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Introduction

Widespread lakes were discovered on Titan by the Cassini mission in 2006 [1]. At Titan surface pressures and temperatures, a mixture of liquid methane and photochemically produced ethane is the most likely liquid. This solution will serve as a solvent for the complex mixture of photochemical products formed in the upper atmosphere, which eventually fall to the surface. The presence of liquid hydrocarbons on the surface of Titan motivates questions about the solubility of surface materials in the liquid, and their fate during possible changes in lake composition and level.

Modeling of lake composition [2] suggests that some species may be present in the lakes at saturation or near saturation. Therefore, lowering of the lake level as a result of evaporation or other processes are likely to induce precipitation of some of the dissolved organics. These organic “evaporites” on the “beaches” or ephemeral lakes may play an important role in Titan’s surface chemistry, and might be identifiable in Cassini VIMS or radar data [3], see Figure 1.

This work describes some of our initial thoughts on how to interpret the notion of ‘beaches’ around the Titan seas. Are these beaches just deposited organics from the atmosphere, materials precipitated out from the ethane/methane lakes or both? Are crystalline or co-crystalline (such as the 1:1 acetylene-benzene co-crystal observed by [4]) complexes formed from the interaction of dissolved materials?

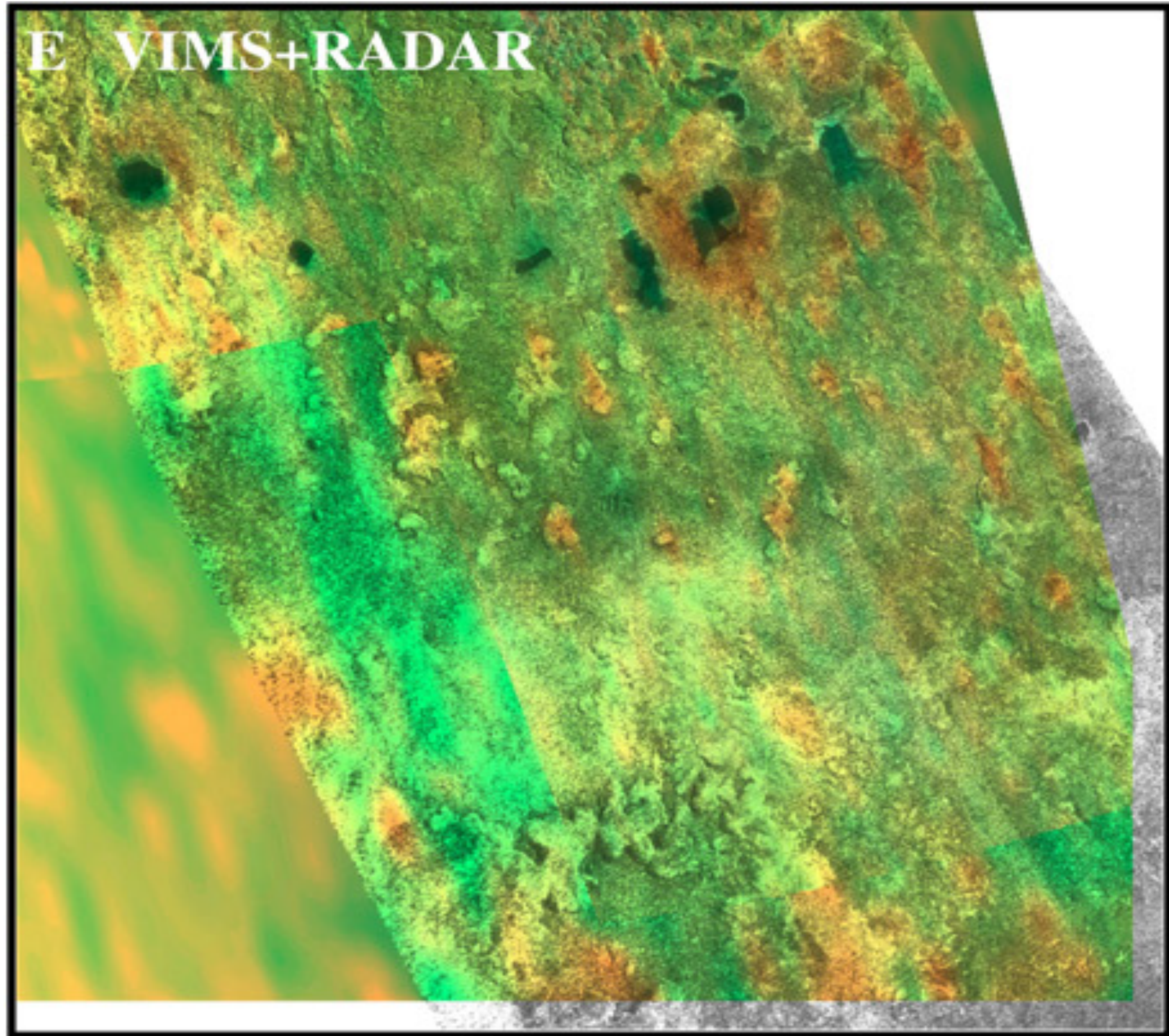


Figure 1: Coupled VIMS-Radar image of Titan’s Northern lakes showing “bedrock” (green) and possible evaporites (yellow to brown). After [3].

References

[1] E. R. Stofan et al., Nature 445, pp. 61-64, 2007.
[2] Cordier, D., Mousis, O., Lunine, J.I., Lavvas, P. and Vuitton, V., Ap. J., Vol. 707, L128, 2009.
[3] Barnes J.W., et al., Icarus 216, 136-140, 2011.
[4] Kirchner MT, Bläser D, Boese R. Chemistry-A European Journal, Vol. 16, 2136-2146, 2010.

Experimental Details

Organic evaporites are produced in a custom built cryostat (Figure 2). Approximately 5 mL of liquid ethane saturated with the solute or solutes of interest is held at 94 K. The liquid solution is transferred by pipette to a Linkam LTS 350 liquid nitrogen-cooled cryostage (Figure 2 inset). Liquid ethane is mixed with solid benzene, and the resulting materials are analyzed by Raman spectroscopy with a Horiba Jobin Yvon LabRam HR confocal Raman microscope.

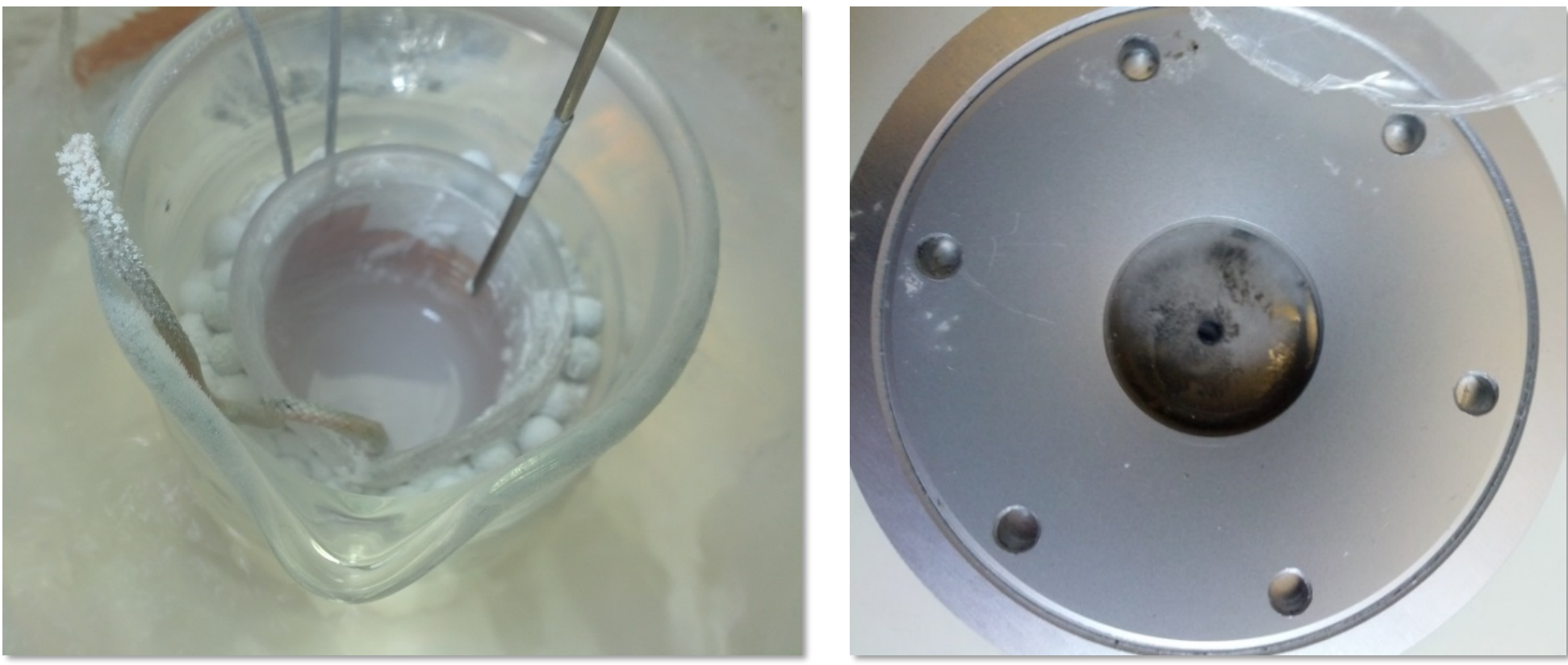


Figure 2: (Left) Liquid cryostat for solution preparation. (Right) Acetylene/benzene precipitate in cryostage.

Results and Conclusions

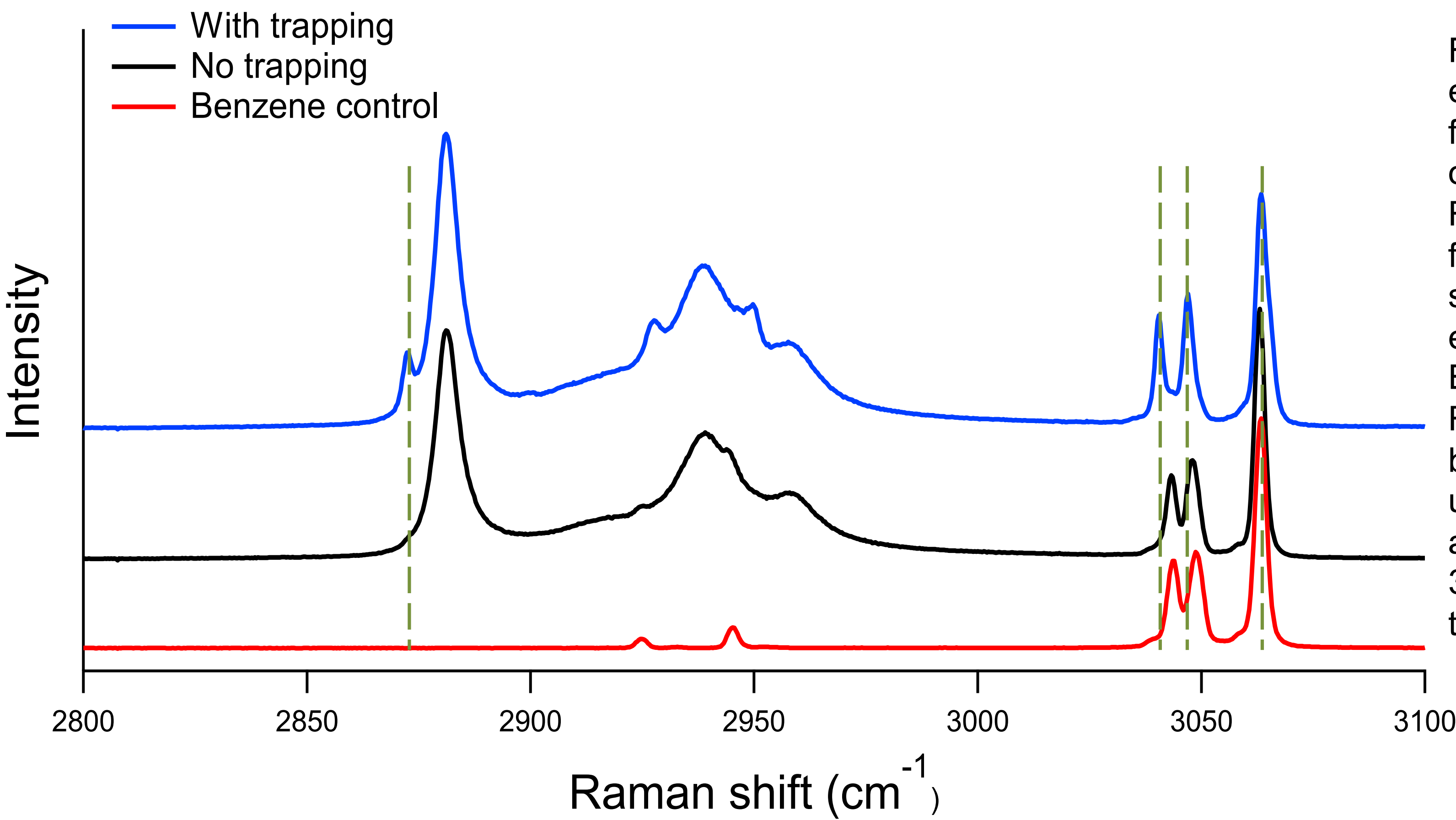


Figure 3: The most compelling evidence for co-crystal formation is a 12 cm⁻¹ red shift of the ν_7 ethane peak in the Raman spectrum. This shift from 2885 to 2873 cm⁻¹ signifies a new molecular environment for Ethane. Red shifts in the Raman frequencies of the ν_7 benzene modes are observed upon ethane trapping: approximately 3 cm⁻¹ for the 3044 cm⁻¹ peak and 2 cm⁻¹ for the 3049 cm⁻¹ peak.

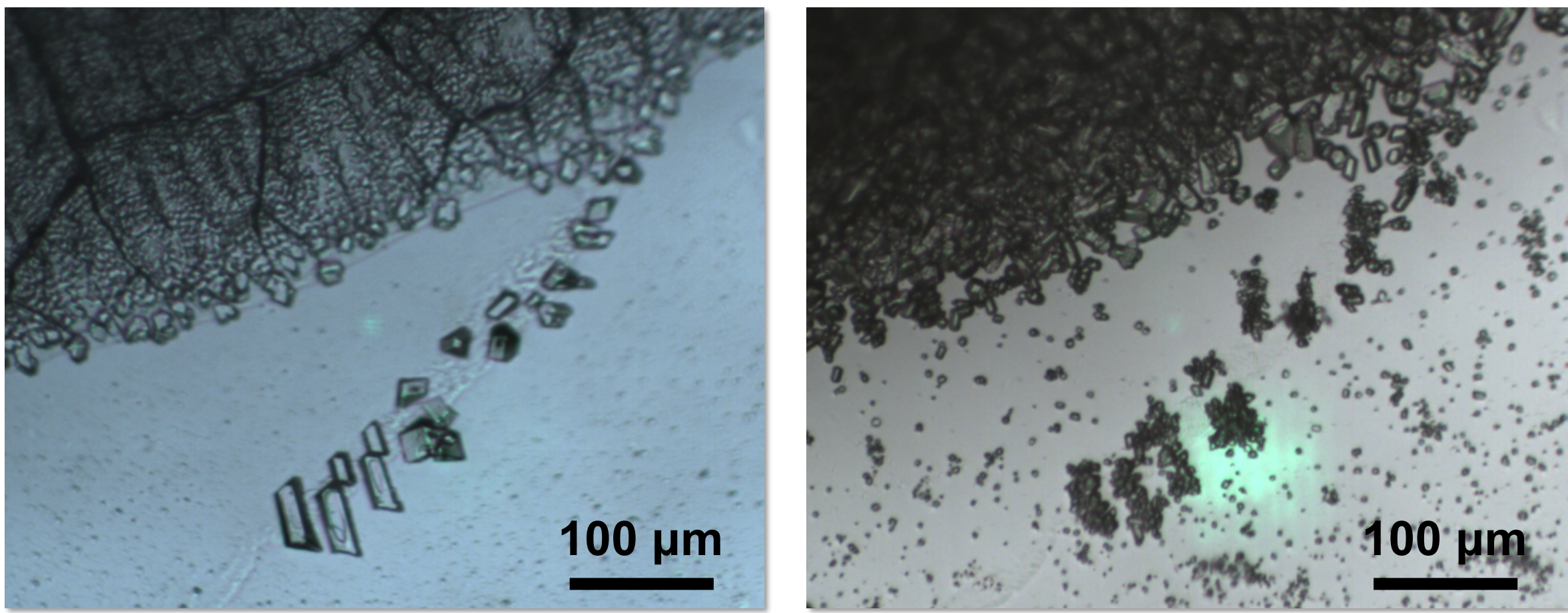


Figure 4: In this experiment, crystalline benzene was immersed in liquid ethane at 90 K (left). After warming to 125 K (right), a clear change in crystal morphology is observed. This is consistent recrystallization of the sample as the strong stacking interaction in benzene is disrupted to accommodate the guest ethane molecules.

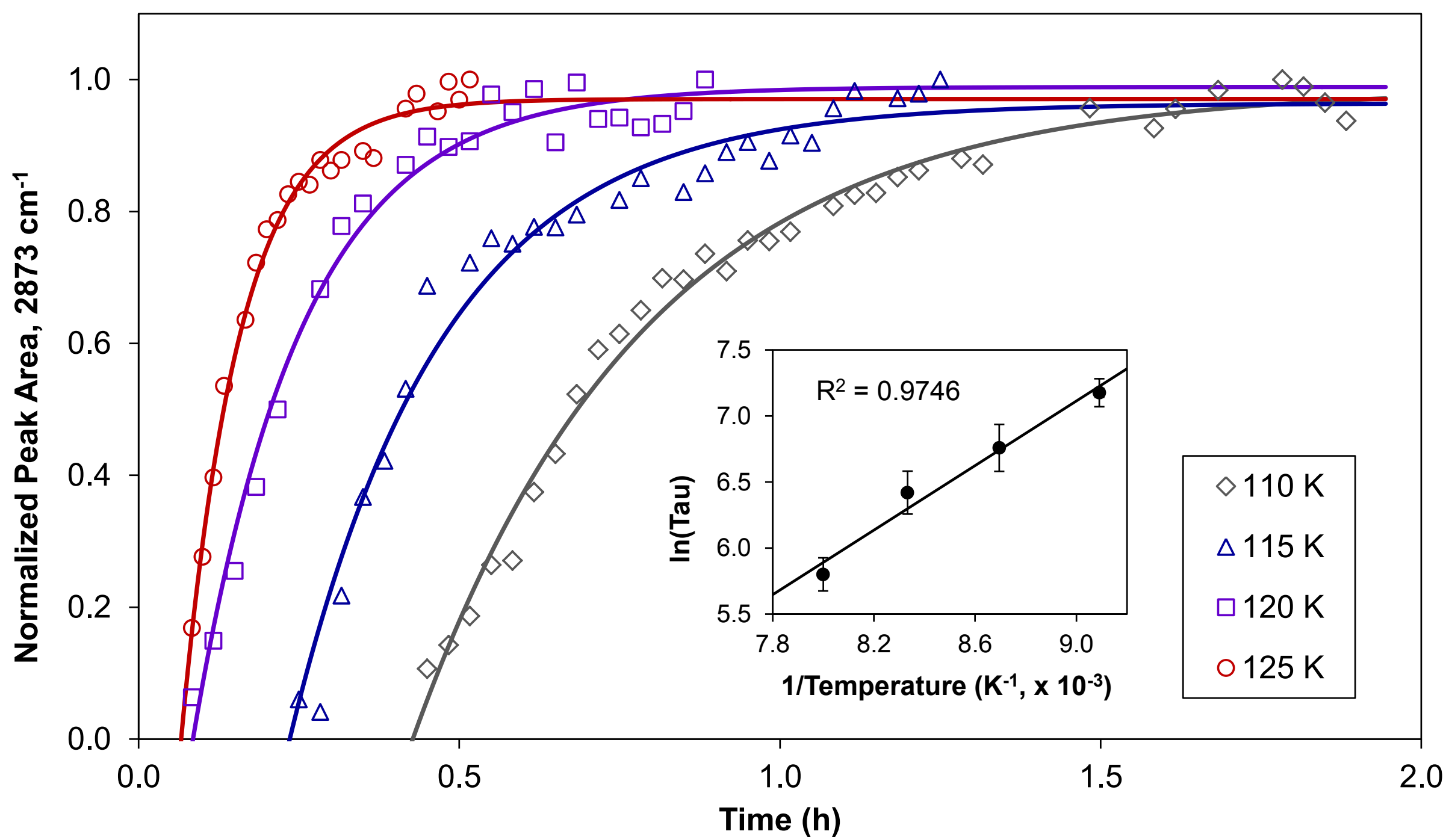


Figure 5: By monitoring the growth in the area of the 2873 cm⁻¹ ethane co-crystal feature at various temperatures, we can study the kinetics of the formation of the co-crystal. An Arrhenius analysis (inset) yields an activation energy of 10.2 ± 0.2 kJ/mol. Extrapolation to Titan surface temperatures indicates co-crystal formation would reach completion in ~18 hours.

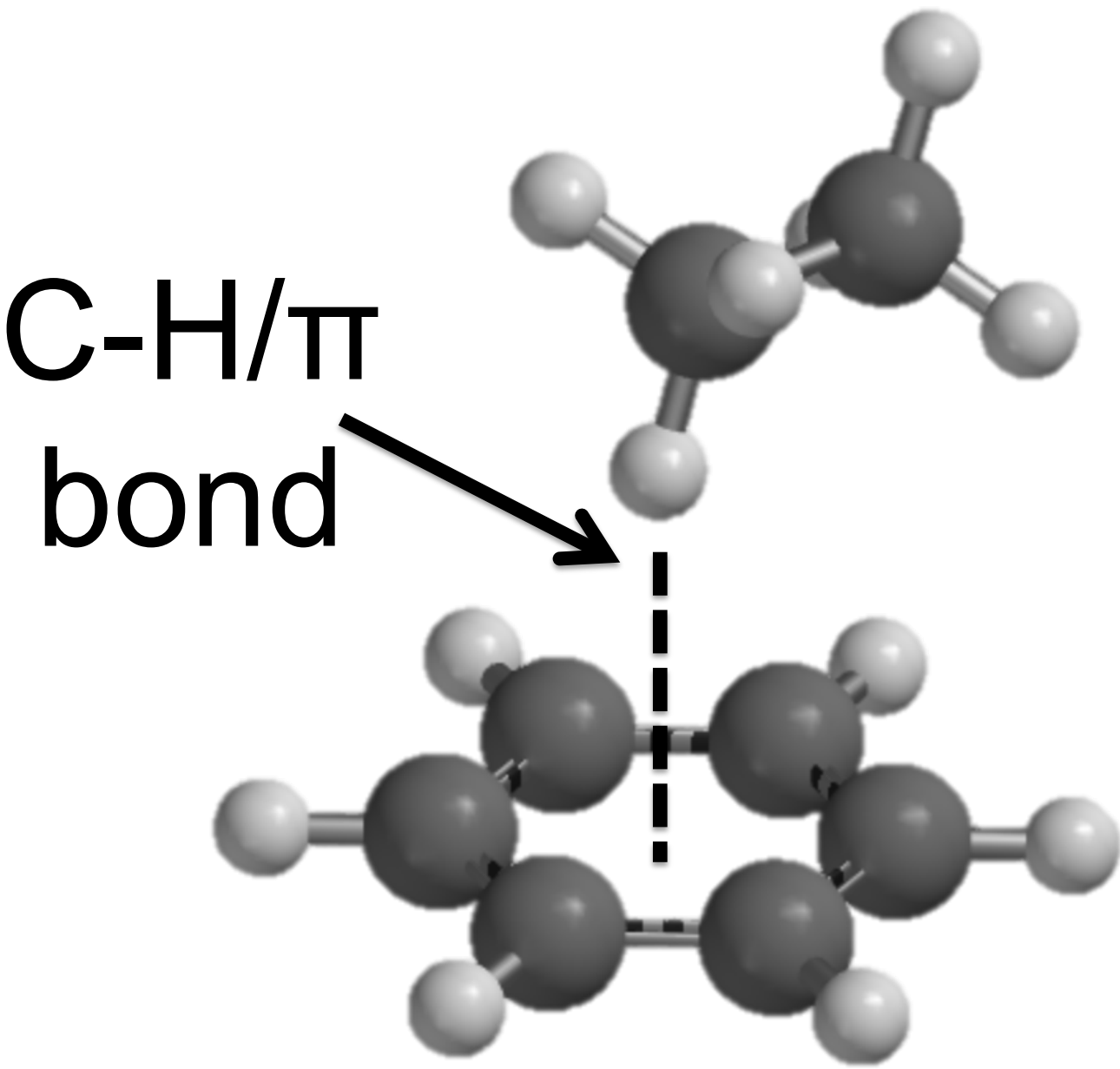


Figure 6: The C-H/ π bond between benzene and ethane.

Benzene and ethane form a co-crystal at Titan surface temperatures, analogous to hydrated minerals on Earth.

Vibrational analysis suggests that the co-crystal is bound through a C-H/ π bond between benzene and ethane, as shown in Figure 6.

The co-crystal may be an important form of benzene where benzene and ethane have coexisted, as in evaporate deposits.

