Molecular Synthesis in Space

The Cradle of Life?

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Introduction

Perhaps the great unanswered questions of modern science is

- Where and how did life begin on Earth?

And

- Is there life elsewhere in the universe?
Introduction

To answer the questions

Where and how did life begin on Earth?

And

Is there life elsewhere in the universe?

We need to answer scientific questions

- Are the conditions for sustaining life common throughout the universe?

- How is the material needed for life (pre-biotic material) formed? **ASTROCHEMISTRY**
The Interstellar Medium is rich in molecules… from the simplest molecule (H$_2$) to those necessary for the formation of life.
## >160 Interstellar Molecules

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### Molecules
- **Acetic Acid**
- **Formic Acid**
- **Glycolaldehyde**
- **Glycine**
- **Benzene**
- **Cyanopolyynes**

[National Radio Astronomy Observatory](http://www.cv.nrao.edu/~awootten/allmols.html)
What chemistry can occur in such environments?

- Temperatures are low ... (As low as 10K)

- In the ISM the density is extremely low ... so probability of collisions is low

- Hence it appears impossible to support chemistry!

But evidence shows there must be complex chemistry!
What chemistry can occur in such environments?

- At low temperatures there is little or no thermal/kinetic energy

- So chemistry must occur through barrierless Reactions.

- Or

- Stimulated reactions (e.g. photon assisted)
What chemistry can occur in such environments?

Ion-Molecule reactions are a typical example of a reaction that may have no activation barrier.

e.g.  
\[
NH_3^+ + H_2 \rightarrow NH_4^+ + H
\]
\[
Ar^+ + H_2 \rightarrow ArH^+ + H
\]
\[
He^+ + H_2 \rightarrow He + H^+ + H
\]
\[
H_2^- + H \rightarrow H + H_2 + e^-
\]

(Note anions as well as cations !)
What chemistry can occur in such environments?

However neutral – neutral reactions can also occur at low temperatures.

\[
\text{H}_2\text{O} + \text{Cl} \rightarrow \text{HCl} + \text{O}
\]

\[
\text{F} + \text{D}_2 \rightarrow \text{DF} + \text{D}
\]

Indeed the reaction rate may INCREASE as the temperature falls.

It has been suggested that the increasing rate of these reactions as the temperature is lowered is related to the changing distribution of reagents over their rotational levels as the temperature is lowered.

- Hence State Selective experiments are required
What chemistry can occur in such environments?

Chemistry on Titan – Huygens 2005

Alone of all the satellites in the solar system, Titan has a significant atmosphere. Titan's peak surface temperature is about 95 K

Cyanoacetylene (HCCCN) is one of the nitrile compounds observed in the atmosphere of Titan

**Formed by CN + RH chemistry (radical - radical) at low temperatures**


Chemistry of Planets
What chemistry can occur in such environments?

Supersonic crossed beam machine for radical-radical studies. CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) to study neutral-neutral reactions and energy transfer processes in the gas phase down to temperatures as low as ~10 K. (Rennes)
What chemistry can occur in such environments?

But such gas phase experiments cannot explain all the chemistry in the ISM.

E.g. the formation of $\text{H}_2$ .... the most common molecule in the ISM cannot be formed in the gas phase.

Instead it is formed by reactions on DUST Surfaces!
Chemistry on Dust grains

• Some of these grains are covered with an icy mantle formed by freezing out of atoms/molecules from the gas phase.

• Hence we need to explore ice chemistry!

• The ices in the mantle are bombarded with cosmic rays, ions, solar UV, electrons.

• Chemical modification occurs.
Ices in the Solar System

Mercury
Earth
Mars
Europa
Ganymede
Callisto
Io
Saturn
Dione
Enceladus
Rhea
Tethys
Mimas
Miranda
Ariel: CO₂
Umbral
Oberon
Neptune
Triton
Pluto & Charon

05th Jan 2006
## Ices in the Outer Solar System

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Nature of Astrochemical Ices and their Environments

- Ices may be broadly characterised in terms of
  - ice thickness, temperature and composition → ice morphology
  - energy, flux and type of processing radiation → ice processing

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<td>10 – 100 K</td>
<td>Stellar UV; Lyman-α photons (H₂ luminescence); Cosmic rays</td>
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<td>1μm – several km</td>
<td>30 – 150 K</td>
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**Experimental Programme at the OU**

_and collaboration with Prof R Kaiser Hawaii_

**OU Portable System:**
- Transmission UV & FTIR Spectroscopy and **Processing** (e/ions/photons)
- Designed to be transported to central facilities → Synchrotrons, RAL, QUB

**OU Static System:**
- TPD, RAIRS and **Processing**
- Molecular synthesis with electrons and photons
- → E-gun, UV lamp

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Diagram of the OU Portable System:
- Cryogen inlet via transfer line
- Cryostat
- Temp controller
- Cryogen inlet via transfer line
- To pumping station
- Thermocouples
- Copper sample mount
- Resistive heater
- MgF₂/ZnSe substrate
- Sources: UV-VIS / FTIR spectrometer, Synchrotron
- Detectors: UV-VIS / FTIR detector, PMT

Diagram of the Proposed TSP:
- Cryostat
- Z-axis feed-through
- Mass spectrometer
- Rotary feed-through
- Gate valve
- Mag-lev turbo-pump
- Ion Gauge
- Sample mount and substrate
- Sources: E-gun, Synchrotron, ECR

**Source:** 300 mm
• HV (UHV) chamber - Portable:
  – $P \sim 10^{-8} - 10^{-10}$ mbar
    • Still > a million times higher than ISM!

• Temperature
  – Continuous flow LHe/LN2 cryostat
    • $12 \text{ K} < T < 450 \text{ K}$

• Substrate
  – $\text{CaF}_2 / \text{MgF}_2$ (VUV) or $\text{ZnSe}$ (IR) window
    • transmission spectroscopy of bulk ices

• Samples
  – deposited in situ by vapour deposition
  – $0.1 - 1 \mu\text{m}$
  – Thick enough to ignore the effects of the substrate
  – Looking at bulk ice reactions
Experiments at Synchrotron Facilities

UK Daresbury   Aarhus Denmark
Recent results on astrochemical ice morphology

- Study electronic state spectroscopy of molecules in the solid phase (photolysis).

- VUV and IR spectroscopy of ice morphology.

- Experiments performed in transmission mode.
VUV Spectrum of water ice <90K

Note: Blue shift in the solid phase
VUV Spectrum of carbon dioxide ice <90K

Note: Blue shift in the solid phase
VUV Spectrum of Methylamine ice CH$_3$NH$_2$
Comparison of gas and solid phase Methylamine

Note absence of low lying bands in solid phase
Some ‘first’ conclusions

• Can not use gas phase data to predict position of electronic bands in the ice phase.

• Some electronic states are ‘missing’ in solid phase spectra.

• Cross sections (hence photodissociation rates) change from gas to solid.
Case study of $\text{SO}_2$ – Morphology and temperature
SO$_2$ Morphology and temperature

- ‘Fast’ deposition at 25 K
  No vibrational structure → Indicates amorphous ice
- Annealed to/deposited at 90 K
  vibrational structure & evidence of Davydov splitting → Indicates crystalline ice
- Slow’ deposition at 25 K
  Weak vibrational structure → evidence of some degree of crystallinity!
• Conclusions

• Rate of deposition is important in determining ice morphology.

• May form mixed amorphous/crystalline ice.

• Crystallinity is not always a signature of temperature or thermal history!
Ammonia gas vs solid (25K)
Ammonia Different T
The band at 194 nm is indicative of ‘exciton’ formation
Different thicknesses of NH₃, all deposited at the same temperature (75 K) and deposition rates.

The exciton band at 194 nm becomes more apparent in the thicker samples. A second band also becomes apparent at 173 nm.

The spectrum of the thinnest sample (0.03 μm) resembles the spectrum of an amorphous sample...

Excitons, if they can be detected, are excellent monitor of morphology.
Ammonia ice in the IR

- 1060 cm\(^{-1}\) peak is evidence of crystalline structure.
- 1070 cm\(^{-1}\) peak is due to amorphous ice.
- The 1100 cm\(^{-1}\) peak indicative of exciton measure of grain boundaries.
**Amorphous:** Disordered structure, thermodynamically unstable

**Semi/polycrystalline:** More ordered structure with crystallite & amorphous mix, thermodynamically stable

**Polycrystalline:** many small crystallites, large number of grain boundaries, thermodynamically stable

**Crystalline:** Large crystallites, few grain boundaries, thermodynamically stable
Ammonia

• Both UV and IR show features that are characteristic of exciton formation

• Complex ice morphology formation of regions of crystalline ice in an ‘amorphos sea’

• Crystallites

• Structure is random/statistical. Each sample is different! Depends on deposition time.
Studies in chemical processing of astrochemical ices

Ices may be processed by UV light or cosmic rays in the ISM

On planetary surfaces interaction with ions from the planetary magnetosphere

e.g. Moons of Jupiter and Saturn
**Ions in the Solar System**

- **Solar wind** → 95% hydrogen/protons + electrons, 4% helium, 1% heavier elements (C, N, O, Ne, Mg, Si & Fe)

- **Cosmic rays** → 86% hydrogen/protons, 11% helium, 1% heavier elements, 2% electrons

- **Plasma in planetary magnetospheres e.g. Jupiter, Saturn...** → include solar wind particles + sputter products off satellites

- **E.g. Jovian Magnetospheric ions comprise of:**
  - H\(^+\), He\(^+\), O\(^6+\) and C\(^6+\) - solar wind
  - H\(^+\), H\(_2^+\) and H\(_3^+\) - ionosphere
  - O\(^+\), O\(^2+\), O\(^3+\), O\(^4+\), S\(^+\), S\(^2+\), S\(^3+\), S\(^4+\), S\(^5+\), S\(_2^+\), SO\(_2^+\), Na\(^+\) and K\(^2+\) - Volcanic emissions from Io
  - H\(_2^+O^+\), H\(_3^+O^+\) and OH\(^+\) - sputtering off icy satellites

- **Low energy and multiply-charged ions constitute a high proportion of the ion flux**
**Ion Interactions with Planetary Surfaces**


**Evidence for sulphur implantation in Europa's UV absorption band**
Arthur L. Lane, Robert M. Nelson & Dennis L. Matson

The International Ultraviolet Explorer (IUE) spacecraft has obtained observations of the galilean satellites over the past 2 years ..........

.......... We report here the discovery of an absorption feature at 280 nm in Europa's reflection spectrum. Observations with the IUE show that this absorption is strongest on Europa's trailing hemisphere (central longitude 270°). We identify the feature as an SO₂ absorption band and hypothesize that SO₂ may form when energetic jovian magnetospheric sulphur ions are injected into Europa's water-ice surface.


**Detection of an oxygen atmosphere on Jupiter's moon Europa**
D. T. Hall, D. F. Strobel, P. D. Feldman, M. A. McGrath & H. A. Weaver

EUROPA, the second large satellite out from Jupiter, is roughly the size of Earth's Moon, but unlike the Moon, it has water ice on its surface¹. ..........

.......... Here we report the detection of atomic oxygen emission from Europa, which we interpret as being produced by the simultaneous dissociation and excitation of atmospheric O₂ by electrons from Jupiter's magnetosphere. Europa's molecular oxygen atmosphere is very tenuous, with a surface pressure about 10⁻¹¹ that of the Earth's atmosphere at sea level.

**Nature 388, 45 - 47 (1997)**

**Detection of ozone on Saturn's satellites Rhea and Dione**
K. S. NOLL, T. L. ROUSH, D. P. CRUIKSHANK, R. E. JOHNSON & Y. J. PENDLETON

The satellites Rhea and Dione orbit within the magnetosphere of Saturn, where they are exposed to particle irradiation from trapped ions. A similar situation applies to the galilean moons Europa, Ganymede and Callisto, which reside within Jupiter's radiation belts. All of these satellites have surfaces rich in water ice¹.² .......... Here we report the identification of O₃ in spectra of the saturnian satellites Rhea and Dione. The presence of trapped O₃ is thus no longer unique to Ganymede, suggesting that special circumstances may not be required for its production.

**Evidence for Crystalline Water and Ammonia Ices on Pluto’s Satellite Charon**
Michael E. Brown¹ and Wendy M. Calvin²

Observations have resolved the satellite Charon from its parent planet Pluto, giving separate spectra of the two objects from 1.0 to 2.5 micrometers. The spectrum of Charon is found to be different from that of Pluto, with water ice in crystalline form covering most of the surface of the satellite. In addition, an absorption feature in Charon's spectrum suggests the presence of ammonia ices. Ammonia ice-water ice mixtures have been proposed as the cause of flowlike features observed on the surfaces of many icy satellites. The existence of such ices on Charon may indicate geological activity in the satellite's past.
Ion v Photon irradiation

- Photoabsorption of a photon interact with single target (selection rules)
  - Dissociation, ionisation, excitation
  - Secondary electrons
- Penetration depth depends on the optical properties of the material

- Ions interact with many atoms/ molecules along the ion tracks
  - Dissociation, ionisation, excitation
  - Dislocations
  - Primary, secondary... knock-on particles
  - Secondary, tertiary... electrons
  - Sputtering
  - Implantation (reactive species)
- Penetration depth depends on the ion energy and mass and the stopping power of the ice
Experiments performed at ECRIS QUB

- 9.0 – 10.5 GHz Electron Cyclotron Resonance Ion Source at QUB
C$n^+$ Irradiation of H$_2$O ice

- Ions: $^{13}$C$^+$ and $^{13}$C$^{2+}$ (45° angle to ice surface)
- Energies: 2 and 4 keV
- Sample Temperatures: 30 and 90 K
- Sample thickness: ~ 300 nm
- Analysis: FTIR transmission

$$Fluence = \frac{It}{eqA} \text{ (ions cm}^{-2}\text{)}$$

- Ion beam size measured for each ion type
- Faraday cup calibrated to determine ion current at the sample for each ion type
- Beam currents < 200 – 600 nA
Results: FTIR Spectroscopy

Redshift and broadening of the H$_2$O O-H stretching band

13CO$_2$
CO₂ Reaction Mechanisms

No CO is observed in the FTIR spectra → efficient conversion to CO₂?

1) C⁺ + e⁻ → C (³P/¹D)
2) H₂O → H + OH
   → O (³P/¹D) + 2H

CO formation (if precursor...)
C addition to O, OH and H₂O

C + O → CO

C + OH → [COH] → CO + H
   ↓
   [HCO]

C (³P/¹D) + H₂O → [COH₂] → CO + 2H/H₂
   ↓
   [HCOH]
   ↓
   [H₂CO]

CO₂ formation

CO + O → CO₂

Barrier...

C + O₂ → \[ \begin{array}{c} \text{C} \\ \text{O} \end{array} \] → CO₂

CO + OH → [COOH] → CO₂ + H

HCO + OH → [HCOOH] → CO₂ + 2H/H₂

C(³P/¹D) + 2H₂O → CO₂ + 2H/H₂

Suprathermal
Temperature Dependence

• In all experiments a higher yield of CO₂ (and H₂O₂ – qualitatively) is observed at lower temperature!

Ice morphology
  – Plays an important role in surface chemistry (surface area, pores…)
  – Density/porosity \(\rightarrow\) affect stopping power and range

• 30 K: ‘spongy’ structure
  – Greater surface area, greater yield?
  – Pore collapse, trapping of reactants?

• 90 K: Mobility (H, O, OH etc.) hindering CO₂ formation?
  – Competitive reactions e.g. O₂ formation \(\rightarrow\) escape?

• Diffusion & trapping of volatiles – O₂, N₂
  – Favouring C + O₂ reaction at lower temperature

• Need to carry out experiments at 10 K
  – Eliminate diffusion
  – Look for intermediates to determine reaction pathways
Proton irradiation of $\text{H}_2\text{O}:\text{CO}_2$

100 keV $\text{H}^+$

5 keV $\text{H}^+$

Chemistry of Planets

05th Jan 2006
Stability and Reactivity of Ozone in Astrochemical Ices
Bio-signatures

Molecules that can be used to detect life elsewhere in the solar system or in deep space

>> Ozone (O₃)

>> Nitrous oxide (N₂O)

These molecules are selected from the planet that already supports organic life form… EARTH !.
Why Ozone?

• Essential component of any atmosphere capable of sustaining life

• Strong evidence that the planet can support life - if not the existence of life itself

• Identified in planetary, satellites surfaces. Ozone chemistry is possible in these ices.

• DARWIN mission --- Biomarker?

How is ozone synthesised in gas and ice phase?
Ozone synthesis

• On Earth atmosphere
  – Stratosphere
  – Chemistry initiated by sunlight

• Planetary ices
  – Ice surface and bulk egs of ices and surfaces
  – Chemistry initiated by energetic particles as well as photons.

How to study ozone chemistry in extreme environments?
Chapman reaction

- \( O_2 + M \rightarrow O + O + M \)
- \( O_2 + O + M \rightarrow O_3 + M \)

- \( M \rightarrow \) Third body (gas phase)
- \( M \rightarrow \) Ice matrix (ice phase)

Ozone produced in the ice phase is stored – is that stable?
In a pure oxygen ice

No significant amount of ozone molecule dissociation
Ozone from oxides of nitrogen

- Ozone produced from the irradiation of solid oxides of nitrogen, like N₂O and NO₂.

**Dissociation pathway**

\[
\begin{align*}
\text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{O} \quad (^{1}\text{D} \text{ or } ^{3}\text{P}) \\
\text{NO}_2 & \rightarrow \text{NO} + \text{O}
\end{align*}
\]

**Formation pathway**

\[
\begin{align*}
\text{O} + \text{O} & \rightarrow \text{O}_2 \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3
\end{align*}
\]
e⁻ irradiation of N₂O

>> Steady ozone growth

>> No dissociation or reduction

>> Less dose -- less NₓOᵧ molecules

Will there be any change with the higher dose irradiation?
H$^+$ irradiation of N$_2$O

>> Ozone loss

>> May be due to dissociation or reaction of ozone molecules

>> Higher the dose, higher N$_x$O$_y$ molecules

Ozone loss due to dissociation or reaction?
Presence of $\text{N}_2\text{O}_5$ in $\text{N}_2\text{O}$ ice

How are the other new molecules produced?
Reactions for $N_2O$ ice

$N_2O + O(^{1}D) \rightarrow (NO)_2$

$NO + O \rightarrow NO_2$

$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$

Will it be the same for an $NO_2$ ice?
Warm-up of the N$_2$O ice

Smaller amounts of ozone stored in the ice before desorption
Conclusion

• Ozone is highly stable in a pure oxygen ice.

• No reaction or significant amount of dissociation in a CO₂ ice.

• But in the presence of oxides of nitrogen, ozone that is produced reacts with NₓOᵧ molecules.
Implications

• Ozone that is produced by the action of energetic particles in astrochemical ices take part in reactions as observed in the Earth’s stratosphere.

• Therefore ozone not only acts as a biomarker but also an active reactant in the icy surfaces similar to Earth’s troposphere/stratosphere.
Questions for Astrochemistry

• Spectral analysis of ices is a useful tool for identifying ice morphology both in the IR and UV.

• Experimentally it is vital that different experiments are calibrated against one another such that the morphology of the ices used are compatible.
Questions for Astrochemistry

• We need a data base of astro-ice spectra to be assembled similar to the large database of gas phase photo-absorption cross sections assembled by the atmospheric community.

• Different temperatures, deposition times and for different substrates
Questions for Astrochemistry

- The mimic of ‘realistic’ astrochemical conditions within the laboratory environment must be addressed.

- Time scales – is our slow deposition still too fast?
Questions for Astrochemistry

• Chemical reactions and their rates depend on surface morphology

• Parameters such as ion charge state, incident energy and secondary electron production are equally important
Questions for Astrochemistry

• The need for a detailed co-ordinated research programme on chemical processes in astrochemical ices is now urgent!

• Needs combination of AMO, Surface Science and Astronomical communities
Need for Astrochemistry

• Can we model ice growth on grain surfaces to explore morphology?

• Look at statistical pattern (e.g. run model many times to provide ‘average’ of ice morphologies)

• To discuss....
Questions for Astrochemistry

• To date have used large bulk ice samples whereas in the ISM dust grains only a few microns in size.

• How is the physics and chemistry influenced by the surface area to volume ratio?
Dust grain chemistry

• Build an ultrasonic trap

• Within which we can suspend ice covered dust particles

• Study spectral characteristics and coalescence properties
Ultrasonic dust trap
**Study of Ice morphology in ultrasonic trap**

- **Studies of ice morphology and grain accretion**
  - Use of ultrasonic trap for IR spectra of ice/dust surfaces

- **Grain sticking** $\rightarrow$ planitesimal building $\rightarrow$ planet formation


Soot and ice agglomerates formed and suspended in an ultrasound field
IR spectra of volcanic ash

Absorbance of low silicate percentage volcanic ash (approx 50%)

Absorbance vs. Wavenumber
IR spectrum of water ice particles in trap: see change from crystal to amorphous on particle surface.
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