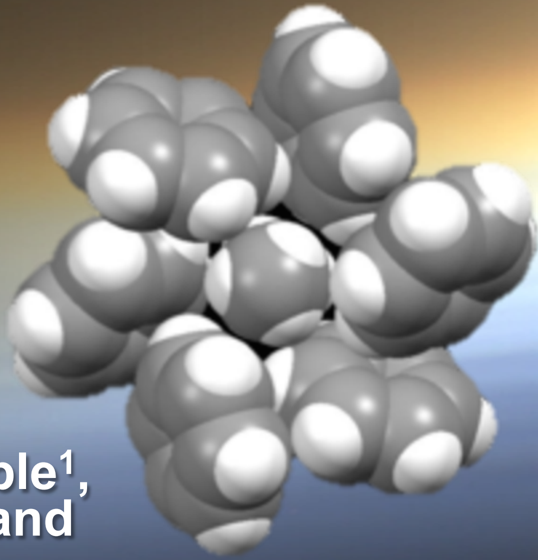
Escape from Waterworld: Chemistry in Hydrocarbons and Supercritical Carbon Dioxide



Robert Hodyss

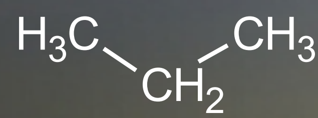
Michael J. Malaska[1], Tuan H. Vu[1], Morgan L. Cable[1], Helen Maynard-Casely[2], Mathieu Choukroun[1], and Patricia Beauchamp[1]

[1]Jet Propulsion Laboratory, California Institute of Technology
[2]Australian Nuclear Science and Technology Organisation

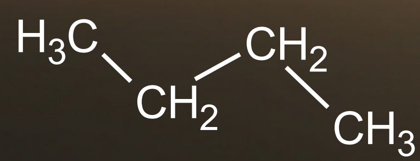
methane CH_4

ethane H_3C-CH_3

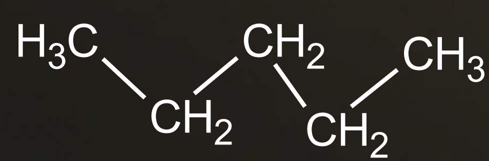
propane



butane



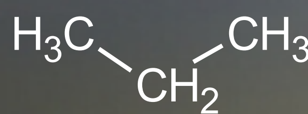
pentane



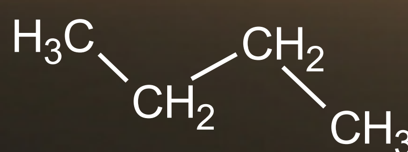
methane CH_4

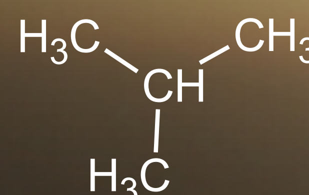
ethane $H_3C{-}CH_3$

propane

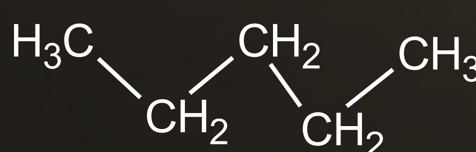


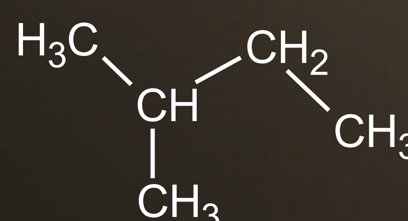
butane

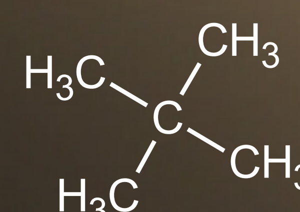




pentane







methane

CH_4

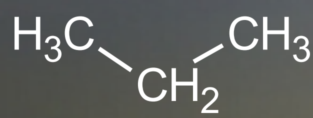
m.p. -183 °C

ethane

H_3C-CH_3

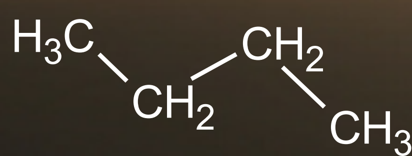
m.p. -183 °C

propane

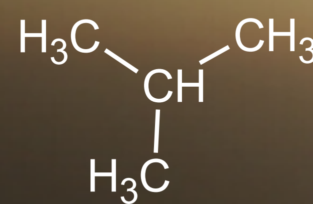


m.p. -189 °C

butane

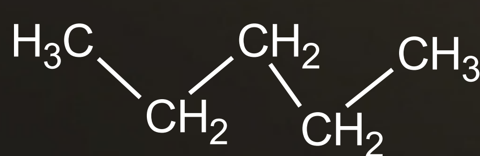


m.p. -138 °C

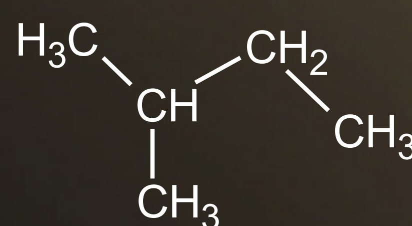


m.p. -160 °C

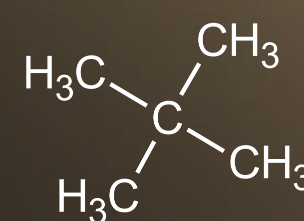
pentane



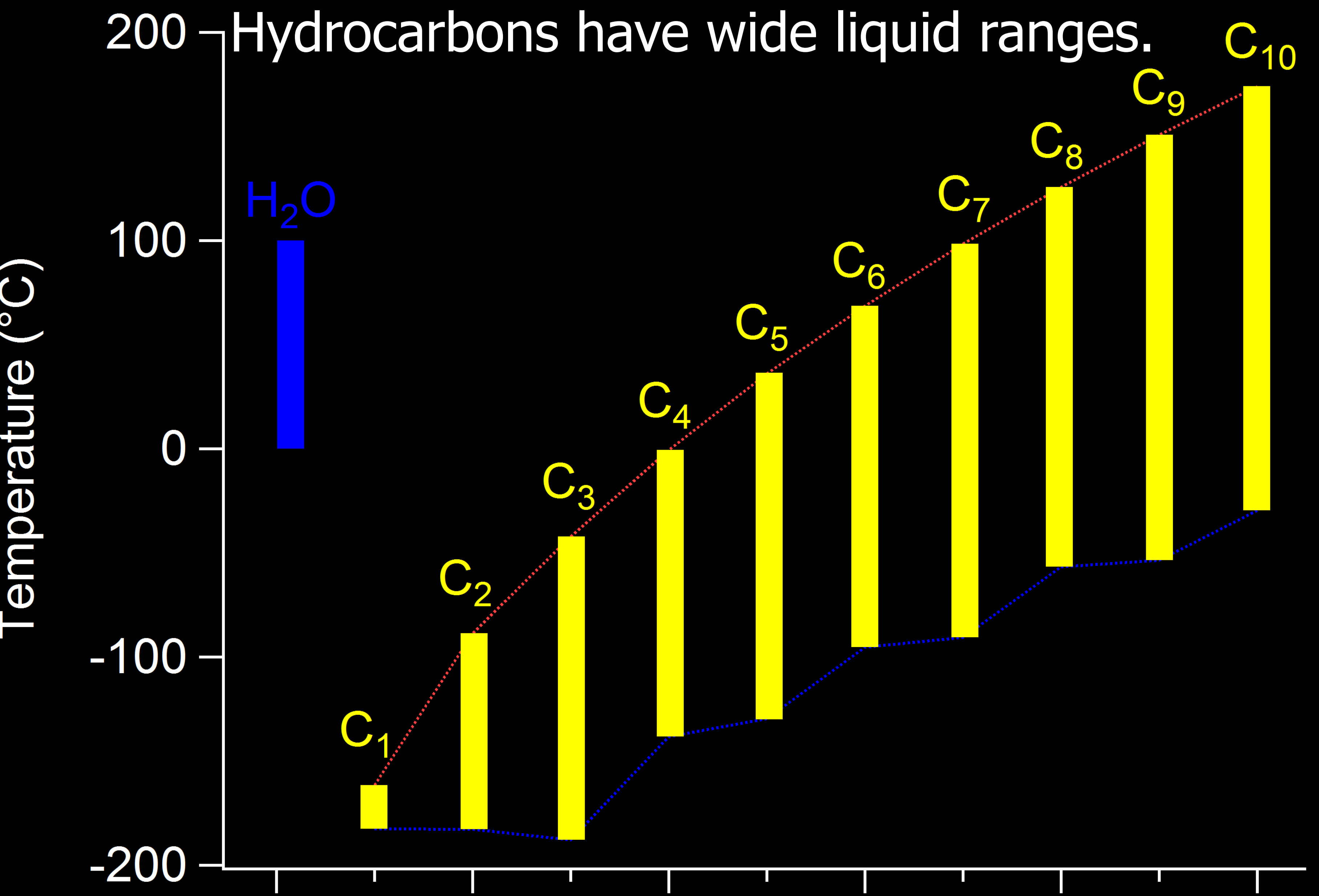
m.p. -130 °C



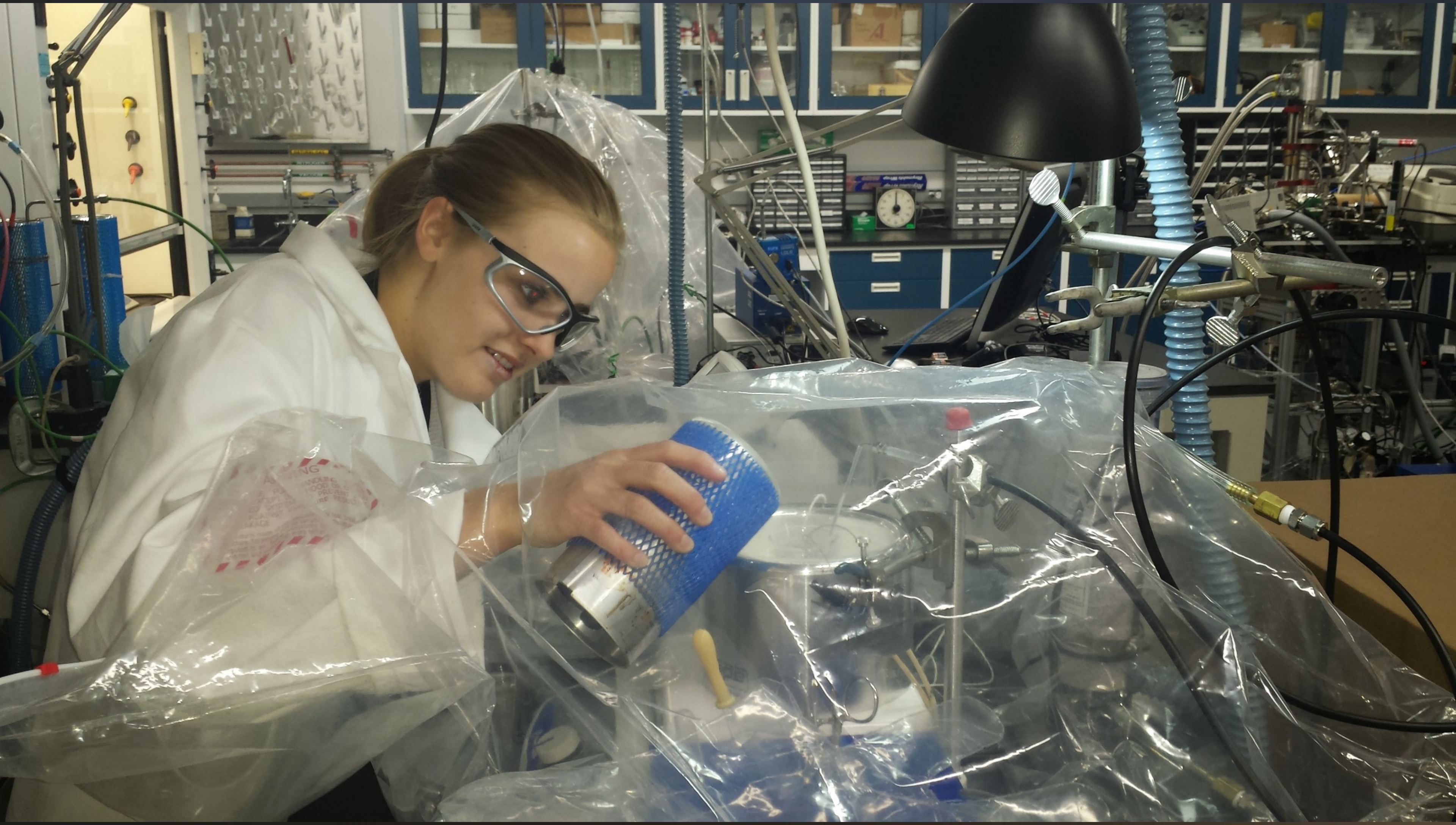
m.p. -160 °C



m.p. -16 °C


Hydrocarbons have wide liquid ranges.
Temperature (°C)
200
100
0
-100
-200
H2O
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10

Low temperatures make life more difficult.

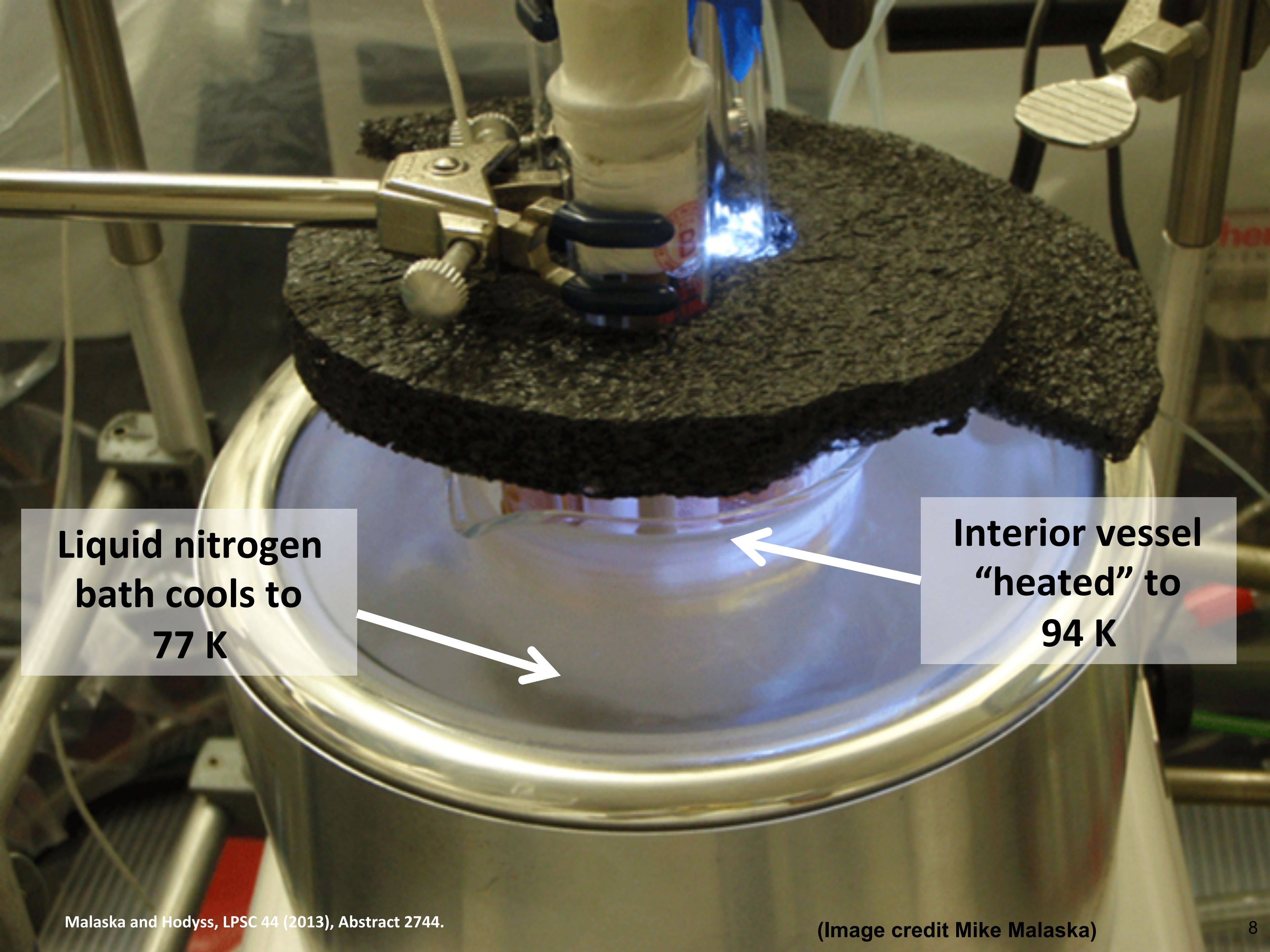


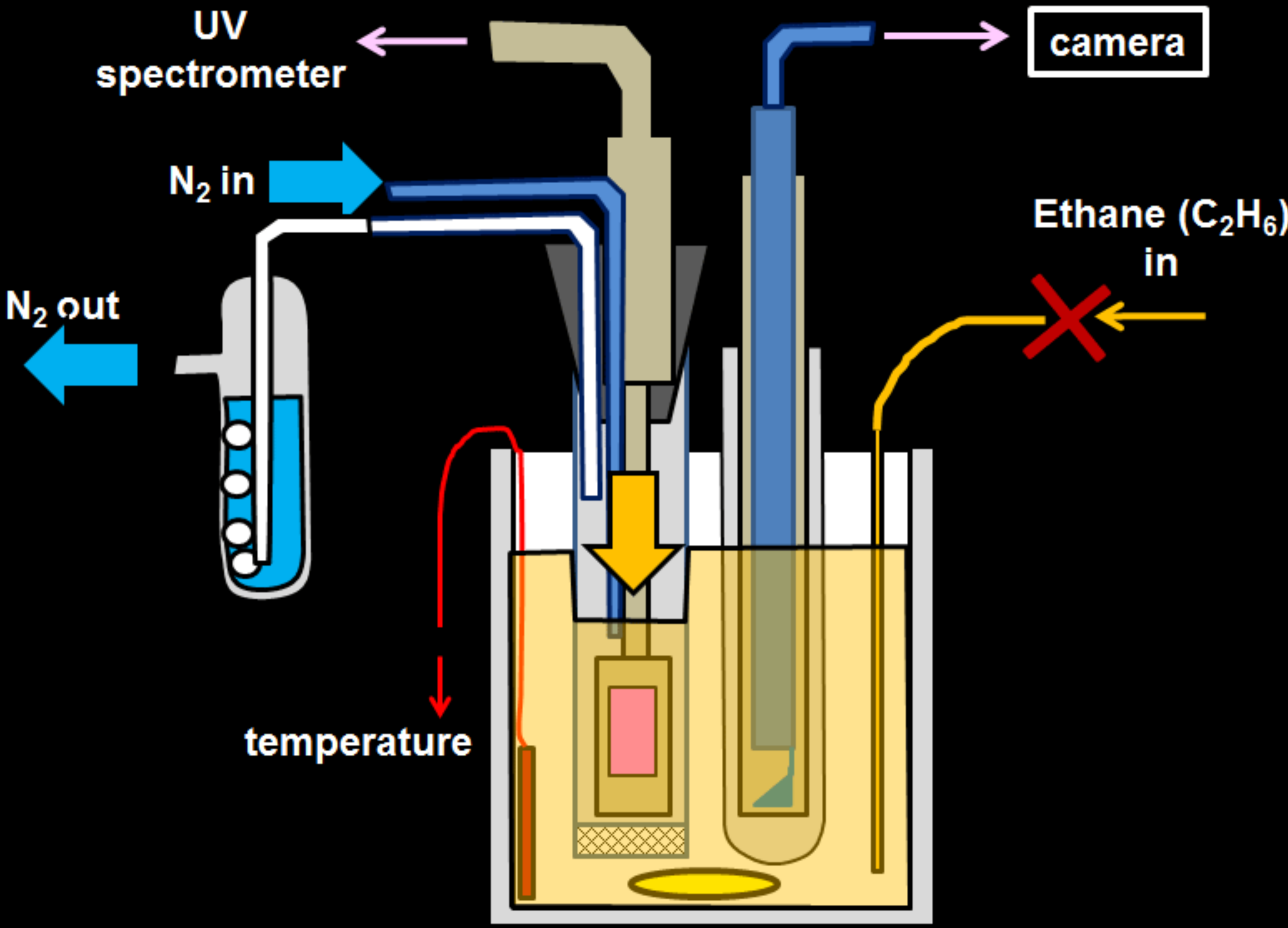
Elyse Pennington (Photo by Morgan Cable)

Low temperatures make life more difficult.

1. Low temperatures reduce solubility.

2. Low temperatures reduce reaction rates.

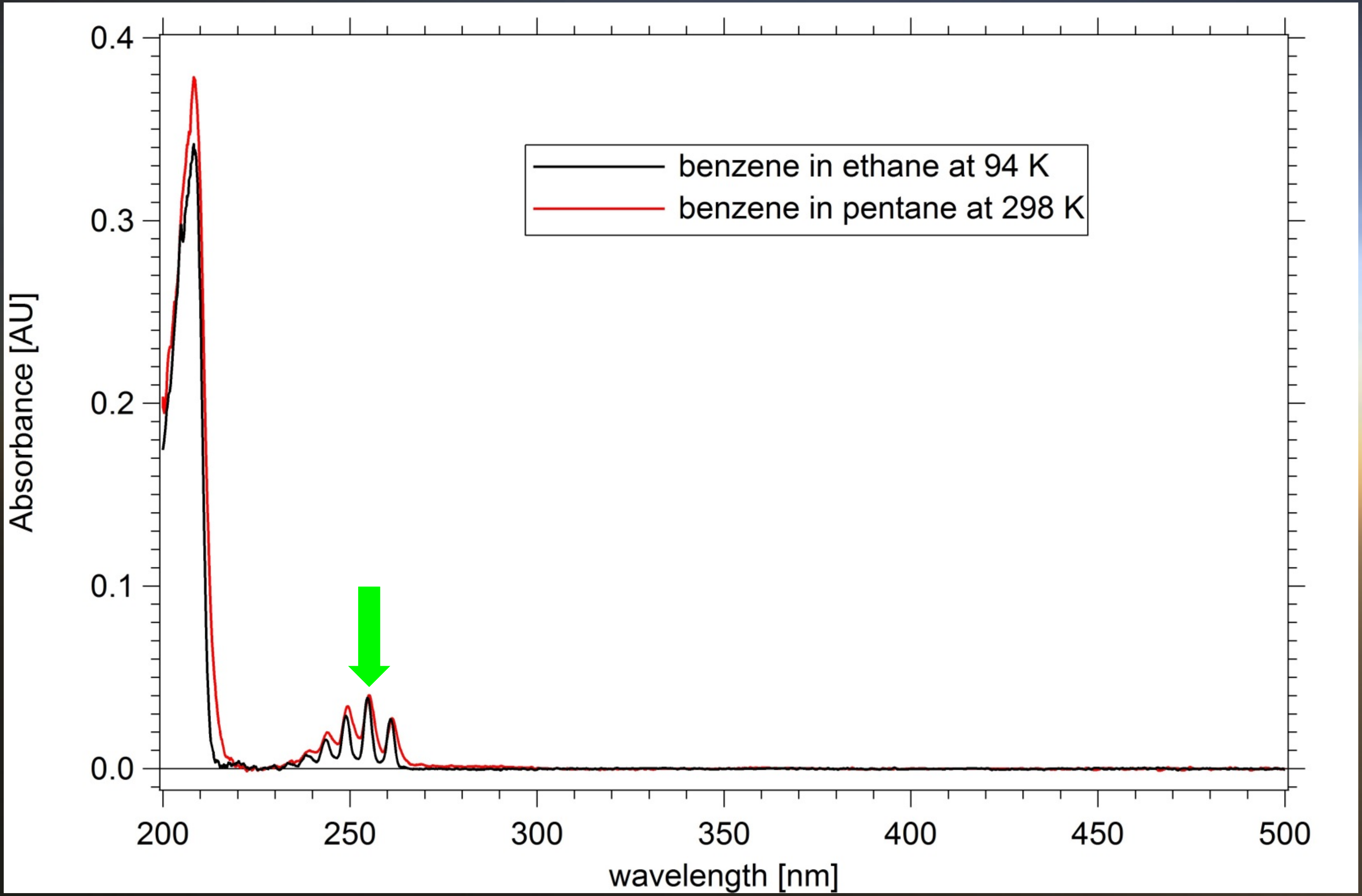

Liquid nitrogen bath cools to 77 K
Interior vessel "heated" to 94 K
Malaska and Hodyss, LPSC 44 (2013), Abstract 2744.
(Image credit Mike Malaska)



Flush and Fill

Benzene UV absorbance at 94 K

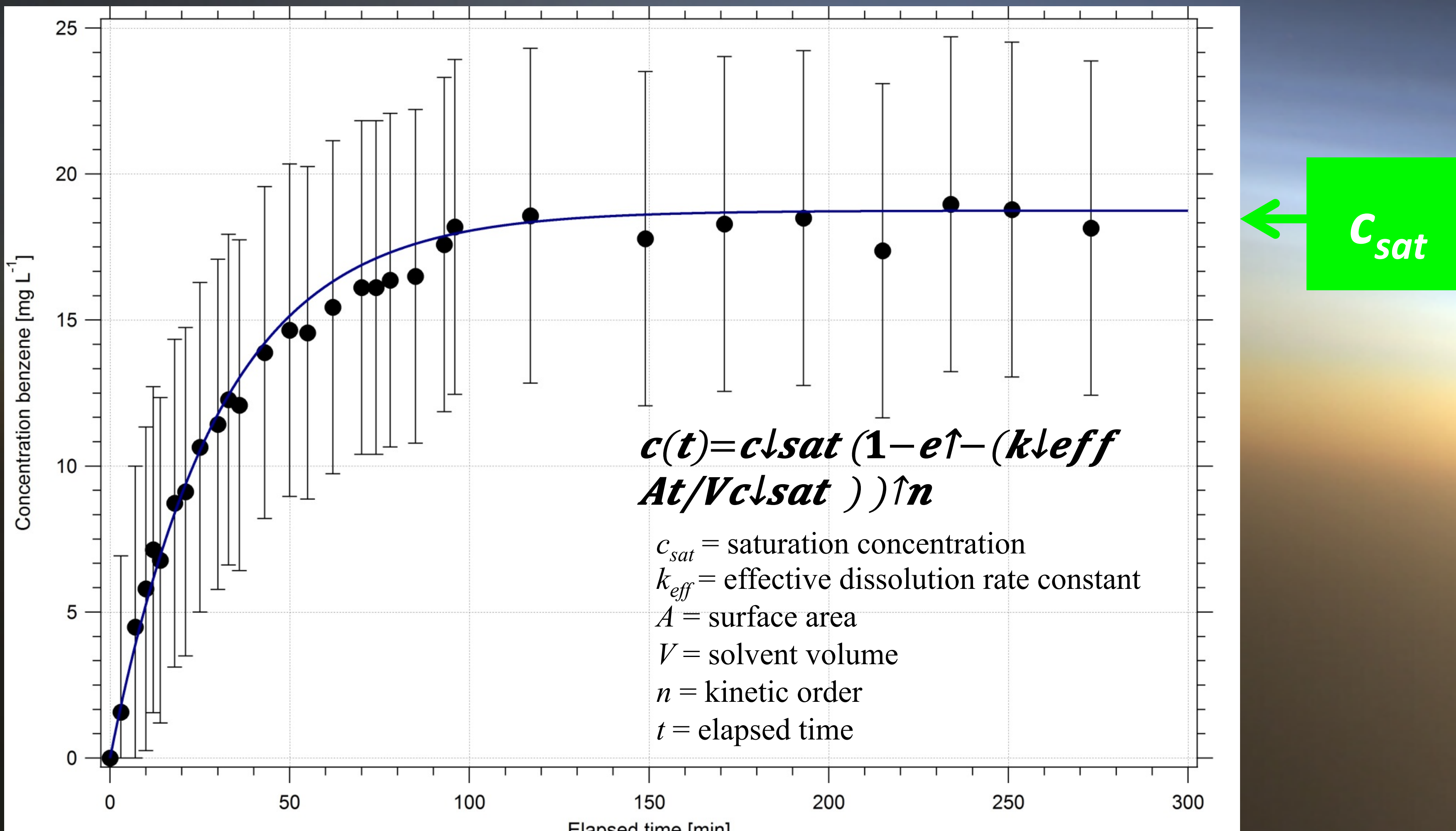
Comparison between ethane and pentane solutions at different temperatures
21-point calibration curve in pentane used for quantitation



Malaska and Hodyss, Icarus 242 (2014), 74-81.

Benzene dissolution is fast at 94 K

Saturation concentration (c_{sat}) and dissolution rate constant (k_{eff}) determined from UV absorbance over time

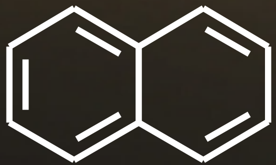
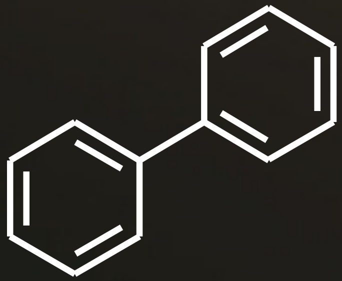


Malaska and Hodyss, Icarus 242 (2014), 74-81.

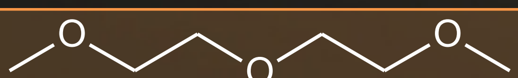
Lab results

How much dissolves? c_{sat}

How fast does it dissolve? k_{eff}

		saturation concentration c_{sat} [mg L^{-1}]	effective rate constant k_{eff} [mmol m^{-2} s^{-1}]
	benzene	18.5 (± 1.9)	3×10^{-6}
	naphthalene	0.159 (± 0.003)	4×10^{-8}
	biphenyl	0.039 (± 0.006)	4×10^{-9}

Malaska and Hodyss, Icarus 242 (2014), 74-81.

		Solubility in CH_4/N_2 (77:23)at 95 K (mg/L)	Solubility in C_2H_6/N_2 (97:3)at 95 K (mg/L)
Hydrogen cyanide	HCN	1080	17000
acetylene	C_2H_2	1300	2600
butane	C_4H_{10}	580	4649
acrylonitrile	C_2H_3CN	3.2	42.4
carbon dioxide	CO_2	44	22
benzene	C_6H_6	0.78	16
		Solubility in CH_4 at 94 K (mole fraction)	Solubility in C_2H_6 at 94 K (mole fraction)
argon	Ar	0.47	0.15
krypton	Kr	0.29	0.43
		Solubility in C_3H_8 at 190 K	
		<1.5 mg/mL	
			

Predicted Titan solubility values from Raulin, 1987 and Cordier, 2009. (for HCN)

Low temperatures make life more difficult.

1. Low temperatures reduce solubility.

2. Low temperatures reduce reaction rates.

But… low temperatures can also enable new interactions.

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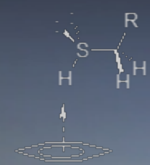
Interaction energies in biological molecules

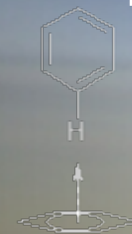
H-bond interactions (typical values)

O-H←:N	**7 kcal/mol**
O-H←:O	**5 kcal/mol**
N-H←:N	**3 kcal/mol**
N-H←:O	**2 kcal/mol**

Aromatic interactions

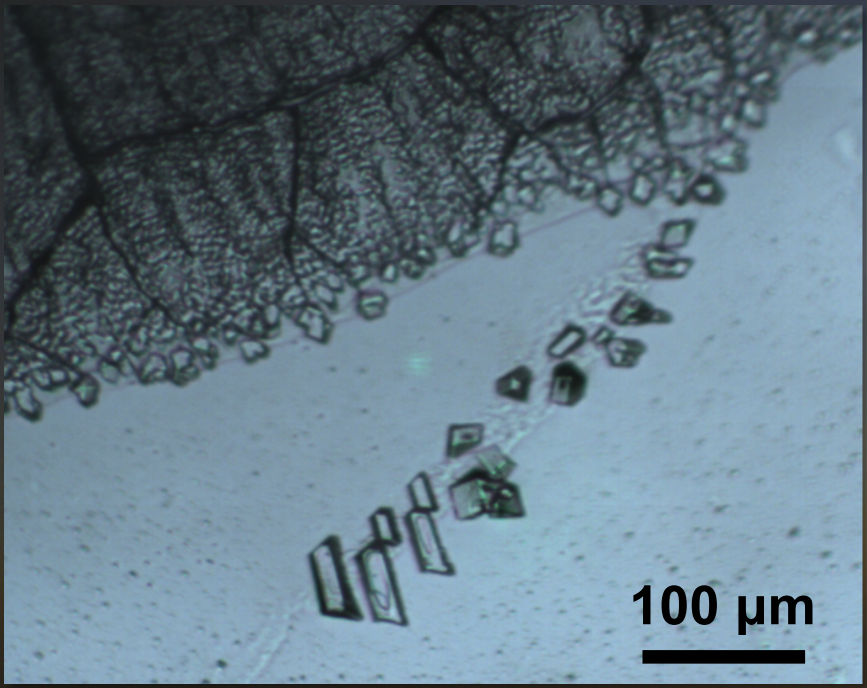


S-H←pi	**2.6 kcal/mol**
N-H←pi	**2.0 kcal/mol**

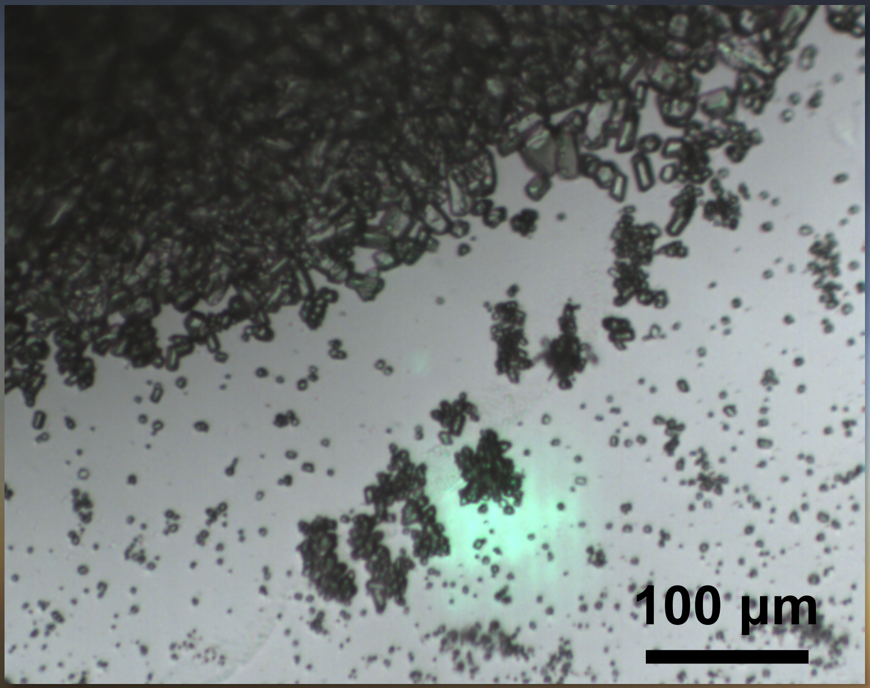


	1.0-2.0 kcal/mol
O-H←pi	**1.5 kcal/mol**
Lone pair S:→pi	**1.5 kcal/mol**
Perpendicular Methyl -pi	**0.75-1 kcal/mol**
In plane Met(S)←H-Arom	**0.75-1 kcal/mol**

But… low temperatures can also enable new interactions.



Before

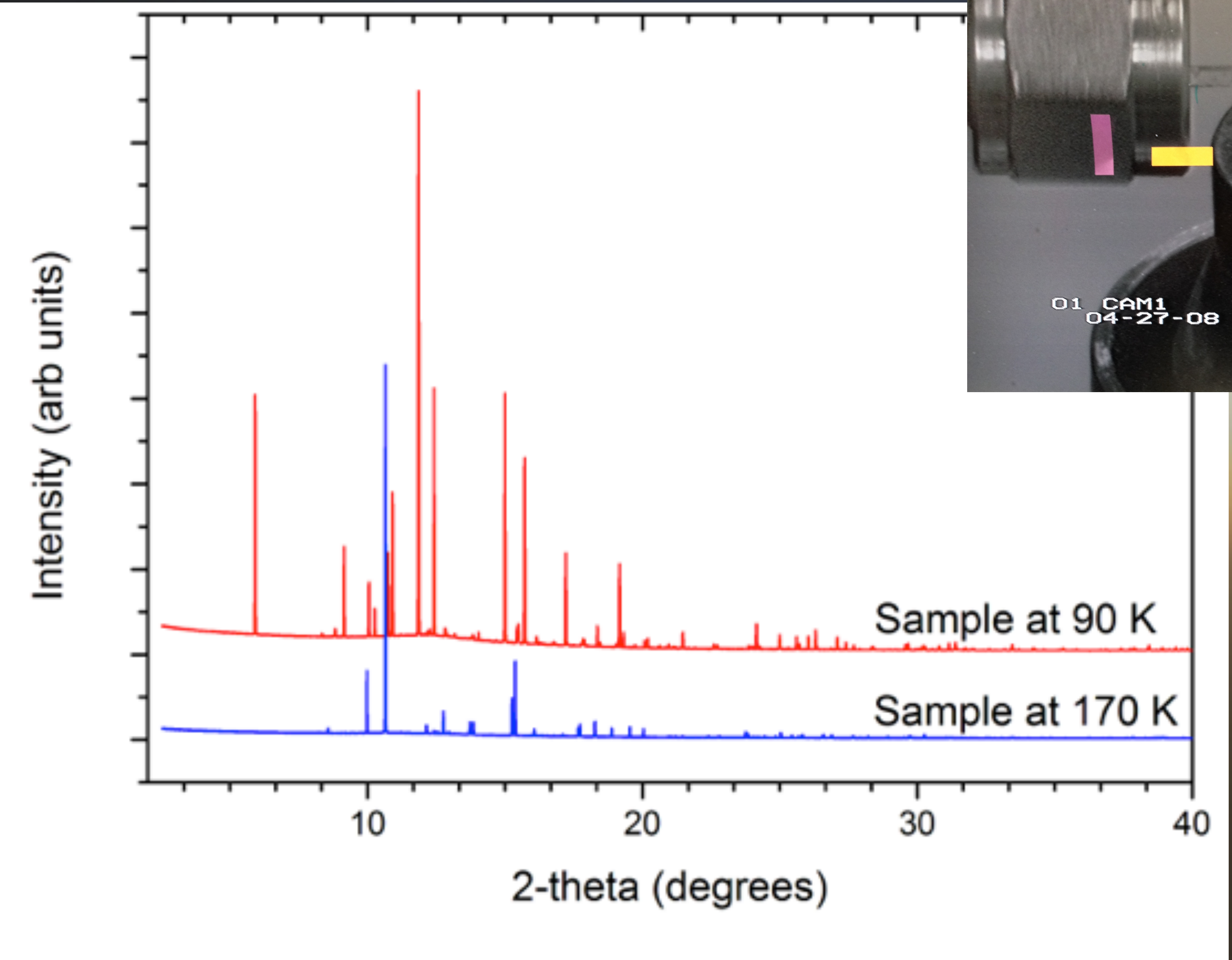


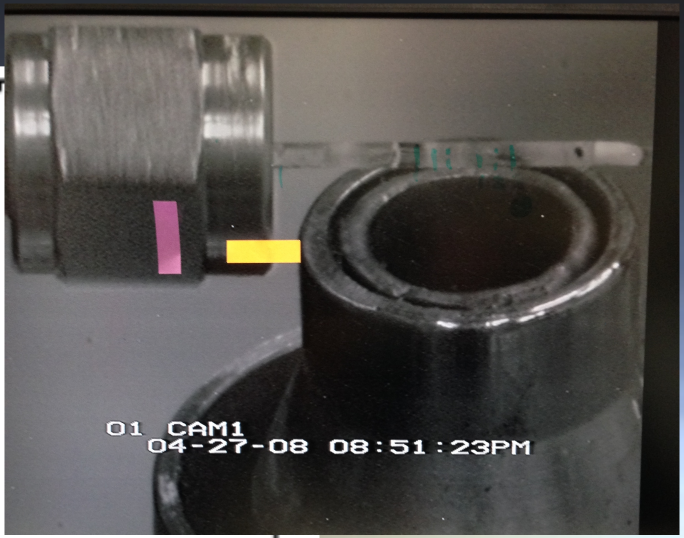
After

Recrystallization occurs when benzene and ethane are mixed.

Cable, M. L. et al., **2014**, *GRL* 41, 5396-5401

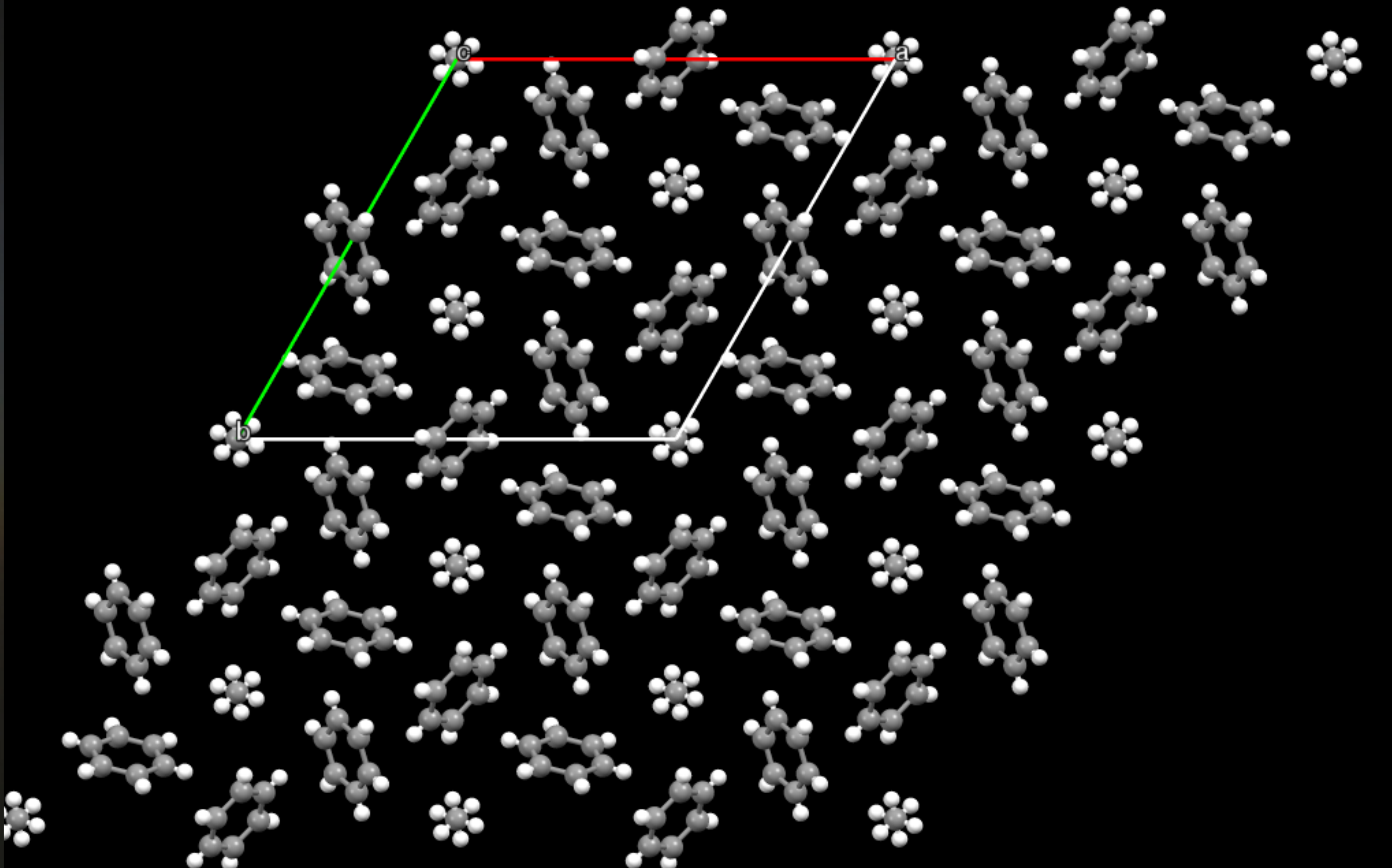
Synchrotron powder diffraction to determine the structure of the co-crystal

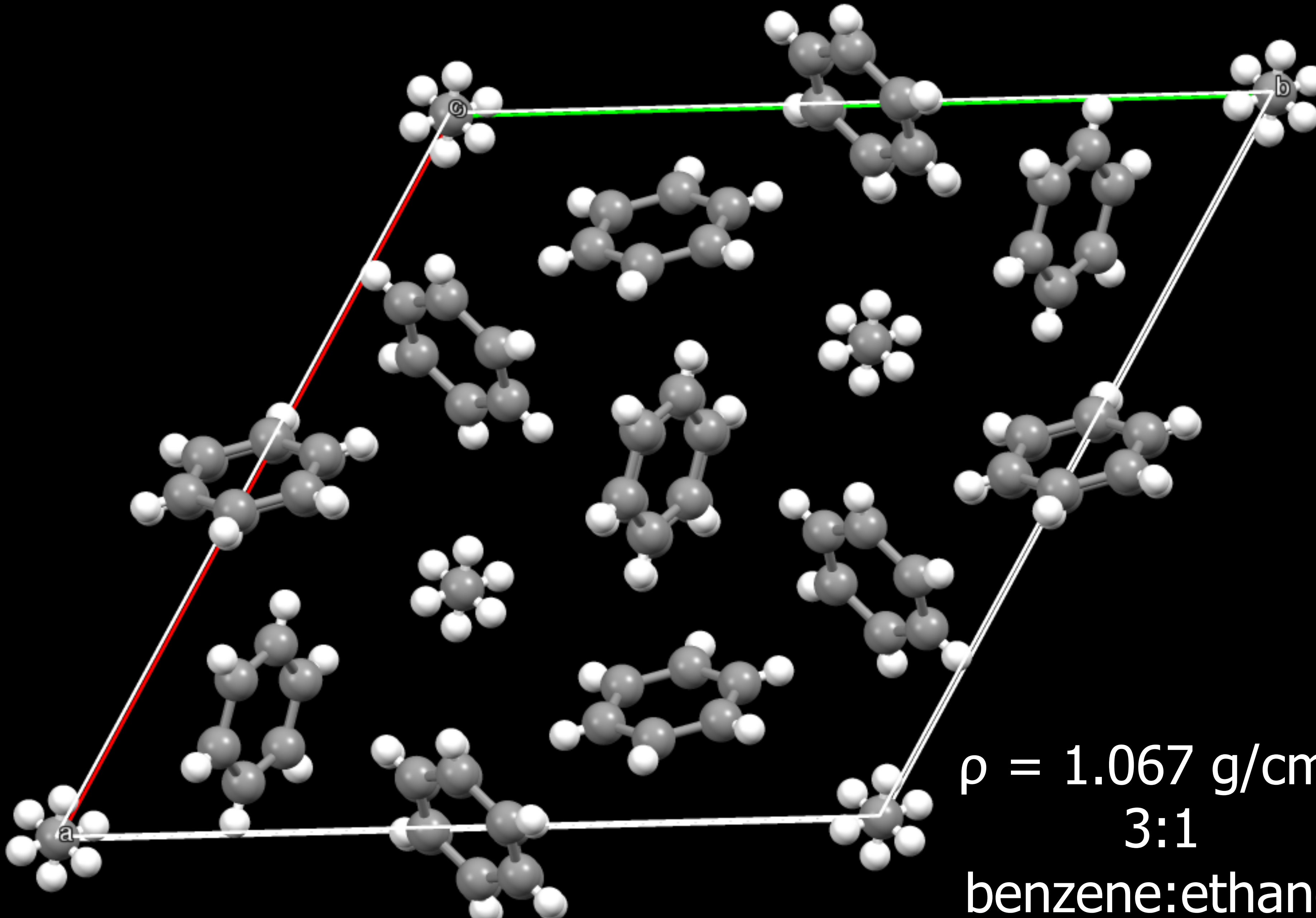




co-crystal

benzene


c
a
b

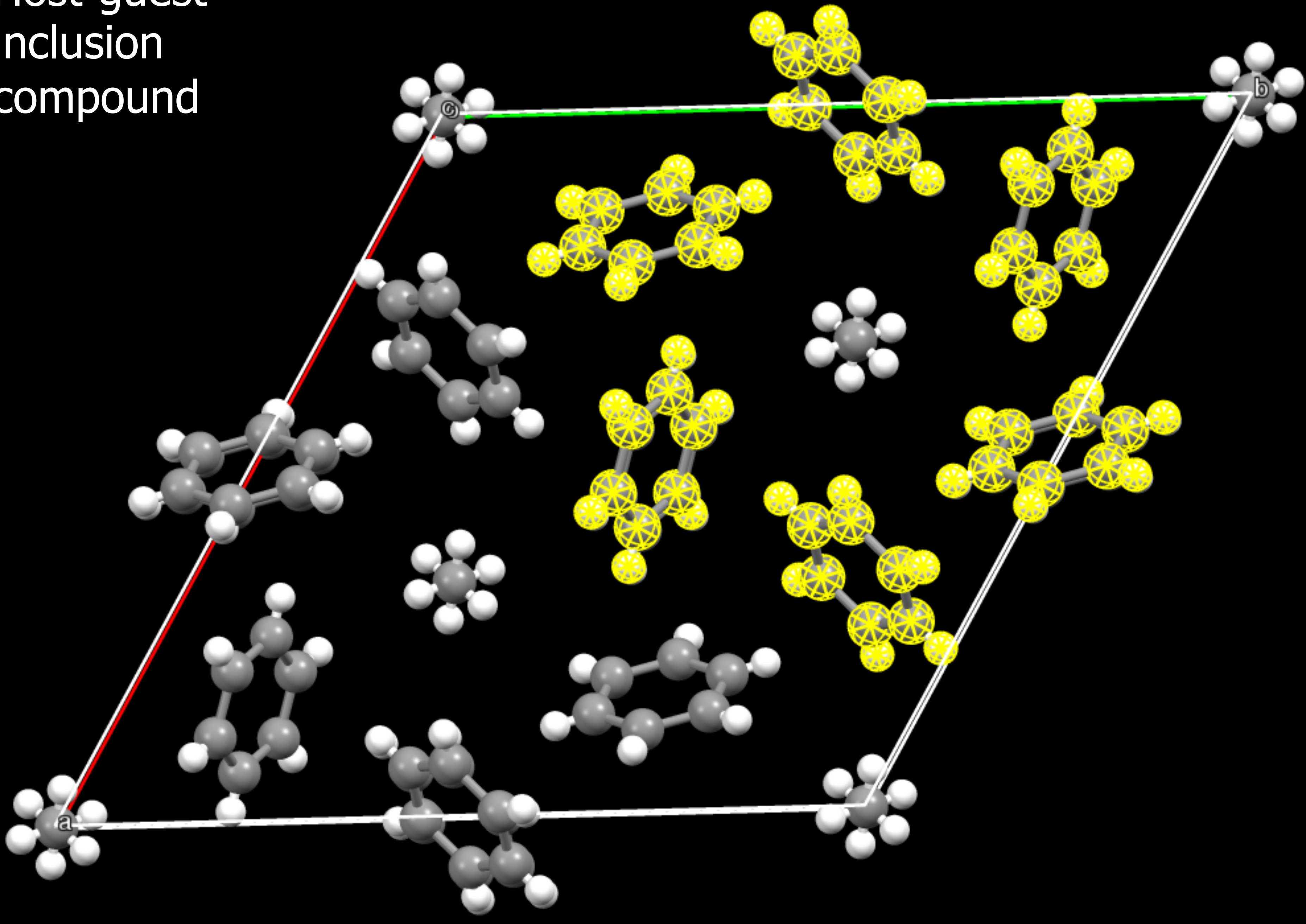


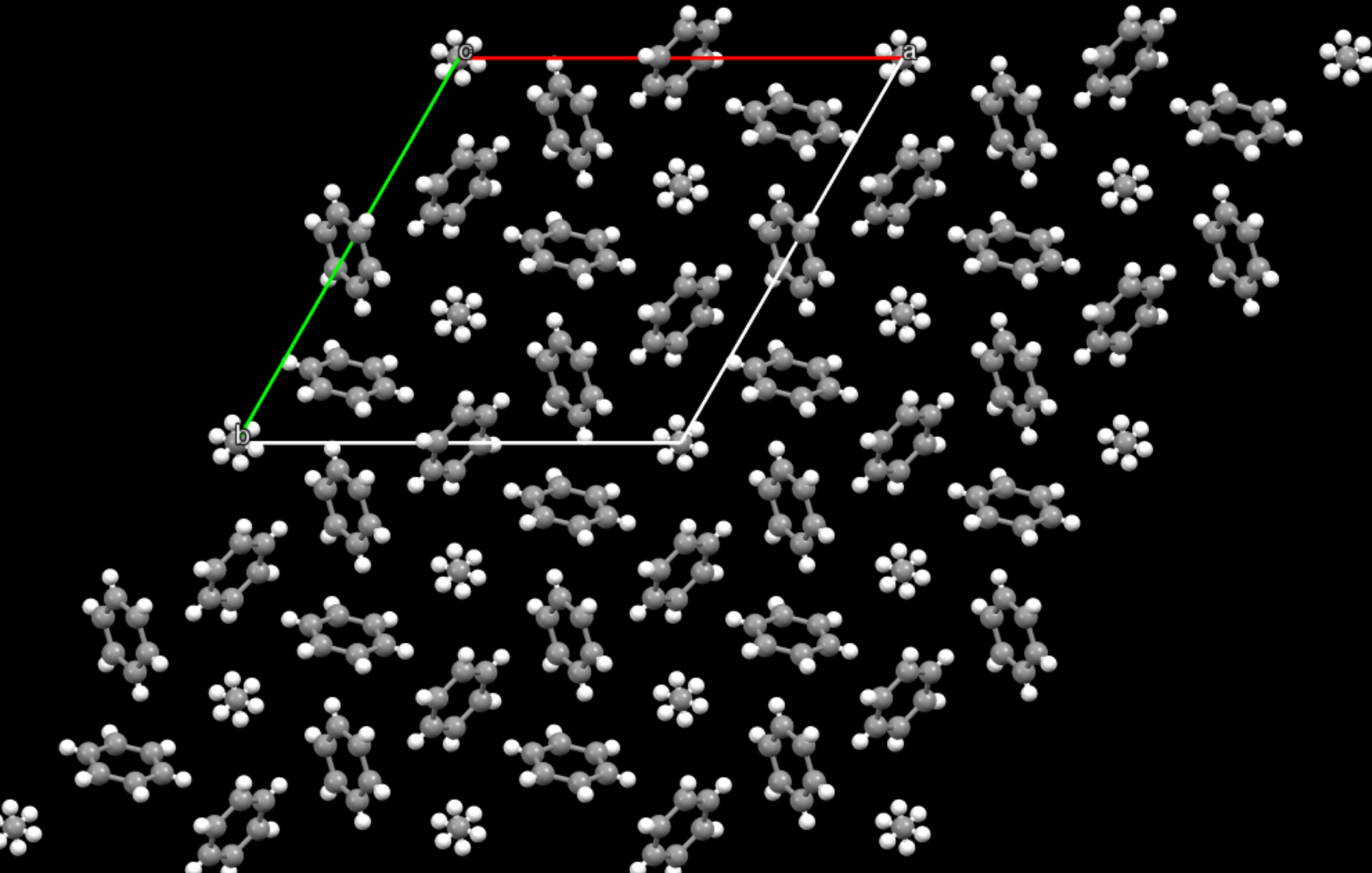
$\rho = 1.067\ g/cm^3$

3:1

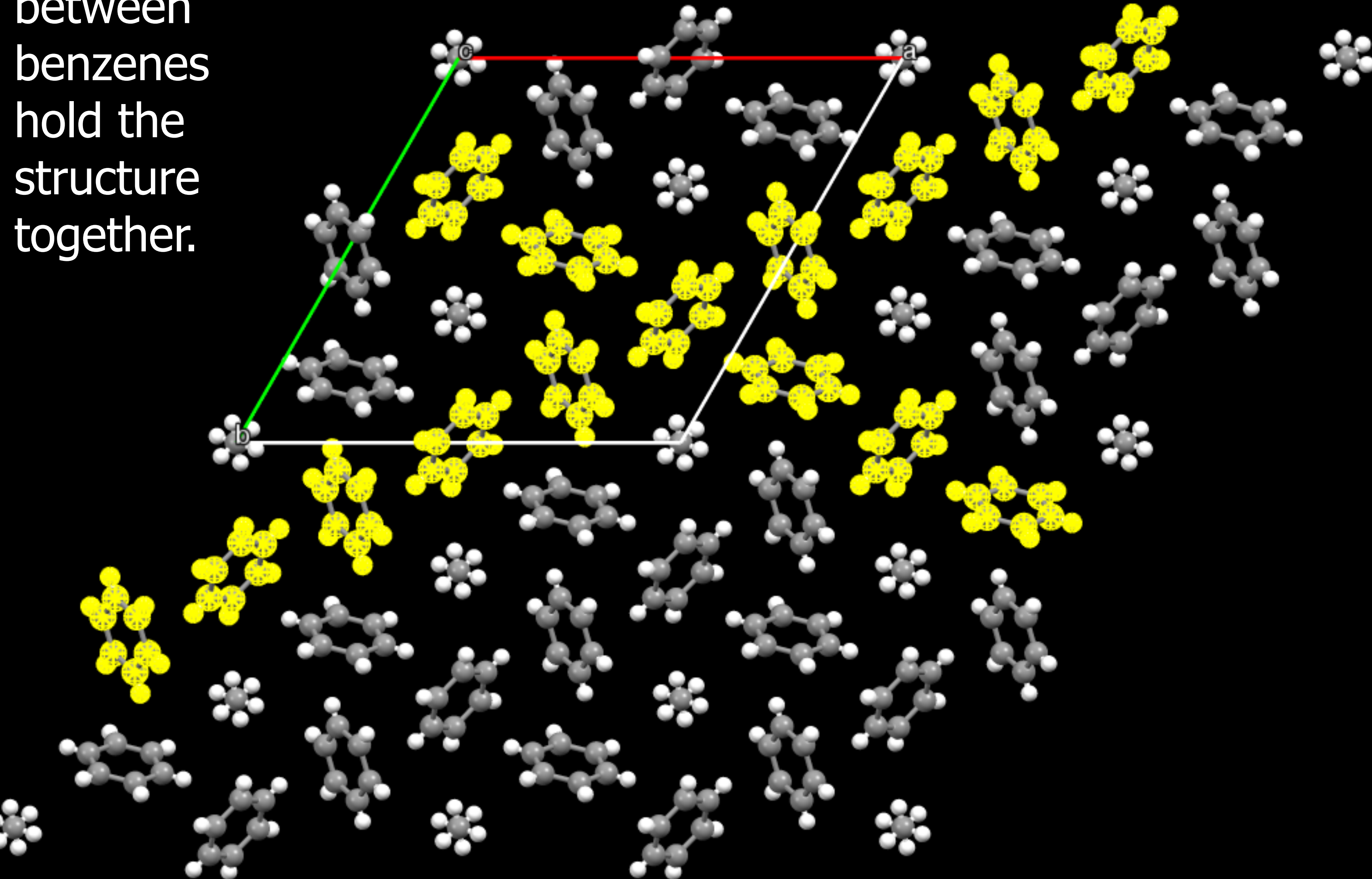
benzene:ethane

Host-guest inclusion compound

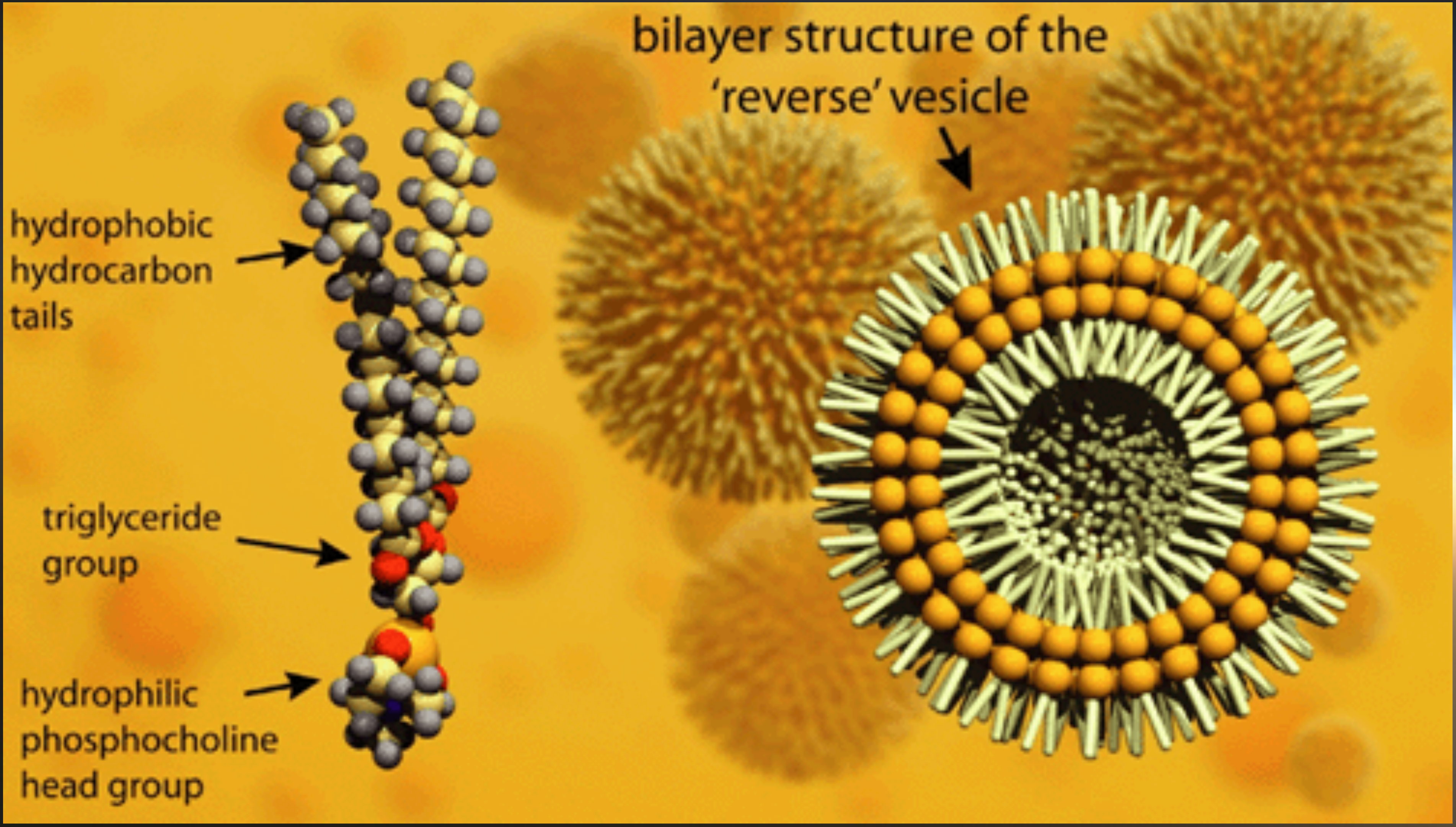



c
a
b

CH-π bonds between benzenes hold the structure together.

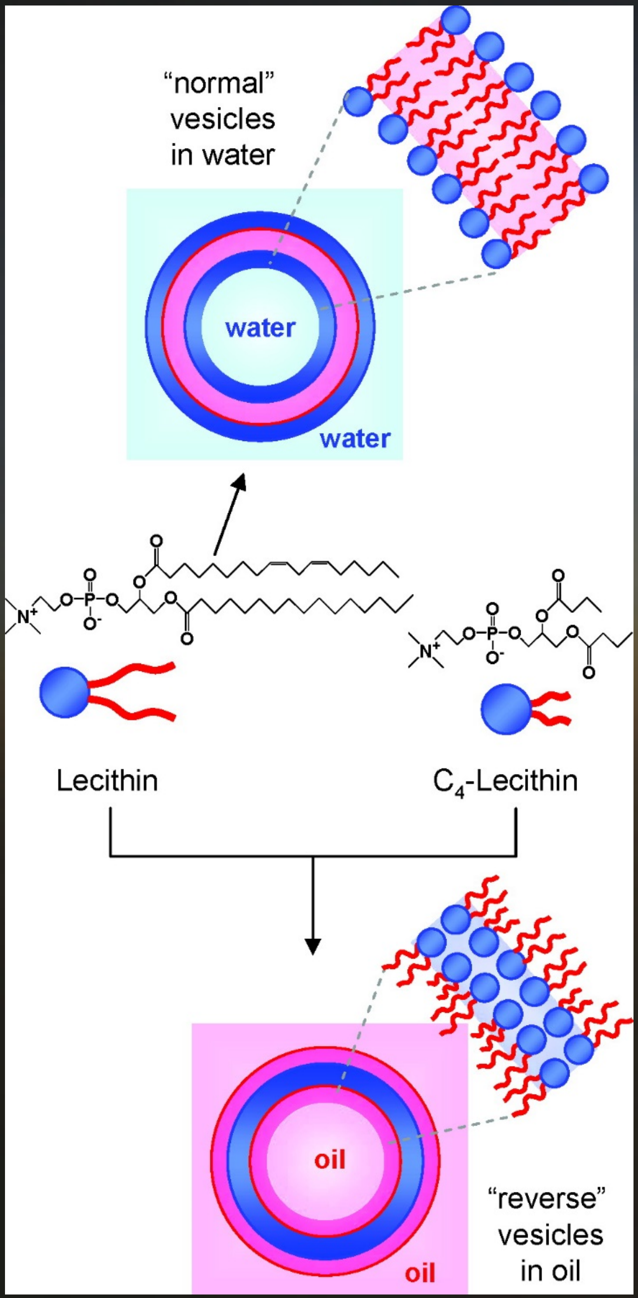


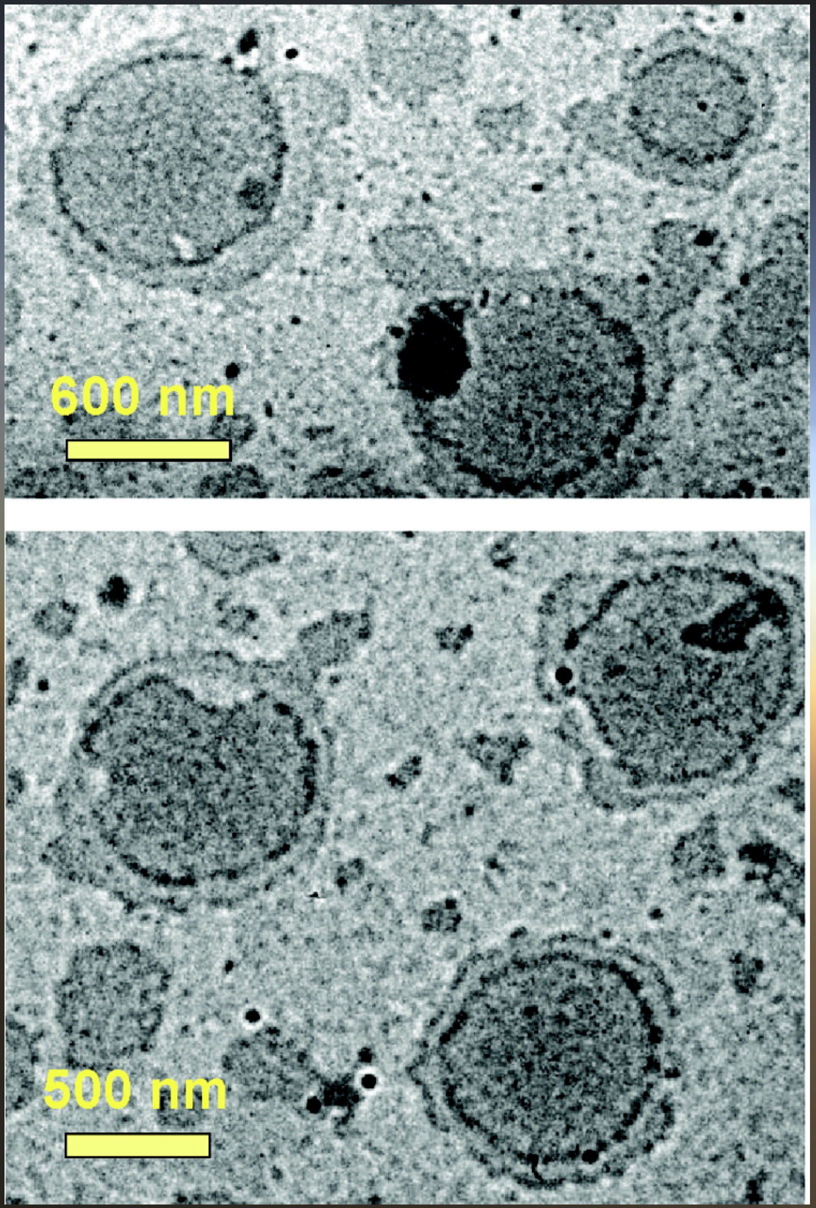
Another sort of self-assembly….?



Norman, L. H. (2011) Astronomy & Geophysics, 52: 1.39–1.42.

Another sort of self-assembly….?

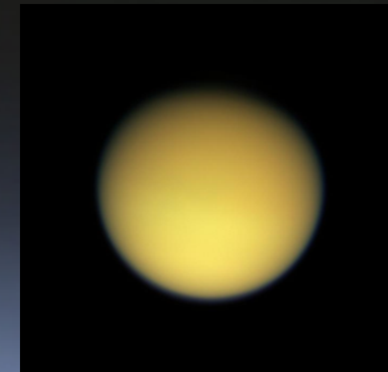


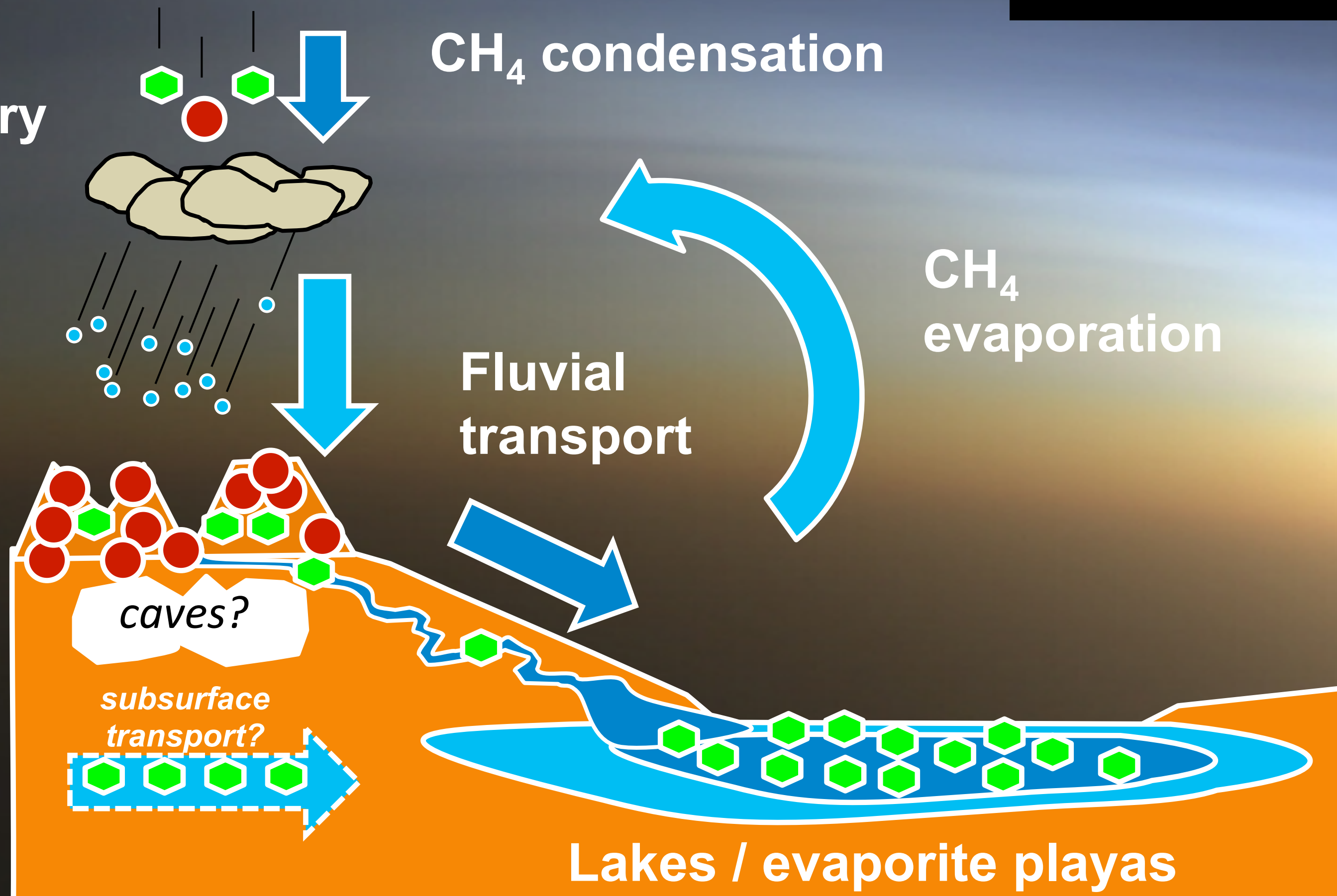


Tung et al. *JACS*, 2008, 130, pp 8813–8817

Titan Organic Cycle

Organics and CH_4

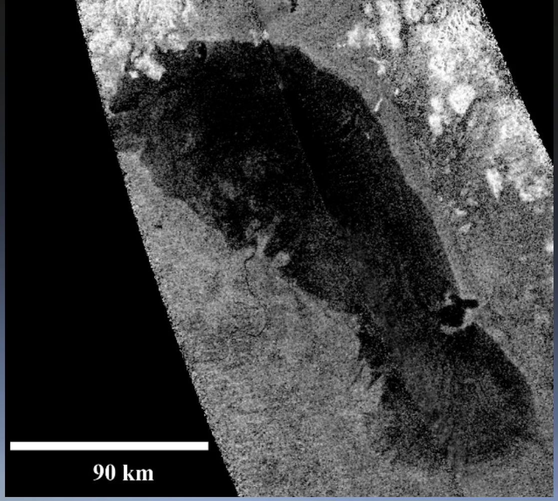




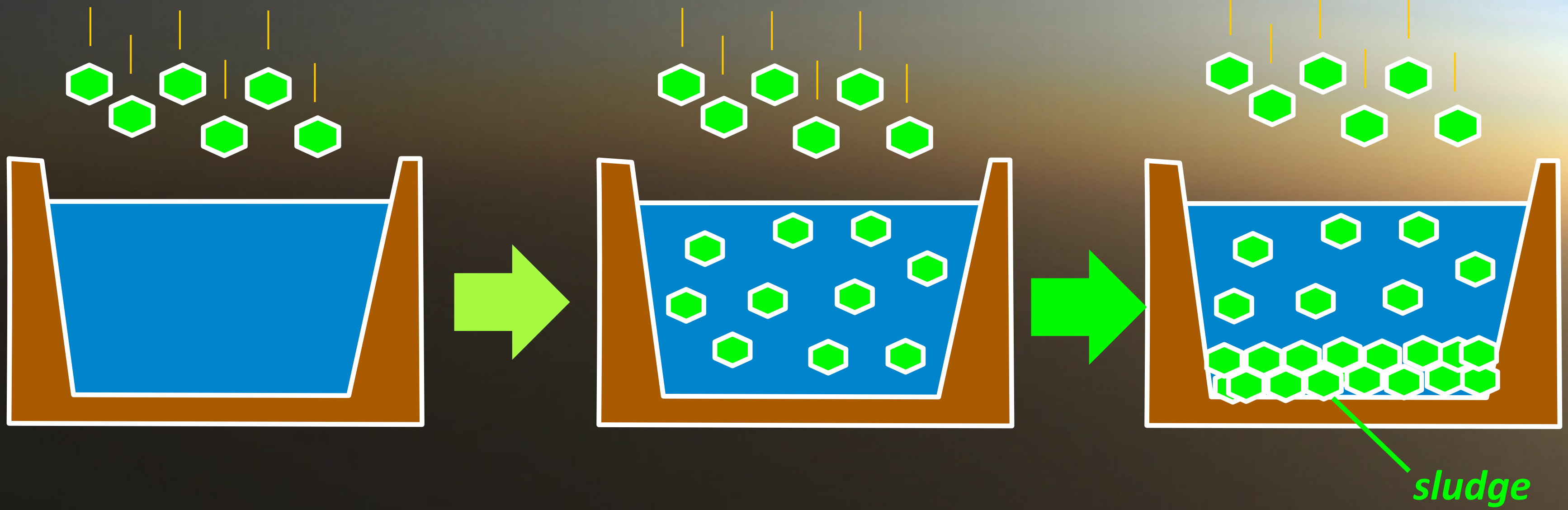
Malaska et al., Workshop on the Habitability of Icy Worlds (2014), Abstract 4020.

Other implications

Ontario Lacus will be saturated from benzene falling out of the atmosphere



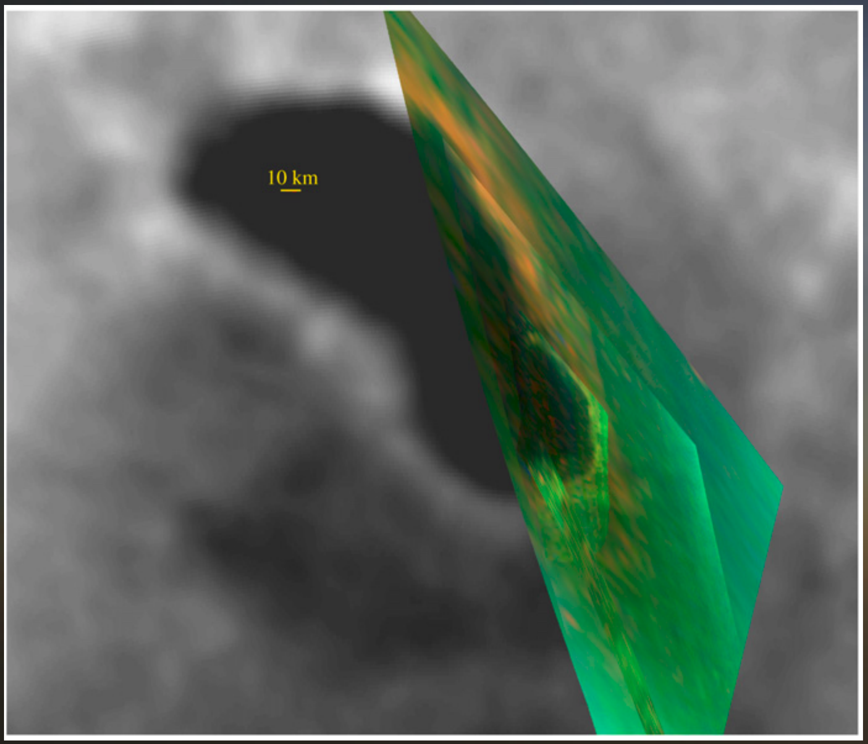
Ontario Lacus surface: 1.5e4 km^2
Ontario Lacus depth: 10 m
Ontario Lacus volume: 1.5e2 km^3 (= 1.5e14 L)
Benzene atmospheric flux rate [1]: 1e6 molecules cm^{-2} s^{-1}

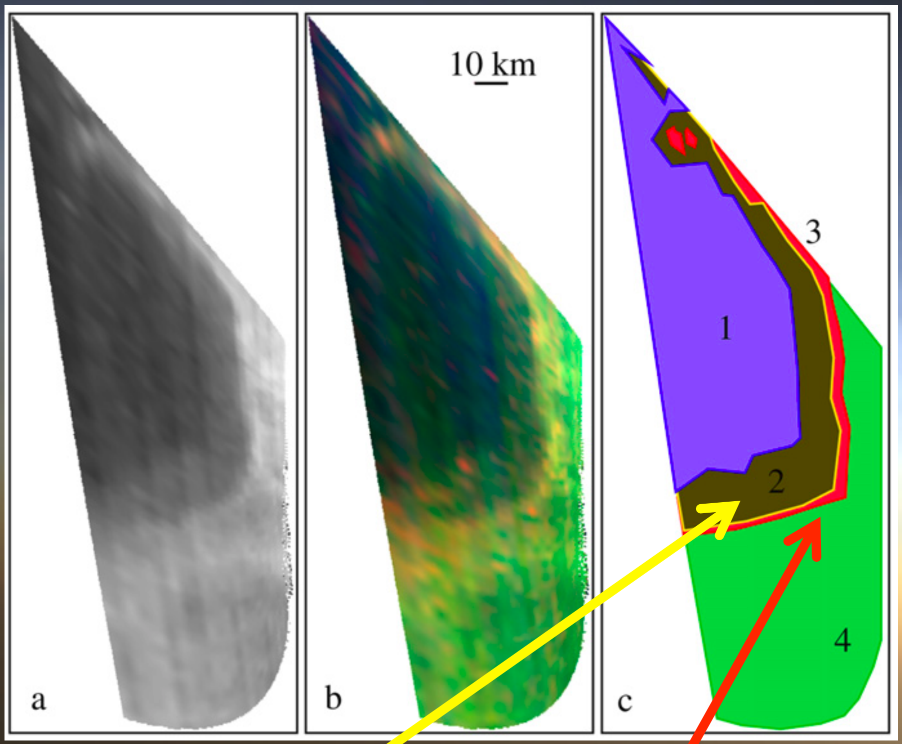


Benzene saturation at 18.5 mg L^{-1} reached in 4.5 Myr

[1] Cordier et al, Ap J 707, L128-L131.

Observed Ontario Lacus evaporite deposits
Hyperspectral imaging shows "Bathtub ring"





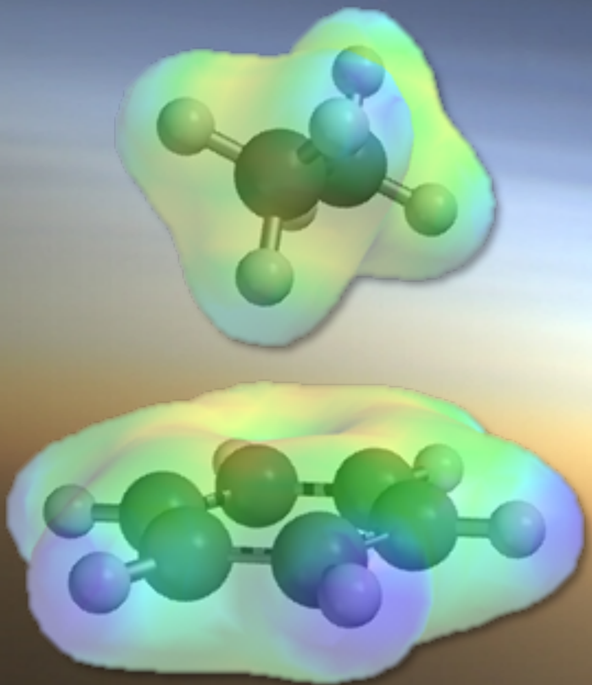
Ontario Lacus VIMS cubes from T38

Unit 2 is dark organic mudflat

Unit 3 is 5 micron bright organic evaporite deposit

Reference:
Barnes et al., Icarus 201 (2009) 217-225. "Shoreline features of Titan's Ontario Lacus from *Cassini/VIMS* observations." (Fig. 4 and 6)
doi:10.1016/j.icarus.2008.12.028

- Solubilities and reaction rates are low in cold hydrocarbon solvents, especially for interesting astrobiological (polar) molecules.
- But – low temperatures enable interactions between molecules that wouldn't readily occur at higher temperatures.
- A wide variety of dynamic chemical processes can occur on hydrocarbon world surfaces.



Thanks to NAI-Titan, NASA-OPR, NASA-SSW.

Cable, M. L., T. H. Vu, R. Hodyss, M. Choukroun, M. J. Malaska, and P. Beauchamp (2014), Experimental determination of the kinetics of formation of the benzene-ethane co-crystal and implications for Titan, *Geophys Res Lett*, *41*(15), 5396-5401.

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Vu, T. H., M. L. Cable, M. Choukroun, R. Hodyss, and P. Beauchamp (2014), Formation of a New Benzene-Ethane Co-Crystalline Structure Under Cryogenic Conditions, *J Phys Chem A*, *118*(23), 4087-4094.

Hodyss, R., M. Choukroun, C. Sotin, and P. Beauchamp (2013), The solubility of Ar-40 and Kr-84 in liquid hydrocarbons: Implications for Titan's geological evolution, *Geophys Res Lett*, *40*(12), 2935-2940.

Cable, M. L., S. M. Horst, R. Hodyss, P. M. Beauchamp, M. A. Smith, and P. A. Willis (2012), Titan Tholins: Simulating Titan Organic Chemistry in the Cassini-Huygens Era, *Chem Rev*, *112*(3), 1882-1909.

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Malaska, M. J., and R. Hodyss (2014), Dissolution of benzene, naphthalene, and biphenyl in a simulated Titan lake, *Icarus*, *242*, 74-81.

Kawai, J., S. Jagota, T. Kaneko, Y. Obayashi, Y. Yoshimura, B. N. Khare, D. W. Deamer, C. P. McKay, and K. Kobayashi (2013), Self-assembly of tholins in environments simulating Titan liquidospheres: implications for formation of primitive coacervates on Titan, *Int J Astrobiol*, *12*(4), 282-291.