Laboratory Studies in Support of Planetary Missions -- Titan

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Premise

- Cassini and Huygens data on Titan require supporting lab work for full interpretation
- Planning for any future mission to Titan will benefit from laboratory studies undertaken over next decade
- Large investments have been made in laboratory installations, but operating funds are lacking

Goal of this Presentation

- A recommendation from OPAG to NASA in support of funding for Titan-directed lab studies is needed.

- Beyond support for current data, new techniques for in situ sampling and analysis on Titan must be developed.
  - Atmospheric gas and aerosols
  - Surface chemistry, wet and dry
  - Emphasis on organic chemistry

Titan’s complexity requires laboratory research in several areas

- Atmospheric chemistry
  - Ionosphere
  - Middle and lower atmospheres
  - Gases and aerosols

- Surface chemistry
  - Surface atmosphere interactions
  - Mixed ices
  - Ice aerosol interactions

- Astrobiology
  - (all of the above)

- Geology
  - Cryovolcanism
  - Impacts and other structures in ice
  - Dune formation
The complexity of Titan’s atmosphere

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Mixing ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>~ 0.98</td>
</tr>
<tr>
<td>Ar</td>
<td>~ 0.07</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>~ 0.018</td>
</tr>
<tr>
<td>H$_2$</td>
<td>1.1 x 10$^{-3}$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>2.0 x 10$^{-5}$</td>
</tr>
<tr>
<td>CO</td>
<td>3.2 x 10$^{-5}$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>5.7 x 10$^{-5}$</td>
</tr>
<tr>
<td>CH$_3$D</td>
<td>1.1 x 10$^{-5}$</td>
</tr>
<tr>
<td>D$_2$H</td>
<td>8.7 x 10$^{-6}$</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>5.5 x 10$^{-6}$</td>
</tr>
<tr>
<td>HC$_3$N</td>
<td>3.0 x 10$^{-7}$</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>2.0 x 10$^{-7}$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>1.2 x 10$^{-7}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.0 x 10$^{-8}$</td>
</tr>
<tr>
<td>C$_3$H$_4$</td>
<td>1.2 x 10$^{-8}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>8.0 x 10$^{-9}$</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>2.0 x 10$^{-9}$</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>1.5 x 10$^{-9}$</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>4.0 x 10$^{-10}$</td>
</tr>
<tr>
<td>C$_5$N$_2$</td>
<td>&lt; 2.0 x 10$^{-9}$</td>
</tr>
<tr>
<td>C$_2$N$_2$</td>
<td>&lt; 1.0 x 10$^{-9}$</td>
</tr>
</tbody>
</table>

Laboratory studies are needed to provide fundamental data to enable modeling.

Rate constants & branching ratios

Photochemistry
Neutral – Neutral
Ion - Neutral

Ionization Reaction Rate at 1 AU, Solar Minimum, Optically Thin Conditions

- H$_2$O + hv $\rightarrow$ H$_2$O$^+ + e^-$
- C$_3$H$_2$ + hv $\rightarrow$ C$_3$H$_2^+ + e^-$
- C$_3$H$_4$ + hv $\rightarrow$ C$_3$H$_4^+ + e^-$
- C$_3$H$_6$ + hv $\rightarrow$ C$_3$H$_6^+ + e^-$
- C$_3$H$_6$ + hv $\rightarrow$ C$_3$H$_4^+ + H_2 + e^-$
- C$_3$H$_6$ + hv $\rightarrow$ C$_3$H$_2^+ + 2H_2 + e^-$
- C$_3$H$_8$ + hv $\rightarrow$ C$_3$H$_6^+ + H_2 + e^-$
- C$_3$H$_8$ + hv $\rightarrow$ C$_3$H$_4^+ + 2H_2 + e^-$
- C$_4$H$_2$ + hv $\rightarrow$ C$_4$H$_2^+ + e^-$

Keller, Anacich, Cravens

Aerosols
Tholins made at Cornell to simulate Titan’s aerosol

Energy deposition in mixtures of simple reducing gases produces complex refractory solid material
Tholin Studies

- Formation
- Optical properties (refractive indices)
- Role of tholins in maintaining CH₄ mixing ratio in atmosphere
- Structure
- Hydrolysis of tholins

![Bernard et al. 2007](image)

Complex refractive indices (optical constants)

Complex refractive index \( m = n + i k \)

- Atmospheric haze
- Radiative transfer
- Surface material
- Surface Reflectance
- Haze
- Thermal structure
- Identification of organic material?
- Systematic study of n & k for various tholins as a function of experimental parameters

Astrobiology

- The irradiation of aromatic hydrocarbons in H₂O ice produces molecules of biological significance.

UV Irradiation of Polycyclic Aromatic Hydrocarbons in Ices: Production of Alcohols, Quinones, and Ethers

Max P. Bernstein, Scott A. Sandford, Louis J. Allamandola, J. Seb Gillette, Simon J. Clemett, Richard N. Zare

Matrix isolation of Polyaromatic Hydrocarbons

Matrix Gas Bulb

Matrix Isolated Sample

Andrew Mattioda & Lindsay Rutter, Astrochemistry Lab, NASA Ames Research Center
**Polycyclic Aromatic Hydrocarbons (PAHs)**

Aliphatic Carbon Molecule

*Propane*

\[ C_3H_8 \]

PAH

*Anthracene*

\[ C_{14}H_{10} \]

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"Endoskeletal" Polycyclic Aromatic Nitrogen Heterocycles, PANHs

N substitution within the carbon skeleton of a PAH produces a depth-dependant blue shift in the position of the dominant CC stretching feature near 6.2 \( \mu \)m.

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**Astrobiological Significance**

Inserting a nitrogen in a PAH...

**Anthracene** \( (C_{14}H_{10}) \)

\[ \rightarrow \]

**Acridine** \( (C_{13}H_{9}N) \)

creates a Polycyclic Aromatic Nitrogen Heterocycle (PANII)

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Influence of Nitrogen on the PAH NIR transitions.
The Surface

Surface Chemistry and interaction with the atmosphere

Ices + Liquids + Aerosol Precipitates

The complexity of Titan’s icy surface

Reflectance spectra of organic ices

Geology
- Cryovolcanism (role of NH₃, if any)
- Impact cratering
- Dune field formation
Ice-Impact Studies of Organic Synthesis

~6 km/sec impacts in ices generate shock and electrical impulses that may initiate organic chemical reactions.

J. Borucki, D. Cruikshank, B. N. Khare, M. P. Bernstein

Irradiation of ices produces new species

Ion irradiation of H$_2$O + CH$_4$

Moore & Hudson, 1998

Some titles from an NSF-sponsored Titan laboratory workshop (Honolulu, Feb. 5-7, 2007) - I

C$_2$H reactions: Low-temp. kinetics and product detection (S. R. Leone)

Photolysis of simulated Titan atmospheres with HCN and CO: Complex refractive index of haze analogs (B. Tran et al.)

Formation of carbon aerosols in Titan’s atmosphere (F. Salama et al.)

Rate constants of neutral-neutral reactions in Titan’s atmosphere (C. Bertelho et al.)

Bimolecular reactions of radicals with unsaturated hydrocarbons—buildup of aerosols (Y. Guo et al.)

Ion imaging of hydrocarbon growth by photochemistry (A. G. Suits et al.)

Tholin influence on CH$_4$ mixing ratio in the atmosphere (B. N. Khare et al.)

Some titles from an NSF-sponsored Titan laboratory workshop (Honolulu, Feb. 5-7, 2007) - II

Role of photoionization in forming complex organic molecules in Titan’s upper atmosphere (H. Imanaka et al.)

Spectroscopy of Titan tholins (E. Quirico et al.)

Cryogenic IR reflectance spectroscopy of organic ices (J. Curchin et al.)


New lab. Studies of titan’s ionospheric chemistry (R. Thissen et al.)

Spectroscopy of hydrocarbon radicals in gas phase and cryogenic matrices (Zhang, X. et al.)

Kinetic measurements of hydrolysis of tholins: Implications for prebiotic chemistry on Titan (C. D. Neish et al.)
NASA’s Laboratory Astrophysics Program

- ROSES solicitation
- Lab astro is a sub-element of APRA (Astronomy and Physics Research and Analysis Program)
- In FY 2006, 33 investigations funded for total of ~$3.8 million
  - 4 infrared
  - 9 supporting interstellar medium studies
  - 5 sub-millimeter spectroscopy
  - 8 UV/optical atomic processes
  - 2 UV/optical molecular and dust formation processes
  - 5 X-ray mission supporting investigations

Information from Hashima Hasan, NASA HQ

Proposal to the American Astronomical Society for a Working Group on Laboratory Astrophysics & Astrochemistry

- Steering Committee consisting of
  - Paul Goldsmith (JPL)
  - Steve Federman (U Toledo) – Chair.
  - Farid Salama (Ames Res. Center)
  - Daniel Savin (U Colombia)
- AAS Council has given its initial encouragement of this effort
- Cruikshank has encouraged Consolmagno (DPS Chair) to support this effort, with some kind of DPS participation

The End