bands. It is such transformation that could be pronounced during the phase transition period. The infrared spectra in Figure 3 were taken during the warm-up period at 10, 91, 92, 94, and 100 K and deliver a detailed

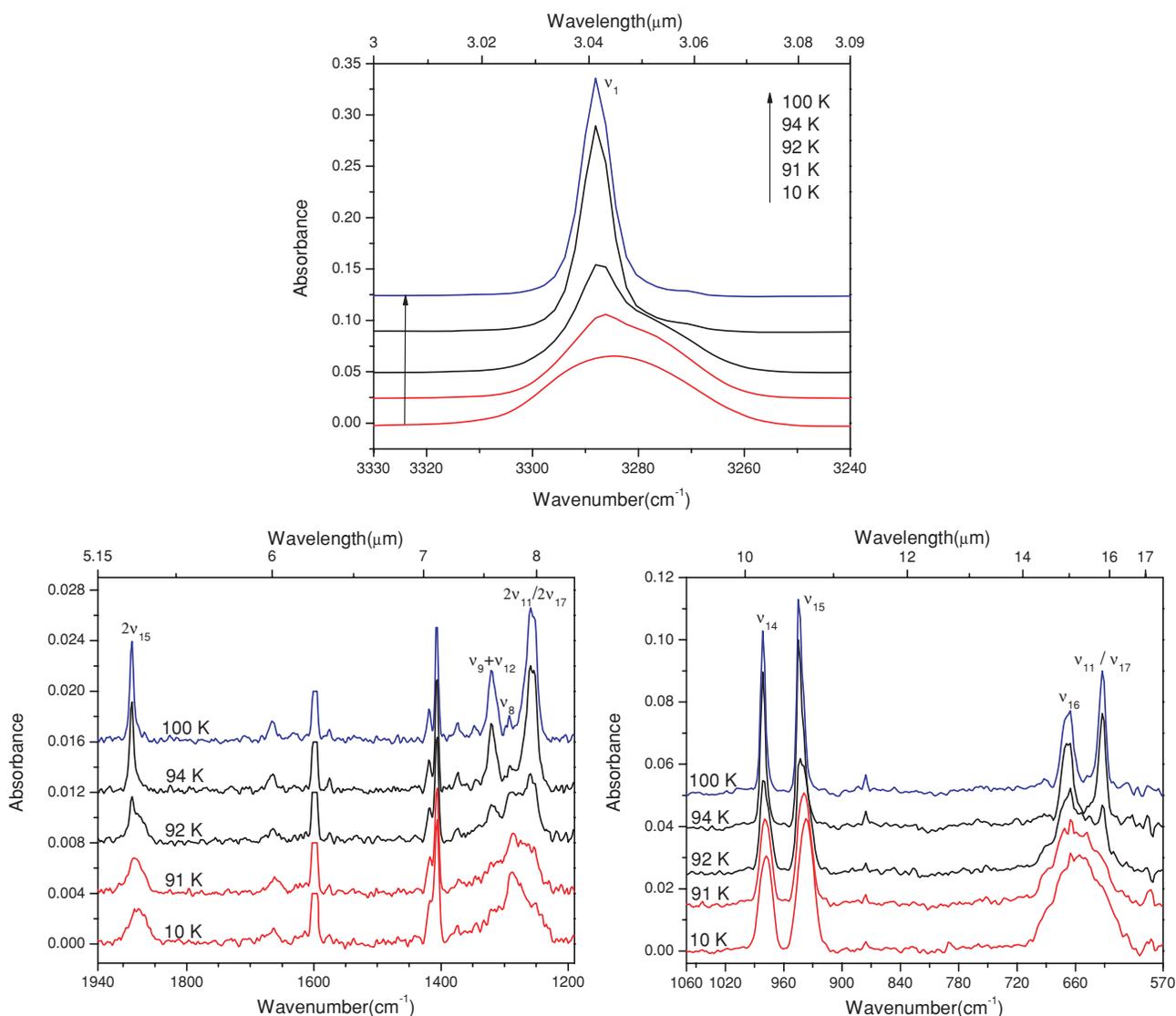


Figure 3 Temperature-dependent infrared spectra taken during warm-up period. The range of phase transition (92, 94 K) is highlighted in black, while amorphous (10, 91 K) ice in red and crystalline (100 K) ice in blue. Three different spectral ranges are selected which highlight the blueshift and the splitting of the bands (see the text for a detailed discussion).

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view on such transformation. Up to 91 K, the amorphous nature remains invariant to the temperature rise. However, the spectra begin to change at about 92 K; this process is complete at 94 K. During this period, C≡C–H deformations, either in fundamental or overtone levels, emerge decisively together with adjacent vibrations. The second signature can readily be observed by comparing the most intense band of the ices, ν_1 at about 3300 cm^{-1} . Upon crystallization, the broad feature becomes visibly narrower and blueshifts. This pattern is also visible on other vibrations such as =CH₂ wagging and its overtone at about 940 and 1880 cm^{-1} , respectively. As detailed in Figure 2, the amorphous bands lying at 3912 (Figure 2(a)), 3284 (Figure 2(b)), 1877 (Figure 2(c)), and 1289 as well as 655 cm^{-1} (Figure 2(d)) experience the splitting and/or the blueshift. Indicative of the crystallization temperature, such spectral changes are very pronounced close to 94 K (Figure 3).

3.3. Sublimation Profile of Solid Vinylacetylene

Amorphous vinylacetylene was initially deposited on the substrate held at 10 K. Heating up the substrate with a gradient

0.5 K minute^{-1} up to 140 K affords to monitor details on the transition from the amorphous ice to the crystalline sample; simultaneously, the sublimation profile of the sample can be monitored with a quadrupole mass spectrometer. As shown in Figure 4, vinylacetylene starts to sublime at about 101 K, reaches a maximum of ion counts at 119 K, and completes at 120 K.

4. CONCLUSION AND IMPLICATIONS FOR SATURN'S SATELLITE TITAN

The current infrared spectrometer aboard the *Cassini* spacecraft is capable of scanning a spectral range of $10\text{--}1500\text{ cm}^{-1}$ at a maximum resolution of 0.5 cm^{-1} (Coustenis et al. 2007; Vinatier et al. 2007). The improved spectral resolution over the past *Voyager* mission is being utilized for untangling the previously blended lines, $600\text{--}700\text{ cm}^{-1}$ range in particular, of the *Voyager* data, aiding to elucidate the abundances of gas phase species such as methylacetylene (C₃H₄), diacetylene (C₄H₂), CO₂, benzene (C₆H₆), and cyanoacetylene (HC₃N) in the Titan's stratosphere. Considering that the far-infrared range is still open to new species discovery (Coustenis et al. 2007), we

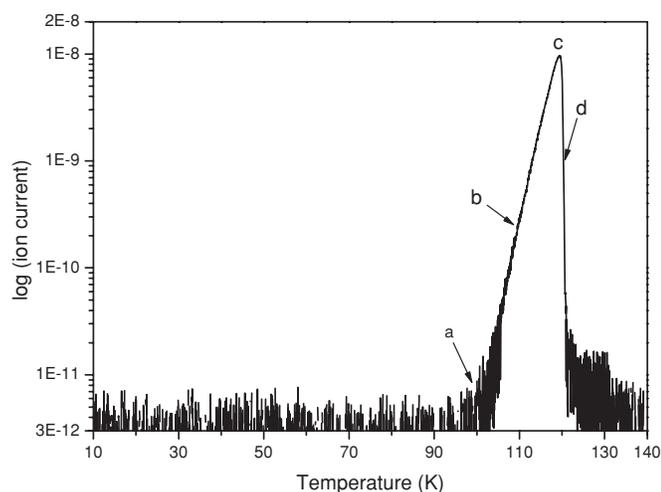


Figure 4 Ion-count profile of vinylacetylene recorded at $m/z = 52$ from 10 K to 140 K. Selected temperatures correspond to (a) 101 K, (b) 110 K, (c) 119 K, and (d) 120 K. Refer to Section 3.3 for details.

propose to search for gas phase vinylacetylene perhaps in the lower stratosphere, focusing on ν_{18} , out-of-plane $C\equiv C$ deformation (Tørneng et al. 1980). The Q -branch of this band near 305 cm^{-1} should be resonant closely lying to that of the methylacetylene (C_3H_4) band at 325 cm^{-1} . Two intense transitions associated with $C\equiv C-H$ deformations may also appear about 630 cm^{-1} , overlapping with those of trace gases such as diacetylene.

So far, the majority of spectroscopic investigations of Titan's constituents have focused on the gas phase. However, an observation of molecules in their solid states can convey important constraints on physical conditions such as pressures and condensation temperatures, as well as on the inherent chemistry and interaction between the gas phase and solid phase (Titan's surface, aerosol particles, haze layers; Lorenz et al. 2008). This in turn provides important clues to how Titan's clouds and the heterogeneous nucleation influence Titan's weather system (Curtis et al. 2008). In the solid state, dicyanoacetylene (NCCCCN, C_4N_2) was detected on Titan via its ν_8 fundamental at 478 cm^{-1} (Samuelson et al. 1997). One decade later, Khanna (2005b) suggested the presence of solid cyanoacetylene (HCCCN) by comparing the absorptions taken toward Titan at 505 and 753 cm^{-1} with laboratory spectra. Coustenis et al. (1999) and Samuelson et al. (1997) indicated that ethane (C_2H_6), acetylene (C_2H_2), cyanoacetylene (HCCCN), and hydrogen cyanide (HCN) also exist in the solid state. From these studies, we recognize that solid hydrocarbons and nitriles may indeed exist in Titan's atmosphere. Here, solid vinylacetylene may exist as either amorphous or crystalline. We recorded temperature-dependent infrared spectra and extracted relative thermal stabilities of both ices. Strong differences unleash the possibility that vinylacetylene ices, if found, will be discernable in the future Titan infrared missions. Furthermore, the characteristic phase transition of solid vinylacetylene ($92\text{--}94\text{ K}$) offers a utility like a molecular-level indicator acting onto the surface temperature (Figure 3). Therefore, the phase transition temperature of vinylacetylene ices, which is close to the surface temperature of Titan, together with the recorded infrared spectra can present a valuable indicator to determine the surface temperature accurately once solid vinylacetylene has been identified on Titan. Also, if vinylacetylene exists on Titan's surface, it would require

transport from those atmospheric regions where it is formed in the gas phase to the surface (Dimitrov & Bar-Nun 1997, 2004). The Antoine equation listed on National Institute of Standards and Technology (NIST) database at <http://webbook.nist.gov> affords to estimate vapor pressure of vinylacetylene at temperatures close to the Titan's atmosphere where condensation may take place. At 140, 120, and 100 K, the vapor pressures of vinylacetylene correspond to the order of 10^{-3} , 10^{-6} , and 10^{-10} Torr, respectively.

Based on our studies, we recommend utilizing the ν_1 and $\nu_{16}/\nu_{11}/\nu_{17}$ fundamentals of solid vinylacetylene and match the 3300 and 650 cm^{-1} positions to determine if crystalline or amorphous vinylacetylene exists in the form of aerosol particles in Titan's atmosphere. The finest approach would be to utilize space-based telescopes to search for these bands in absorption against the reflected light from the Sun or against the continuum emission. Also, future missions to Titan shall probe the surface in situ via infrared spectroscopy. Here, our spectra are of crucial importance to identify if vinylacetylene exists as an amorphous solid or in a crystalline phase.

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