Contents lists available at ScienceDirect

Planetary and Space Science

Infrared spectroscopy of crystalline and amorphous diacetylene (C_4H_2) and implications for Titan's atmospheric composition

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ARTICLE INFO

ABSTRACT

New laboratory spectra of crystalline and amorphous diacetylene ice have been recorded in the range of 7000–500 cm^{-1} (1.4–20 μm) to aid in the identification of solid diacetylene on Saturn's moon Titan. We have established that amorphous diacetylene ice is stable only at temperatures less than 70 ± 1 K. With respect to observations on Titan, the best approach would be to utilize future space-based telescopes to search for the v_4 (3277/3271 cm^{-1}) in absorption against the reflected light from the sun and the slightly weaker v_8 absorption bands (676/661 cm^{-1}) in absorption against the continuum emission.

1. Introduction

The composition of the nitrogen-rich atmosphere of Saturn's moon Titan has been studied extensively for more than two decades since the early days of the Voyager 1 and 2 missions in 1980 and 1981. In the gas phase, about fifteen molecular species have been identified mainly via infrared spectroscopy. The molecules observed fall into three categories. The first are hydrocarbons such as CH_4 (methane), CH_3D (d1-methane), C_2H_2 (acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), C_3H_4 (methylacetylene), C_3H_8 (propane), C_4H_2 (diacetylene), and C_6H_6 (benzene) identified via their infrared absorptions (Coustenis et al., 2007; Hebrard et al., 2007). The second are nitriles – molecules carrying a cyano (CN) group – such as HCN (hydrogen cyanide), HCCCN (cyanoacetylene), and C_2N_2 (cyanogen) (Coustenis et al., 2007; Hebrard et al., 2007). Finally, oxygenated species – CO_2 (carbon dioxide), CO (carbon monoxide), and H_2O (water) – were observed in the infrared regime of the electromagnetic spectrum. It should be stressed that Cassini–Huygens mission to Titan not only confirmed the chemical makeup of Titan, but also provided latitude- and height dependent mixing ratios of these chemicals (Teanby et al., 2008; Coustenis et al., 2007).

Surprisingly little is known on the constituents in the condensed phase. Dicyanoacetylene (NCCCCN, C_4N_2), a molecule which has been proposed as the first condensable species on Titan and potential building-block of the organic haze layers, was detected by Samuelson et al. from Voyager observations at a resolution of 4.7 cm^{-1} via its v_8 fundamental at 478 cm^{-1} (Samuelson et al., 1997). In 2005, Khanna proposed the existence of solid cyanoacetylene (HCCCN) by comparing the absorptions taken toward Titan as obtained from Voyager data (resolution: 4.7 cm^{-1}) at 505 and 753 cm^{-1} with laboratory spectra (Khanna, 2005a); at the same time, Khanna proposed the presence of solid acetylene (C_2H_2) via its absorptions in the 700–800 cm^{-1} range (Khanna, 2005b). Based on laboratory studies, his group also suggested solid propionitrile (C_2H_5CN) to be present on Titan (Khanna, 2005b). From these studies, we recognize that solid hydrocarbons and nitriles may indeed exist in Titan's atmosphere. These solids may have also accumulated on Titan's surface (Lorenz et al., 2008).

Considering that solid acetylene (HCCH) and cyanoacetylene (HCCCN) have been probed in Titan's atmosphere, it is surprising that solid diacetylene (HCCCCH) has not been identified so far. Note that gas phase diacetylene was detected in the stratosphere of Titan by Kunde et al. (1981); two bands at 220 and 628 cm^{-1} correspond to the v_9 and v_8 fundamentals of diacetylene, respectively. The mole fraction of diacetylene varies strongly depending on the altitude (Vinatier et al., 2007). Due to its photochemical activity (Yung et al., 1984; Okabe, 1983; Laufer and

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Bass, 1979), diacetylene, which can be formed by the bimolecular neutral–neutral reaction of ethynyl radicals (C_2H) with acetylene (C_2H_2) (Kaiser et al., 2002), is considered as an important precursor to form larger hydrocarbon molecules, in particular polyacetylenes; the latter can polymerize easily (Kuriyama et al., 1996) and may contribute significantly to the formation of the organic haze layers in Titan's atmosphere. The infrared spectrum of gas phase diacetylene is well known (Koops et al., 1984; Gabalov et al., 1986), but as for the condensed phase, only a few limited studies exist in the matrix (Patten and Andrews, 1986; Chang and Graham, 1982). Khanna investigated the infrared absorptions of crystalline diacetylene at 70 K (Khanna et al., 1988). Due to the importance of diacetylene and to assist in the identification of diacetylene in the solid state, we recorded infrared spectra of crystalline and of amorphous diacetylene in the laboratory at temperatures from 10 to 96 K. These are combined with experiments to elucidate the temperature at which amorphous diacetylene ices change to well-defined crystalline structures. We would like to stress that so far, no systematic study on the infrared spectra from 10 K to the sublimation of diacetylene have been conducted; likewise, there is no systematic comparison of the spectra of crystalline and amorphous diacetylene. Differences and similarities of the infrared spectra of the crystalline and amorphous phases are utilized to propose prospective search strategies of solid diacetylene in Titan's atmosphere.

2. Experimental

Diacetylene was synthesized according to the literature (Jones, 1952; Okabe, 1981). Briefly, 9 g of 1,4-dichloro-2-butyne ($ClCH_2CCCH_2Cl$) were dissolved in 15 ml ethyl alcohol (C_2H_5OH) and warmed up to 353 K. Sixty percent aqueous sodium hydroxide (NaOH) solution was added dropwise while stirring. White diacetylene vapor evolved and was carried away in a stream of helium carrier gas. The diacetylene gas was bubbled through a 13% aqueous sodium hydroxide solution, dried over calcium chloride, and frozen in a liquid nitrogen trap (77 K). Gas mixtures of 5% diacetylene in helium (99.9999%; Gaspro) were prepared at 293 K and at a pressure of 3 atm. These mixtures were stable for months. The purity of the diacetylene was checked via mass spectrometry and was found to be 99.5% +; without the calcium chloride, a higher yield, but a lower purity of only 99% was achieved.

Diacetylene ices were prepared in a contamination-free ultra-high vacuum chamber which can be evacuated to pressures as low at 3×10^{-11} torr (Bennett et al., 2004). A two-stage closed-cycle helium refrigerator coupled with a rotary platform is attached to the main chamber of the machine and holds a polished silver mirror. The latter serves as a substrate for the diacetylene ice condensation. With the combination of the closed-cycle helium refrigerator and a programmable temperature controller, the temperature of the samples can be regulated very precisely to ± 0.3 K between 10 and 350 K. A fine regulation valve coupled to a glass capillary array is utilized to condense diacetylene gas at pressures of typically 1.5×10^{-7} torr for 10 min on the silver mirror at 10 K. A Fourier transform infrared spectrometer (Nicolet 6700 FTIR) was employed to measure the infrared spectra of the sample online and in situ. The thickness of the diacetylene was estimated to be about 66 ± 10 nm based on the integrated infrared absorption coefficient (A_{ref}) of the v_4 band in the 3320 cm^{-1} regime ($A_{ref} = 3.3 \times 10^{-17}$ cm molecule^{-1}) (Silva et al., 2008) and utilizing a modified Lambert–Beers relationship accounting for the ingoing and outgoing beam and for the angle of the infrared beam with respect to the surface normal (Bennett et al., 2004). The
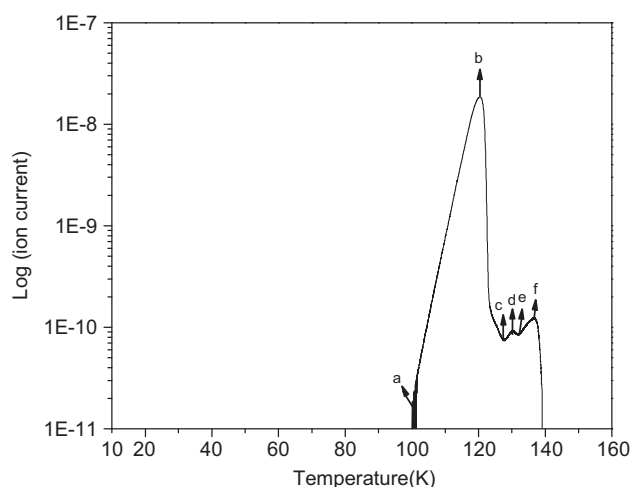

Fig. 1. Ion count profile of diacetylene recorded at $m/z = 50$ from 10 to 160 K. Temperatures at selected points correspond to 101 K (a), 120 K (b), 128 K (c), 130 K (d), 132 K (e), and 136 K (f), respectively. The crystalline sample was heated at a rate of 0.5 K min^{-1}.

sublimation of the diacetylene sample was monitored in the gas phase via ion counts at $m/z = 50$ ($C_4H_2^+$) through a quadrupole mass spectrometer (Balzers QMS420). Samples of crystalline diacetylene were prepared by annealing the amorphous diacetylene ices at a rate of 0.5 K min^{-1} to 96 K and cycling the sample with 0.5 K min^{-1} back to 10 K. Temperatures higher then 96 K were avoided since diacetylene starts subliming at 101 K (Fig. 1(a)). The ion currents up to the ion current peak at 120 K (b) can be attributed to diacetylene molecules subliming from the diacetylene bulk ice. It should be mentioned that the sublimation temperatures in the laboratory differ from those on Titan since our laboratory setup and Titan have different pressures. Due to the molecular structure of the diacetylene molecules and the interaction of the π electron density with metal surfaces, Muniz-Miranda et al. (2005) and Giorgetti et al. (2006) suggested that physisorbed diacetylene molecules can stick to the surface of metals; this might also lead to a sticking on the silver surface in our experiments. The enhanced binding energy would result in a delayed release in the gas phase, i.e. a higher temperature compared to the bulk diacetylene molecules. Therefore, the smaller peaks at 130 K (d) and 136 K (f) might be correlated with diacetylene molecules subliming from physisorbed sites of the silver target.

3. Results

The infrared spectra of the crystalline and amorphous diacetylene ices are shown in Fig. 2; both spectra were recorded at 10 K. Considering a linear, gas phase diacetylene molecule with six atoms, we would expect thirteen fundamental bands. Four fundamental bands (v_6–v_9) are doubly degenerate; also the v_7 (482 cm^{-1}) and v_9 (231 cm^{-1}) absorptions fall outside the range of our detector; therefore, seven fundamental bands should be observable. In the diacetylene ices, we monitored the fundamental bands at around 3271–3293 cm^{-1} (v_1/v_4), 2179 cm^{-1} (v_2), 2006–2011 cm^{-1} (v_5), 845 cm^{-1} (v_3), and 661–676 cm^{-1} (v_6/v_8). Compared to Khanna et al. (1988), we were also able to monitor the $2v_4$ overtone band. It should be stressed that the shapes of the v_1/v_4, v_5, and v_6/v_8 bands differ significantly in the amorphous ice to the crystalline structure. Here, bands in

the amorphous ices are typically very broad; upon change from the amorphous to the crystalline structure, we also observe pronounced fine structures in the v_1/v_4, v_5, and v_6/v_8 bands.

Besides the fundamental bands, we were also able to observe seven combination bands as compiled in Table 1. Here, the v_4+v_6 absorption also splits upon changing from the amorphous to the
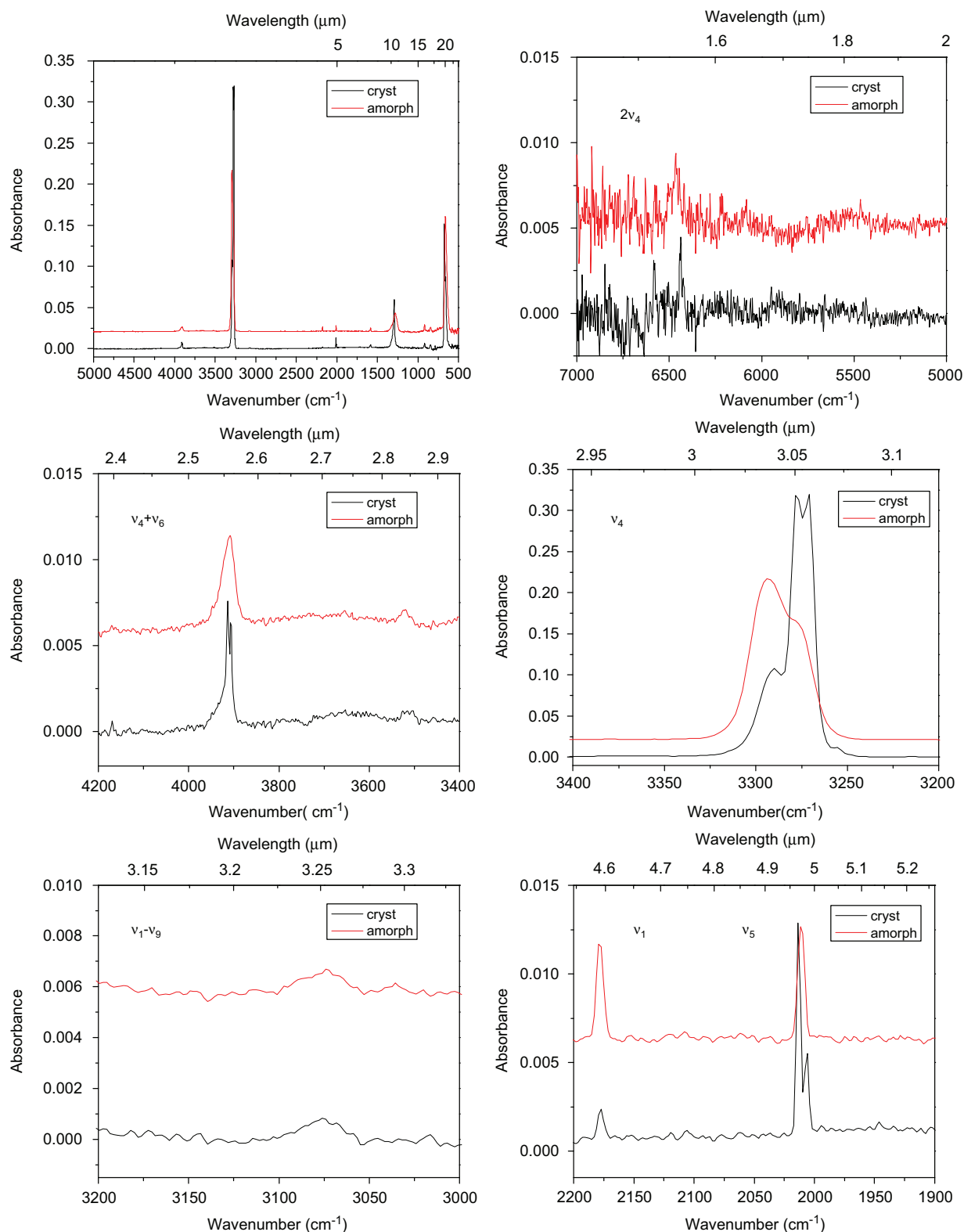

Fig. 2. Infrared spectra of crystalline and amorphous diacetylene ices recorded at 10 K. The peak positions are compiled in Table 1.
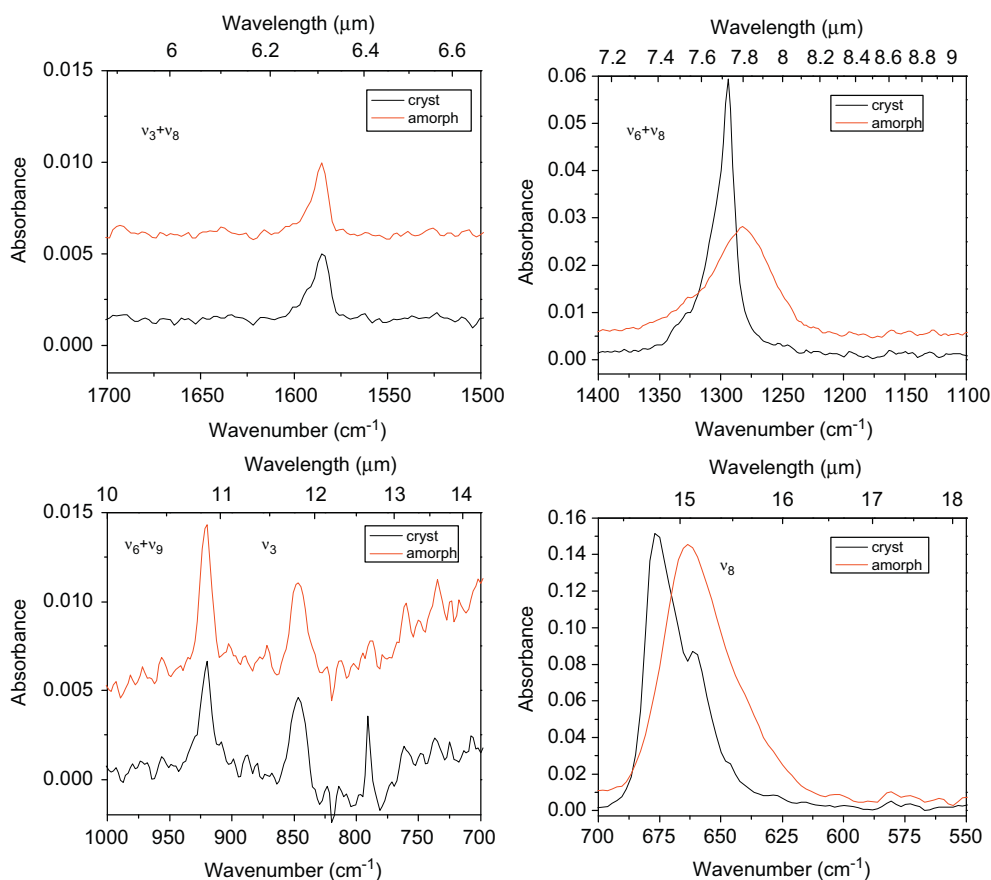
Fig. 2. (*Continued*)

Table 1
Positions of fundamentals, overtones, and combination bands of crystalline and amorphous diacetylene ices recorded in our laboratory.

Amorphous[a] (10 K)	Crystalline[a] (10 K)	Crystalline[a] (94 K)	Literature[b] (gas phase)	Literature[c] (crystalline)	Assignments	Carrier
6465	6439	6443			$2v_4$	Overtone
3908	3913, 3907	3914, 3907	3939		v_4+v_6	Combination
3522	3518	3520	3554		v_1+v_9	Combination
3293	3277, 3271	3278, 3273	3324	3272	v_4	CH stretch
			3293		v_1	CH stretch
3074	3075	3075	3109		v_1-v_9	Combination
2179	2178	2178	2184		v_2	C$\equiv$C str.
2011	2013, 2006	2013, 2007	2018	2013	v_5	C$\equiv$C str.
1586	1585	1585			v_3+v_8 (?)	Combination
1282	1294	1292	1240	1363/1310	v_6+v_8	Combination
921	920	920	845		v_6+v_9	Combination
845	847	847	874		v_3	C–C str.
788	790	788	701		v_7+v_9	Combination
664	676, 661	674	630	652	v_8	CH bend
			627		v_6	CH bend
				252	v_9	C$\equiv$C–C bend

[a] Literature data were taken from Koops et al. (1984).
[b] Gabalov et al. (1986).
[c] Khanna et al. (1988).

crystalline phase. The fine structure in the crystalline ices can be attributed to distinct lattice modes of diacetylene.

Having outlined the assignments of the absorptions of diacetylene, we now examine the temperature dependence of the infrared spectra (Fig. 3). This helps us to elucidate the temperature at which amorphous diacetylene converts to a crystalline phase. Fig. 3 shows (from the bottom to the top) the absorption of the amorphous diacetylene recorded at 10–100 K. The temperature was increased starting at 10 K. The final spectrum depicts the crystalline sample at 10 K. As evident from
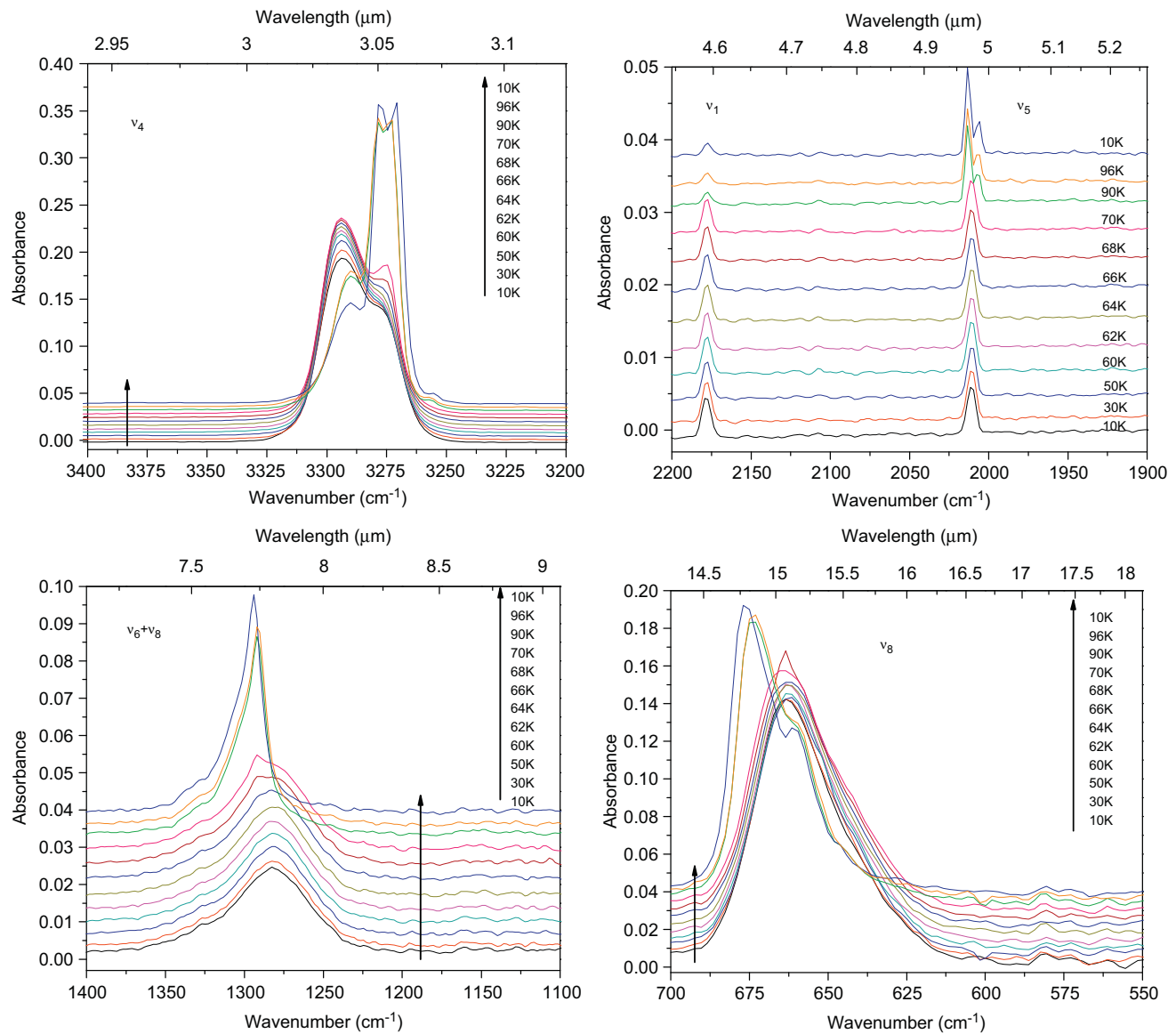
Fig. 3. Infrared spectra of crystalline and amorphous diacetylene ices recorded at 10 K. The shape in the spectra can be clearly seen when annealing amorphous diacetylene ice from 10 K to about 70 K with a constant rate of 0.5 K min^{-1}. The 96 K sample was cycled back to 10 K to investigate the temperature effects on the bands of the crystalline diacetylene sample. See text for a detailed discussion.

Fig. 3, four absorptions show a strong temperature dependence. These are: v_4, v_5, v_6+v_8, and v_8. From 10 to 64 K, the v_4 band is almost temperature invariant. As the temperature reaches 66 K, a pronounced peak emerges from the shoulder at 3275 cm^{-1}. A further increase of the temperature to 68 K changes the spectrum dramatically: the absorption at 3300 cm^{-1} decreases substantially, and the peak at 3275 cm^{-1} splits into two components. An additional temperature increase closer to the sublimation point does not influence the peak shape much. These patterns are also reflected in the temperature dependence of the shapes of the v_5 fundamental and of the v_6+v_8 combination band. From 10 to 68 K, the absorption looks essentially identical. Considering the v_5 band, a small shoulder emerges at the low frequency side at about 2007 cm^{-1} at 68–70 K. In case of the v_6+v_8 combination band, a pronounced blue shift and line sharpening is observable at 70 K. This is similar to the v_8 fundamental which depicts a blue shift

and change in shape at this temperature. Based on these considerations, we would like to suggest that a conversion of the amorphous diacetylene to crystalline diacetylene ice occurs at 70 ± 1 K.

4. Observational implications

The laboratory spectra showed explicitly that it is feasible to discriminate amorphous and crystalline diacetylene samples (Figs. 2 and 3) if solid diacetylene exists on Titan—either on Titan's surface or in form of aerosol particles. Note that solid diacetylene was suggested to produce significant condensate material near 78 km at 117 K (Coustenis et al., 1999). The temperature to convert amorphous to crystalline diacetylene was determined to be about 70 K. This presents the very first exact

determination of the transition from amorphous to crystalline diacetylene. Therefore, on the surface of Titan (about 94 K) and at heights of 78 km, solid diacetylene should exist in its crystalline phase. This has been postulated previously, for instance, by Khanna et al. (1988) and by Coustenis et al. (1999), however, without the knowledge of a precise transition temperature from the amorphous to the crystalline stage.

What would be a sensible approach to search for crystalline and/or amorphous diacetylene in our Solar System, such as on Saturn's moon Titan? Based on the temperature dependence of the spectra and the intensity of the absorptions, it would be best to study the strong v_4 (3293 cm^{-1}) and v_8 absorption bands (664 cm^{-1}) and observe the peak position within an accuracy of 5 cm^{-1}. Is it feasible to monitor these bands via terrestrial telescopes or from space? Considering the atmospheric transmission and the accessible wavelength range of, for instance Mauna Kea, only the 6465 cm^{-1} (1.55 μm), 3293 cm^{-1} (3.05 μm), 2011 cm^{-1} (4.95 μm), and 1282 cm^{-1} (7.75 μm) spectral regions are accessible. If we look at the near infrared spectrum of Titan in the range of 20,000–2000 cm^{-1} (0.5–5 μm) (Geballe et al., 2003), deep bands of methane block the 6465 cm^{-1} (1.55 μm) and 3293 cm^{-1} (3.05 μm) bands of diacetylene. At 2011 cm^{-1} (4.95 μm), the spectra would be unreliable due to variable water vapor absorption in the terrestrial atmosphere. From the thermal infrared spectrum recorded by Coustenis et al. (2007), we see that the spectrum is completely dominated by methane emission from the stratosphere, thus making the detection of the less prominent 1282 cm^{-1} (7.75 μm) band very challenging. For completeness, we would like to recall that Khanna et al. (1988) also observed the v_9 at 223 and 252 cm^{-1}. Features of this mode of diacetylene have been searched for unsuccessfully previously on Titan (Coustenis et al., 1999; Samuelson et al., 1997). Therefore, it will be challenging to monitor crystalline and/or amorphous diacetylene on Titan utilizing terrestrial telescopes. The best approach is to use future space-based telescopes to search for the v_4 (3277/3271 cm^{-1}) in absorption against the reflected light from the sun and the slightly weaker v_8 absorption bands (676/661 cm^{-1}) in absorption against the continuum emission.

Acknowledgements

References

Bennett, C.J., Jamieson, C., Mebel, A.M., Kaiser, R.I., 2004. Untangling the formation of the cyclic carbon trioxide isomer in low temperature carbon dioxide ices. Phys. Chem. Chem. Phys. 6, 735.

Chang, K.W., Graham, W.R.M., 1982. The near-ultraviolet spectrum of diacetylene trapped in solid argon at 9 K. J. Mol. Spectrosc. 94 (1), 69–78.

Coustenis, A., et al., 2007. The composition of Titan's stratosphere from Cassini/CIRS mid-infrared spectra. Icarus 189, 35–62.

Coustenis, A., Schmitt, B., Khanna, R.K., Trotta, F., 1999. Plausible condensates in Titan's stratosphere from Voyager infrared spectra. Planet. Space Sci. 47, 1305–1329.

Gabalov, B., Dudev, T., Nicolova, B., Orville-Thomas, W.J., 1986. Interpretation and prediction of vibrational intensities in infrared spectra: fluorinated methanes. J. Mol. Struct. 120, 276–283.

Geballe, T.R., Kim, S.J., Noll, K.S., Griffith, C.A., 2003. High-resolution 3 micron spectroscopy of molecules in the mesosphere and troposphere of Titan. Astrophys. J. 583, L39.

Giorgetti, E., Muniz-Miranda, M., Margheri, G., Giusti, A., Sottini, S., Alloisio, M., Cuniberti, C., Dellepiane, G., 2006. UV polymerization of self-assembled monolayers of a novel diacetylene on silver: a spectroscopic analysis by surface plasmon resonance and surface enhanced Raman scattering. Langmuir 22 (3), 1129–1134.

Hebrard, E., Dobrijevic, M., Benilan, Y., Raulin, F., 2007. Photochemical kinetics uncertainties in modeling Titan's atmosphere: first consequences. Planet. Space Sci. 55, 1470–1489.

Jones, A.V., 1952. Infrared and Raman spectra of biacetylene. Proc. R. Soc. London, Ser. A 211, 285.

Kaiser, R.I., Stahl, F., Schleyer, P.v.R., Schaefer III, H.F., 2002. Atomic and molecular hydrogen elimination in the crossed beam reaction of d1-ethinyl radicals $C_2D(X^2\Sigma^+)$ with acetylene, $C_2H_2(X^1 \Sigma_g^+)$: dynamics of d1-diacetylene (HCCCCD) and d1-butadiynyl (DCCCC) formation. PCCP 4, 2950–2958.

Khanna, R.K., Ospina, M.J., Zhao, G., 1988. Infrared band Intensities and complex refractive indices of crystalline C_2H_2 and C_4H_2. Icarus, 527–535.

Khanna, R.K., 2005a. Condensed species in Titan's atmosphere: identification of crystalline propionitrile (C_2H_5CN, CH_3CH_2CN) based on laboratory infrared data. Icarus 177, 116–121.

Khanna, R.K., 2005b. Condensed species in Titan's stratosphere: confirmation of crystalline cyanoacetylene (HC_3N) and evidence for crystalline acetylene (C_2H_2) on Titan. Icarus 178, 165–170.

Koops, T., Visser, T., Smit, W.M.A., 1984. The harmonic force field and absolute infrared intensities of diacetylene. J. Mol. Struct. 125, 179–196.

Kunde, V.G., Aikin, A.C., Hanel, R.A., Jennings, D.E., Maguir, W.C., Samuelson, R.E., 1981. C_4H_2, HC_3N, and C_2N_2 in Titan's atmosphere. Nature (London) 292, 686–688.

Kuriyama, K., Kikuchi, H., Kajiyama, T., 1996. Solid-state polymerization behaviors of crystalline diacetylene monolayers on hydrophilic surfaces. Langmuir 12, 2283.

Laufer, A.H., Bass, A.N., 1979. Photochemistry of acetylene. Bimolecular rate constant for the formation of butadiyne and reactions of ethynyl radicals. J. Phys. Chem. 83, 310.

Lorenz, R.D., Stiles, B.W., Kirk, R.L., Allison, M.D., Persi del Marmo, P., Lunine, J.I., Ostro, S.J., Hensley, S., 2008. Titan's rotation reveals an internal ocean and changing zonal winds. Science 319, 1649–1651.

Muniz-Miranda, M., Giorgetti, E., Margheri, G., Del Rosso, T., Sottini, S., Giusti, A., Alloisio, M., 2005. SERS investigation on the polymerization of carbazolyl-diacetylene monolayers on gold surfaces. Macromol. Symp. 230 (Polymer Spectroscopy), 67–70.

Okabe, H., 1981. Photochemistry of acetylene at 1470 Å. J. Chem. Phys. 75 (6), 2772–2778.

Okabe, H., 1983. Photochemistry of acetylene. Can. J. Chem. 61, 850.

Patten Jr., K.O., Andrews, L., 1986. Infrared spectra of diacetylene–hydrogen fluoride complexes in solid argon. J. Phys. Chem. 90, 3910–3916.

Silva, R., Gichuhi, W.K., Huang, C., Doyle, M.B., Kislov, V.V., Mebel, A.M., Suits, A.G., 2008. H elimination and metastable lifetimes in the UV photoexcitation of diacetylene. Proc. Nat. Acad. Sci. U.S.A. 105, 12713–12718.

Teanby, N.A., Irwin, P.G.J., de Kok, R., Nixon, C.A., Coustenis, A., Royer, E., Calcutt, S.B., Bowles, N.E., Fletcher, L., Howett, C., Taylor, F.W., 2008. Global and temporal variations in hydrocarbons and nitriles in Titan's stratosphere for northern winter observed by Cassini/CIRS. Icarus 193, 595–611.

Samuelson, R.E., Mayo, L.A., Knuckles, M.A., Khanna, R.J., 1997. C_4N_2 ice in Titan's north polar stratosphere. Planet. Space Sci. 45, 941–948.

Vinatier, S., Bezard, B., Fouchet, T., Teanby, N.A., de Kok, R., Irwin, P.G.J., Conrath, B.J., Nixon, C.A., Romani, P.N., Flasar, F.M., Coustenis, A., 2007. Vertical abundance profiles of hydrocarbons in Titan's atmosphere at 15°S and 80°N retrieved from Cassini/CIRS spectra. Icarus 188, 120–138.

Yung, Y.L., Allen, M., Pinto, J.P., 1984. Photochemistry of the atmosphere of Titan: comparison between model and observations. Astrophys. J., Suppl. Ser. 55, 465.