Polymeric Hydrogen Cyanide and its Potential Prebiotic Role on the Surface of Titan

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An Interdisciplinary Study



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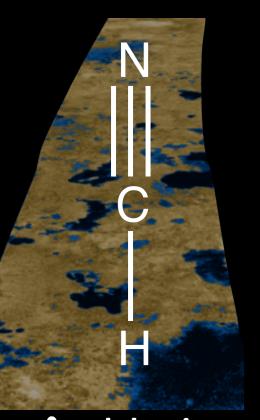
The Keck Institute for Space Studies (NASA-JPL/Caltech)

The National Science Foundation

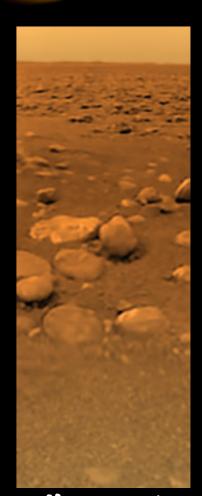
The Templeton Foundation

Saturn's moon Titan

- * The only other body in the solar system with liquids on its surface (CH₄ and C₂H₆)
- Thick hazy atmosphere, 1.5 atm @ surface. nitrogen bearing organics.
- * No liquid water (and no oxygen)
- * Surface temperature of 90-94K
- * HCN exists in ample amounts in the atmosphere (formed from CH₄ and N₂)
 - Presumed key molecule in prebiotic chemistry



Cassini radar imaging of surface *



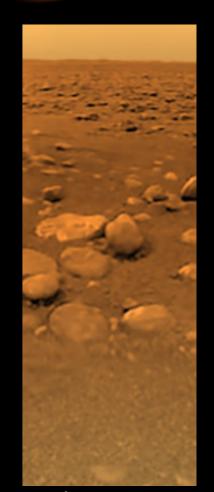
Huygens' landing site

Saturn's moon Titan

- HCN is expected to condense into aerosols, which drop down onto the surface.
- No HCN has been detected on the surface. Instead, unidentified reaction products have been observed

What is the fate of Titan's HCN?

What chemistry is possible?could prebiotic processes go on?



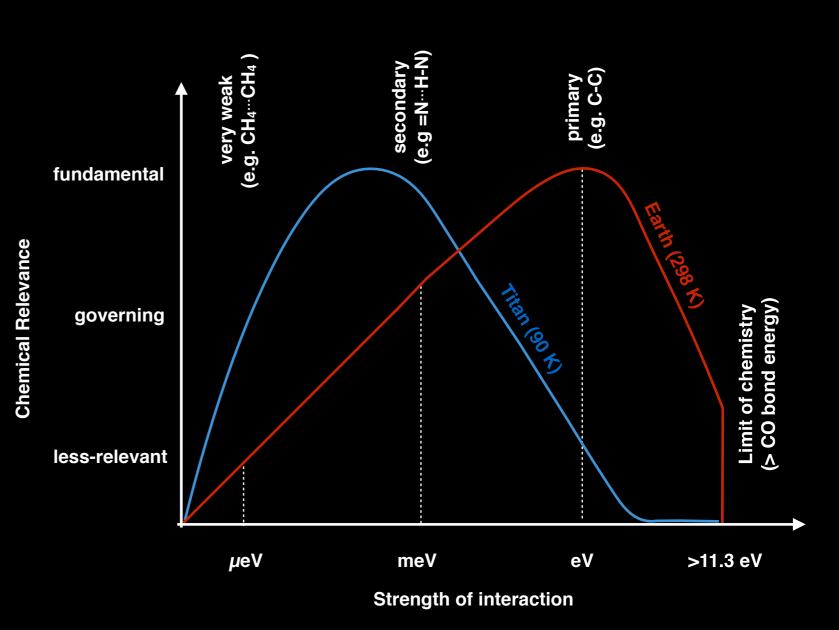
Huygen's landing site



Cassini radar imaging of surface

Limits of Chemistry and requirements for dynamic processes

- Earth and Titan are very different!
- Pynamic processes require reversible thermodynamics, and allowed kinetics (time scales)
- * Weak dispersion interactions and =NH...H- hydrogen bonds on Titan may take up the role of stronger OH...H- hydrogen bonds and covalent bonds on Earth.
- Available energy sources and catalysis may change the situation



Polymers of HCN

- * Proposed component of "Tholins" on Titan
- * Polymerized HCN is poorly understood.
- The structure of polymerized HCN is controversial.
- # Hydrolysis of polymeric HCN results in the formation of amino acids and nucleobases and, possibly routes to polypeptides.

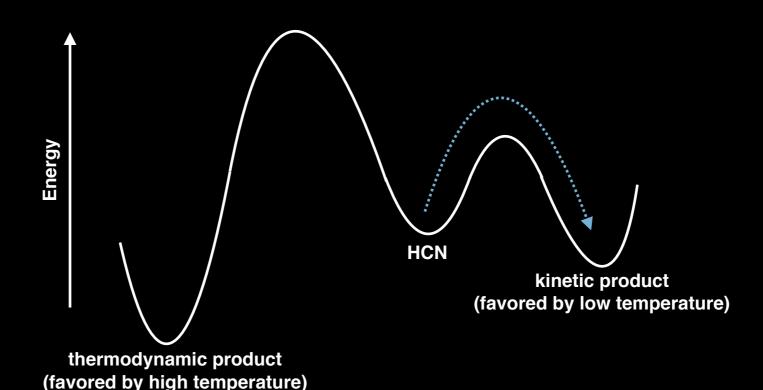
$$N \left[N \right]_{n} N$$

$$\begin{array}{c|c} & NH_2 \\ & & \\ N & & \\ N & & \\ N & & \\ N & & \\ NH_2 \end{array}$$

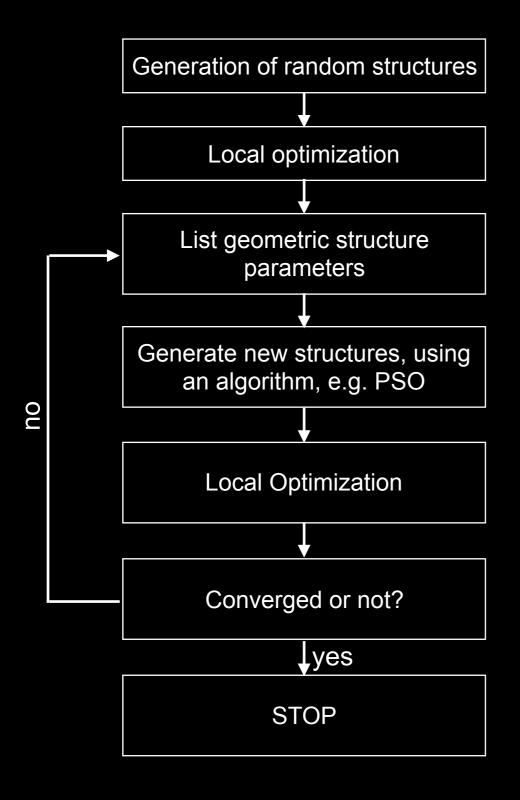
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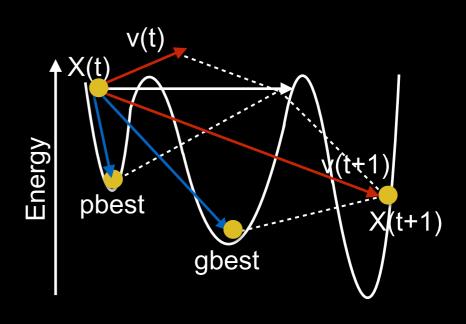
A Computational Study

- * Removes some ambiguity (well defined materials can be studied)
- * Ordered materials are unlikely on Earth, but more likely on Titan (kinetic control)
- Pensity Functional Theory (DFT) used to calculate energies and properties of different materials
- * Structure search algorithms used to predict possible materials from the H,C,N stoichiometry.

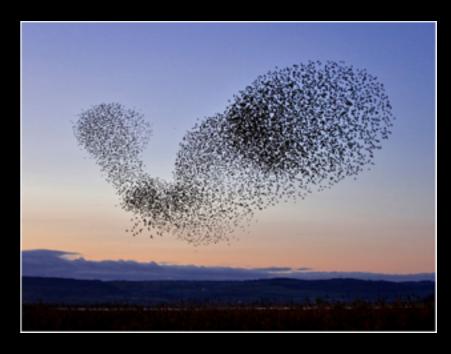


Structure Prediction





Particle-Swarm Optimization (PSO) algorithm

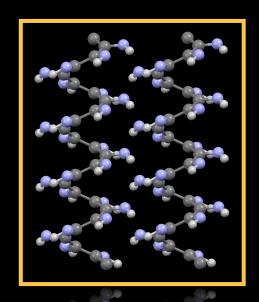


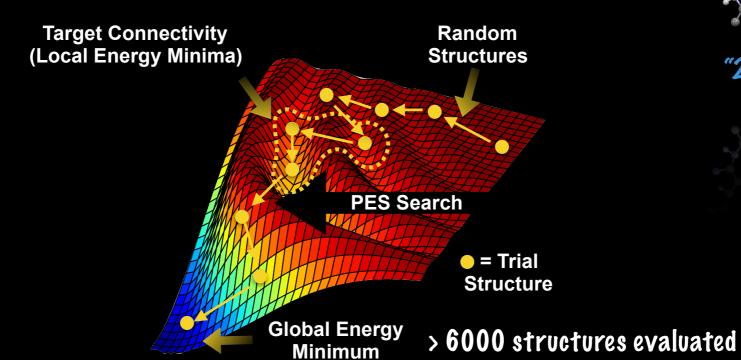
Structure Searching



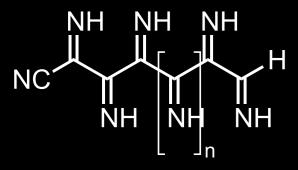


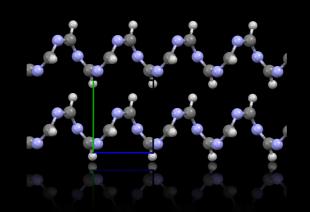
"10" polymers











30 networks

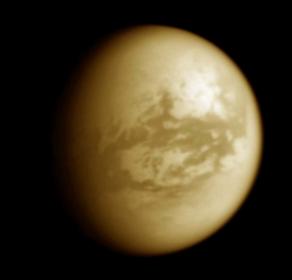
or as a physicist put it:

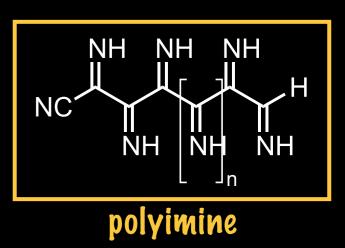
"Nitrogen-doped cubic gauche structure of carbon hydride"

"20" sheets

Polyimine (pl)

- ca 75% of polymeric HCN has been attributed to polyimine (multinuclear and multidimensional NMR spectroscopy).
- Reaction outcomes are dependent on reaction conditions, and this assignment remains controversial.
- On Earth, HCN polymerizes to an disordered material. On Titan, kinetic control may allow for more well defined materials.
- * We have chosen to focus on this one polymer, its polymorphs, properties, and their potential chemical function on the surface of Titan





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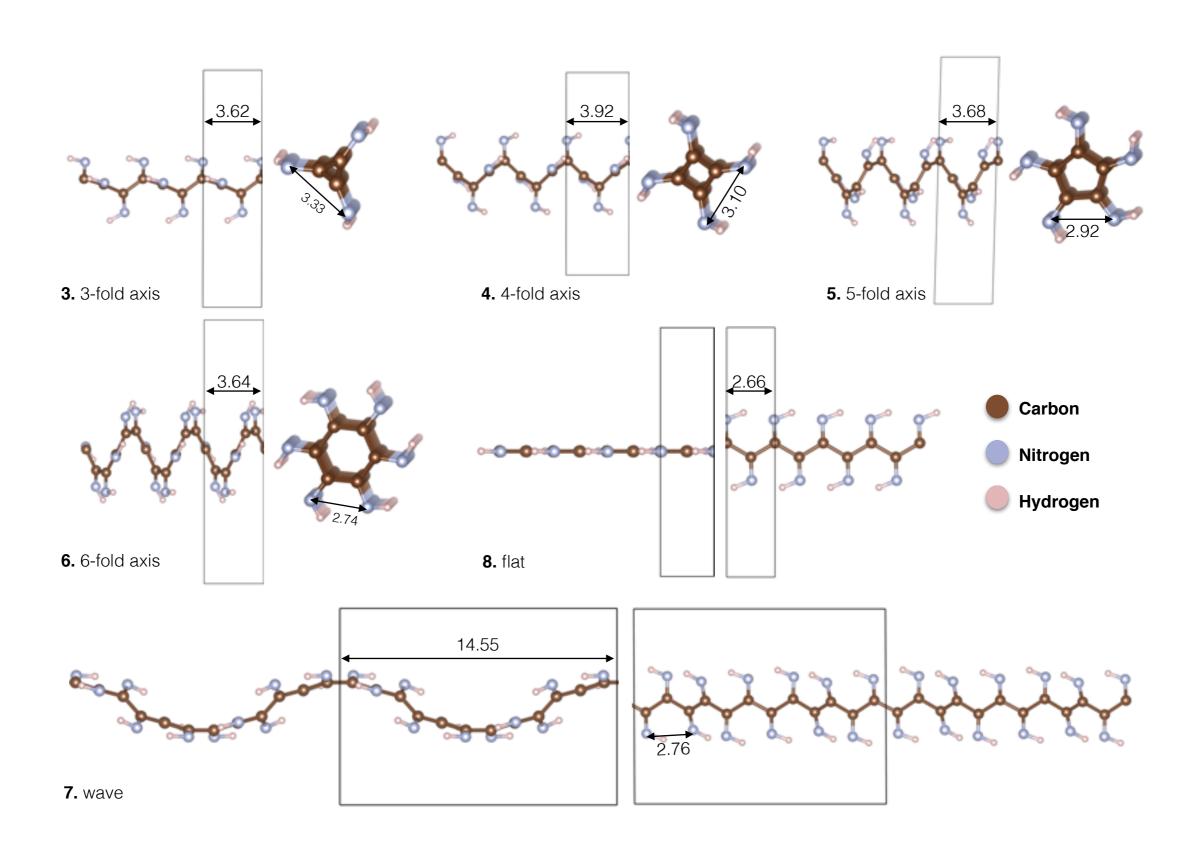
Atomic and Ionic Radii of Elements 1-96

Dr. Martin Rahm ☑, Prof. Dr. Roald Hoffmann ☑, Prof. Dr. N. W. Ashcroft

Just out NOW!

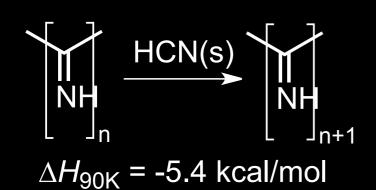
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3	3s ¹ 2.25	3s ² 2.40	3	4	111 Ang: 5	ström (6	7	8	9	10	11	12	3s ² 3p ¹ 2.39	3s ² 3p ² 2.32	3s ² 3p ³ 2.23	3s ² 3p ⁴ 2.14	3s ² 3p ⁵ 2.06	3s ² 3p ⁶ 1.97
	K	Ca			V	Cr	Mn				Cu				As	Se	Br	Kr
4	4s ¹ 2.34	2.70	4s ² 3d ¹ 2.63	4s ² 3d ² 2.57	4s ² 3d ³ 2.52	4s ¹ 3d ⁵ 2.33	4s ² 3d ⁵ 2.42	4s ² 3d ⁶	4s ² 3d ⁷	4s ² 3d ⁸	4s13d10	4s ² 3d ¹⁰	4s ² 4p ¹	4s ² 4p ²	4s ² 4p ³	4s ² 4p ⁴	4s ² 4p ⁵	4s ² 4p ⁶
			2.03 Y					2.26	2.22 Rh	2.19	2.17	2.22	2.33 In	2.34 Sn	2.31 Sb	2.24 Te	2.19	2.12 Xe
5	Rb _{5s1}	5s ²	5s ² 4d ¹	Zr 5s ² 4d ²	Nb 5s ¹ 4d ⁴	5s ¹ 4d ⁵	5s ² 4d ⁵	5s ¹ 4d ⁷	5s ¹ 4d ⁸	4d ¹⁰	Ag 5s ¹ 4d ¹⁰	5s ² 4d ¹⁰	5s ² 5p ¹	5s ² 5p ²	5s ² 5p ³	5s ² 5p ⁴	5s ² 5p ⁵	5s ² 5p ⁶
	2.40	2.79	2.74	2.68	2.51	2.44	2.41	2.37	2.33	2.15	2.25	2.38	2.46	2.48	2.46	2.42	2.38	2.32
6	Cs 6s1	Ba 6s ²	Lu 6s ² 5d ¹	Hf 6s ² 5d ²	Ta 6s ² 5d ³	W 6s ² 5d ⁴	Re 6s ² 5d ⁵	Os 6s ² 5d ⁶	6s ² 5d ⁷	Pt 6s ¹ 5d ⁹	Au 6s ¹ 5d ¹⁰	Hg 6s ² 5d ¹⁰	TI 6s ² 6p ¹	Pb 6s ² 6p ²	Bi 6s ² 6p ³	Po 6s ² 6p ⁴	At 6s ² 6p ⁵	8n 6s ² 6p ⁶
	2.49	2.93	2.70	2.64	2.58	2.53	2.49	2.44	2.33	2.30	2.26	2.29	2.42	2.49	2.50	2.50	2.47	2.43
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			2.84	2.82		2.84	2.83	2.80	2.80	2.77	2.76	2.75	2.73	2.72	2.71	2.77	Valence configu	
		7	7s ² 6d ¹	7s ² 6d ²	7s ² 5f ² 6d ¹	7s ² 5f ³ 6d ¹	Np 7s ² 5f ⁴ 6d ¹	7s ² 5f ⁶	7s ² 5f ⁷	7s ² 5f ⁷ 6d ¹							Rad	dius
			2.93	2.89	2.85	2.83	2.80	2.78	2.76	2.64							Hat	iius

Polymorphs of Polyimine

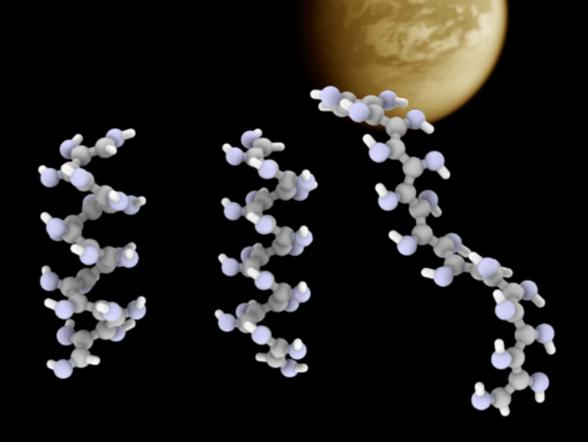


Dynamic ground state geometry

- Infinite chains and 20-mer models have been calculated to study the properties of possible polymorphs.
- The identified lowest energy polymorph has a wave-like conformation
- Polymerization of HCN(s) into pl is thermodynamically reversible, even at 90K.
- Polymerization of acetylene is irreversible.







	ΔE^a	N=C-C=N
Polymorph:	kcal/mol	dihedral angle (°
1. HCN (g)	17.8	-
2. HCN (s)	9.6	-
3. pI 3-fold helix	1.7	110
4. pI 4-fold helix	2.4	68
5. pI 5-fold helix	4.5	39
6. pI 6-fold helix	2.1	26
7. pI wave	0.0	~3 ^b
8. pI planar	0.8	0

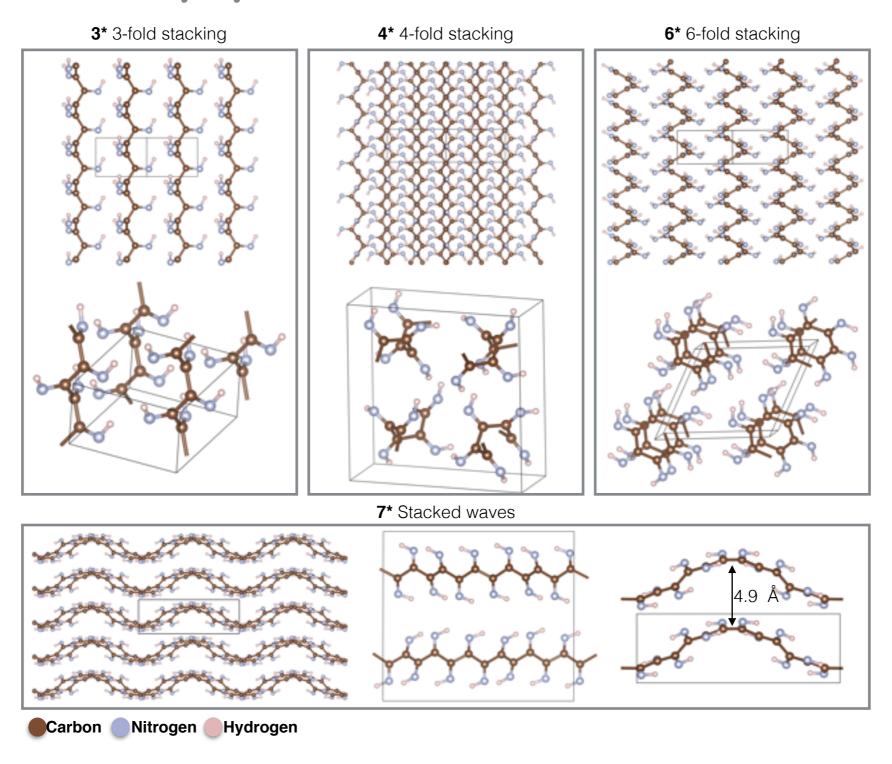
^a Energy per unit of HCN are from periodic HSE06 calculations.

^bAverage value for all N=C-C=N dihedral angles in the unit cell.

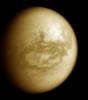
Crystal Packing



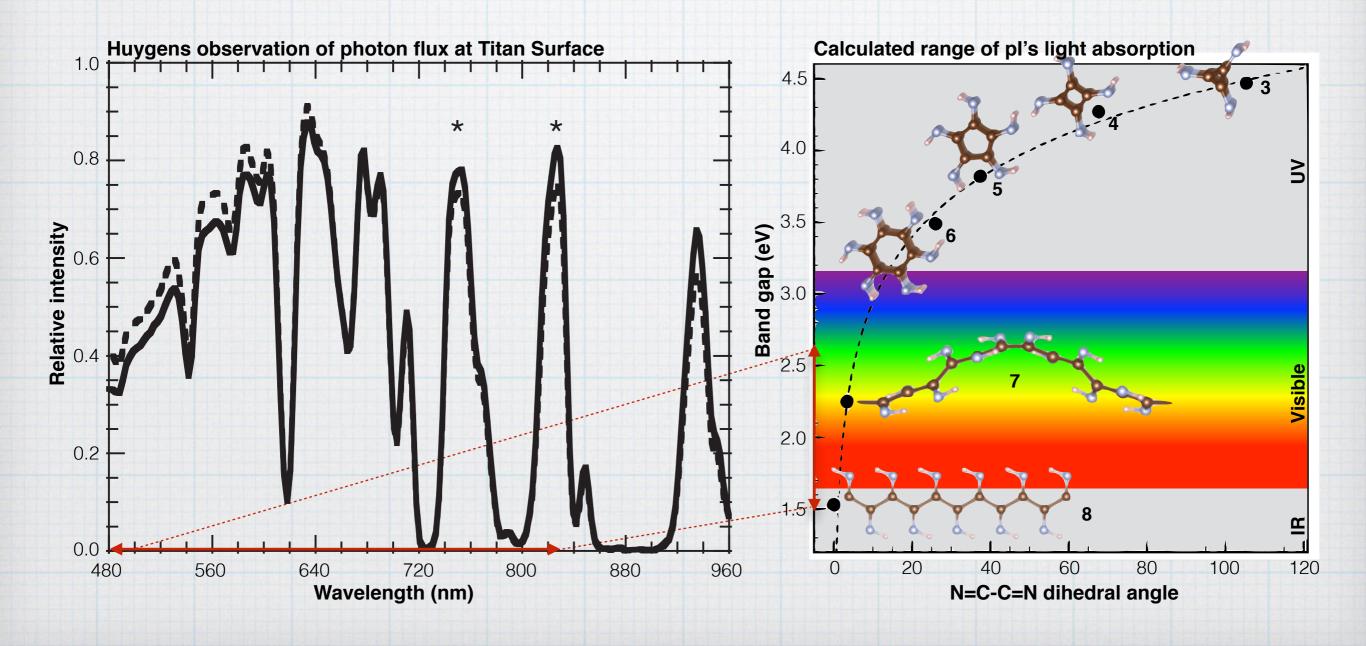
Low temperature may allow for more ordered structures, with * characteristic properties



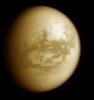
Light Absorption

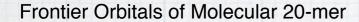


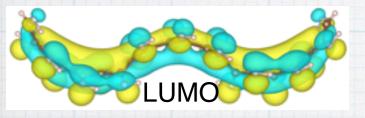
- * pl can absorb photons in a region of relative transparency on Titan
- * Could this allow for photochemistry, and covalent bond making and breaking, despite cryogenic conditions?

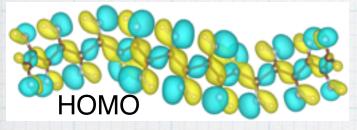


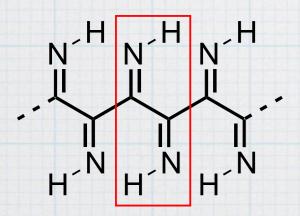
Electronic Structure

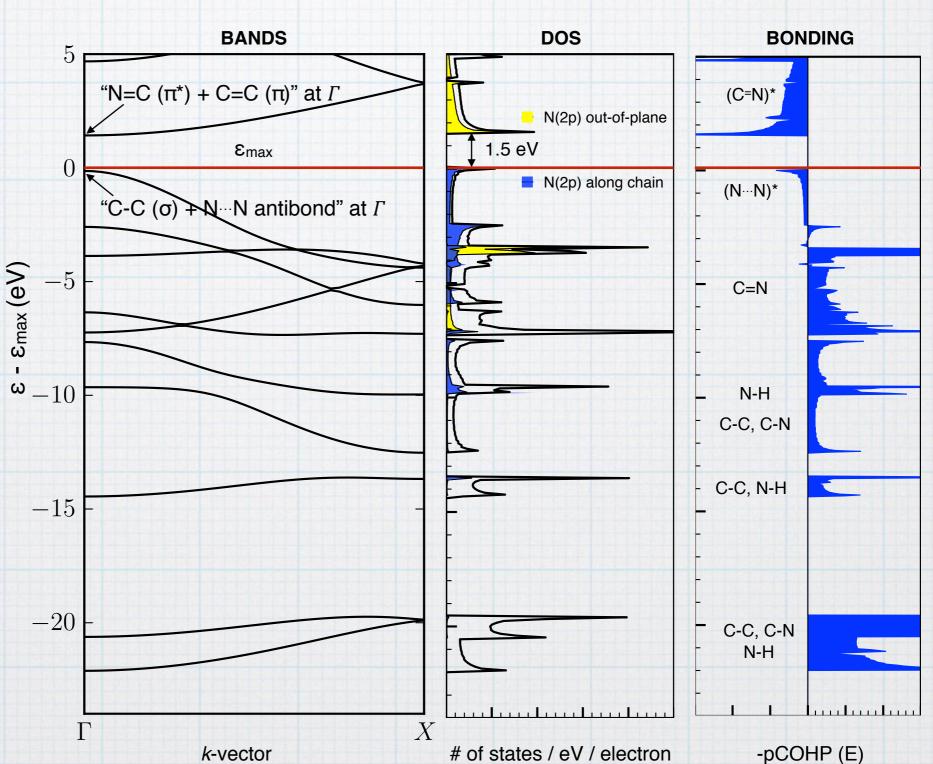




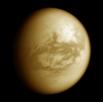


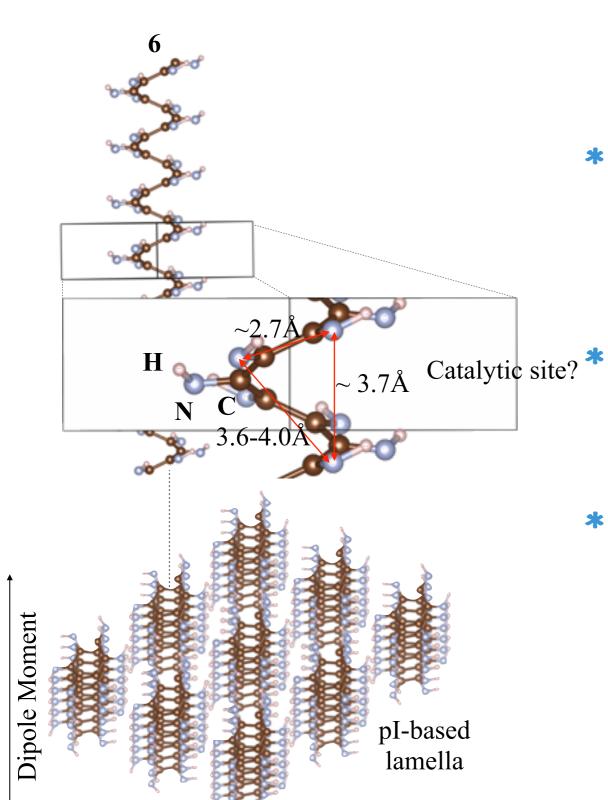






Catalytic Activity?





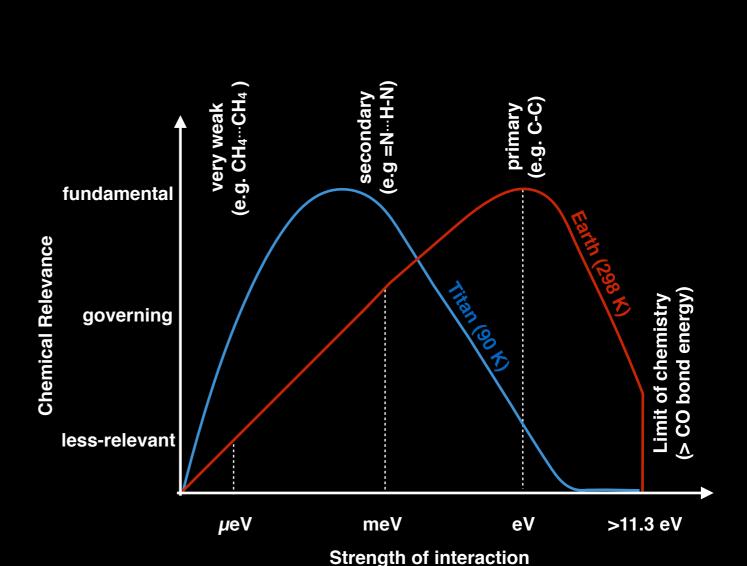
* The ability of some polymorphs to generate electric fields by the alignment of =NH groups may give rise to materials capable of catalysis via electrostatic preorganization.

The pl backbone can give rise to structures reminiscent of "oxyanion holes", catalytic sites in some enzymes.

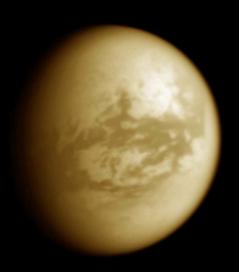
Photon absorption may synergize with such structures, allowing for more selective chemical transformations.

Petection on Titan

- Pensities of considered structures are 1.2-1.4 g cm⁻³, considerably higher than that of Titan's seas (0.4-0.7 g cm⁻³).
- * The polymers will be solid
- Pefects and lacunae, copolymerization or heterodispersion with polyacetylene could reduce density.
- * If we are after dynamic chemistry, the most promising regions are likely shore regions.
- * Pefinite material identification is not possible with remote sensing.
- * We have considered "normal chemistry". Dynamic chemical processes ongoing on Titan are likely to rely on extremely weak interactions.



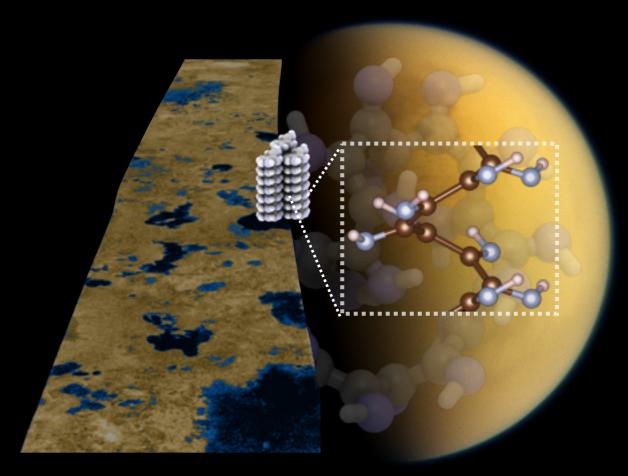
Future Research

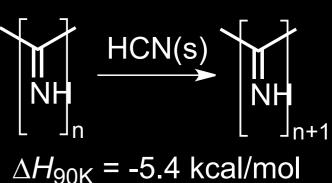


- * Computational evaluation of other HCN-based polymers
- * Prediction of detection characteristics
- Identification of key reaction steps for their formation (considering tunneling, excited states)
- Catalysis, synthesis

Conclusions

- * Formation of polyimine (pl, and other polymers) may explain the lack of HCN on the surface of Titan.
- * Dynamic insertion and removal of HCN from pl is thermodynamically allowed, even at 94K.
- Inter and intra-molecular hydrogen bonds may drive the formation of ordered structures.
- Primary photon absorption is predicted in regions of relative transparent on Titan.
- pl may be photochemically and catalytically active
- * HCN-based materials are good model materials for exploring structure function relationships.





Final Thoughts

- * Titan is a natural laboratory for exploring the possibility of prebiotic chemistry without water (and thus limits of life). However...
- * The solubility of anything is <u>near-zero</u> at 90K. Unless materials are floating on the surface, or accumulate at the bottom, the seas may not be very interesting, chemically.
- * The most dynamical regions are likely to be shore regions.
- * Submarine to Kraken Mare is being considered.
- * If you want insane media attention (as a chemist) drop whatever you do, and pursue planetary science.



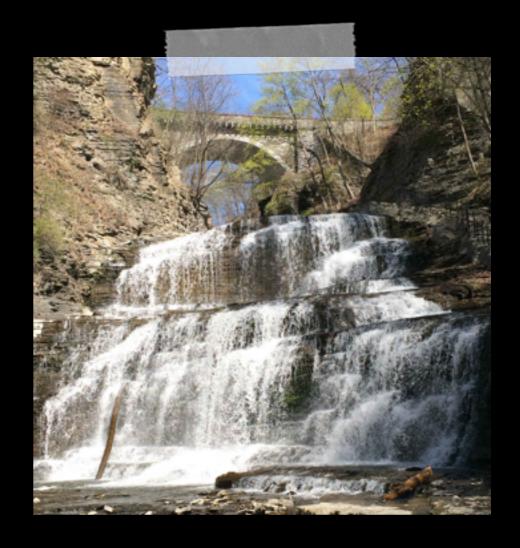
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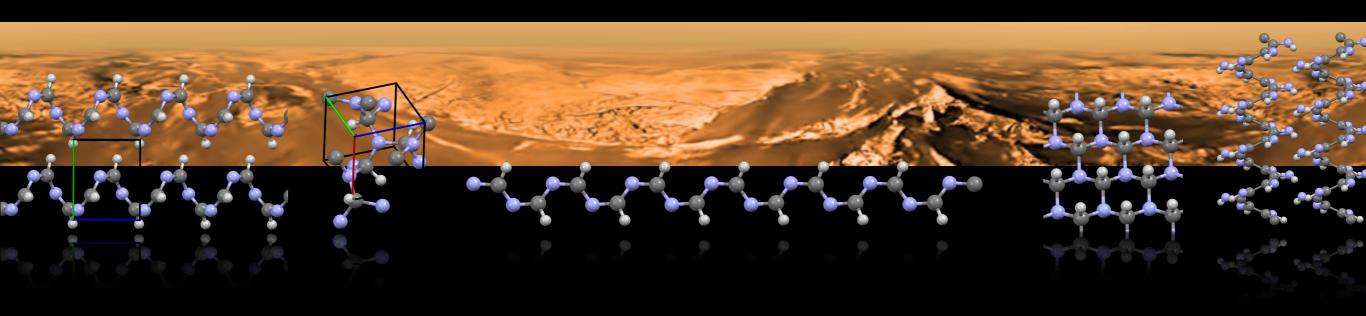
Jonathan Lunine Pavid Shalloway Pavid Usher

Roald Hoffmann

The Keck Institute for Space Studies

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Thank you!

Questions?

