Formation of molecules on the surface of laboratory interstellar grain analogues

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Chemistry in the ISM

Chemical processes leading to the formation of molecules in the interstellar medium (ISM)

Gas phase reactions

Grain surface reactions

Carbon- or silicate-based particles
Chemistry in the ISM

Origin of Life

Prebiotic molecules

ISM

Earth
Cold phases of the ISM

Molecular clouds

Planet-forming disks

Outer parts of envelopes of evolved stars
Formation of ice/dust grains in the ISM
Formation of ice/dust grains in the ISM
Formation of ice/dust grains in the ISM

Molecular ices: $\text{H}_2\text{O}$, CO, $\text{CO}_2$, $\text{NH}_3$, $\text{CH}_4$, $\text{CH}_3\text{OH}$
Formation of ice/dust grains in the ISM
Formation of ice/dust grains in the ISM
Cosmic dust grains

- Heat
- Atom bombardment
- UV irradiation
- Cosmic rays

Dust grains

- $\text{H}_2\text{O}$
- $\text{O}_2$
- $\text{CO}_2$
- $\text{CH}_4$
- $\text{CH}_3\text{OH}$
- $\text{CH}_3\text{NH}_2$
- $\text{CO}$
- $\text{OH}$
- $\text{H}$
Chemistry on the surface of interstellar ice analogues

- UV irradiation
- Heat
- Atom bombardment
- Cosmic rays

Molecules:
- $\text{H}_2\text{O}$
- $\text{CO}_2$
- $\text{CH}_4$
- $\text{CH}_3\text{OH}$
- $\text{NH}_3$
- $\text{OH}$
- $\text{H}$
- $\text{O}_2$
- $\text{CO}$
Huge number of studies from simple molecules to amino acids
Chemistry on the surface of interstellar ice analogues

Bernstein et al., Nature 2002

Munoz Caro et al., Nature 2002
Chemistry on the surface of interstellar grain analogues

- UV irradiation
- Heat
- Atom bombardment
- Cosmic rays

Dust grains

- H\(_2\)O
- CO\(_2\)
- CH\(_4\)
- CH\(_3\)OH
- CO
- NH\(_3\)
- OH
- O\(_2\)
Chemistry on the surface of interstellar grain analogues

- UV irradiation
- Heat
- Dust grains
- OH
- Atom bombardment
- Cosmic rays

Direct participation of dust molecules
Catalytic effects of the grains surface

Our Astro-Chemical History: Past, Present, and Future
Chemistry on the surface of interstellar grain analogues

Heat
Atom bombardment
UV irradiation
Cosmic rays

O₂
H₂O
O
OH
H
H₂O₂
CH₄
CO₂
CO
NH₃
O₂
UV irradiation
Heat
Dust grains
OH
Atom bombardment
Cosmic rays

Direct participation of dust molecules
Catalytic effects of the grains surface

Our Astro-Chemical History: Past, Present, and Future
Chemistry on the surface of interstellar grain analogues

A handful of works

$\text{CO}_2$ in $\text{H}_2\text{O}$ ice covering **hydrogenated carbon grains** by ion irradiation (Mennella et al., 2004)

$\text{CO}$ and $\text{CO}_2$ in $\text{H}_2\text{O}$ ice covering **hydrogenated carbon grains** by UV irradiation (Mennella et al., 2006)

$\text{CO}_2$ in $\text{O}_2$ ice covering **atomic carbon foil** by UV irradiation (Fulvio et al., 2012)

$\text{CO}_2$ in $\text{H}_2\text{O}$ ice covering **atomic carbon foil** by proton irradiation (Raut et al., 2012)

$\text{CO}$ and $\text{CO}_2$ in $\text{H}_2\text{O}$ ice covering **hydrogenated carbon grains** by proton irradiation (Sabri et al., 2015)

$\text{CO}$ and $\text{CO}_2$ in $\text{H}_2\text{O}$ ice covering **graphite films** by UV irradiation (Shi et al., 2015)
Chemistry on the surface of interstellar grain analogues

UV irradiation (Ly$\alpha$)

Cosmic rays (protons or ions)

Formation of CO and CO$_2$
Chemistry on the surface of interstellar grain analogues

Heat
Atom bombardment
UV irradiation
Cosmic rays

Dust grains

H₂O
O₂
OH
H
CO₂
NH₃
CO
CH₄
CH₃OH
Chemistry on the surface of interstellar grain analogues

Diffuse, translucent, and dense interstellar clouds
Our study

Atom bombardment (H + O)
Interstellar grain analogues in the laboratory

Ablation chamber  Particle beam  Deposition chamber
Interstellar grain analogues in the laboratory

Amorphous hydrogenated fullerene-like carbon grains

Grains on a substrate

TEM image

Our Astro-Chemical History: Past, Present, and Future
Atom bombardment (addition)

Dissociation yields - 15% and 40% for H$_2$ and O$_2$
Experimental details

Sample - fixed on a cryogenic polished copper mirror

High vacuum chamber with a base pressure of $10^{-9}$ mbar

Temperature of the mirror - 10 K

Bombardment – 30 minutes, final atom fluence $1.8 \times 10^{20}$ atoms cm$^{-2}$

IR spectra - transmission-reflection mode between 5000 and 500 cm$^{-1}$ with a resolution of 0.5 cm$^{-1}$ using a Bruker FTIR spectrometer
O addition: IR spectra at 10 K

(a) carbon grains
(b) after O bombardment of carbon grains
(c) difference spectrum
O/H addition: IR spectra at 10 K

(a) carbon grains
(b) after H bombardment of carbon grains
(c) after O/H bombardment of carbon grains ([O$_2$]/[H$_2$] = 1/60)
(d) after O/H bombardment of carbon grains ([O$_2$]/[H$_2$] = 10/70)
O/H addition: Difference IR spectra at 10 K

(a) after O/H bombardment of carbon grains ([O_2]/[H_2] = 1/60)
(b) after O/H bombardment of carbon grains ([O_2]/[H_2] = 10/70)
O/H addition: Difference IR spectra at 10 K

(a) after O/H bombardment of carbon grains ([O₂]/[H₂] = 1/60)
(b) after O/H bombardment of carbon grains ([O₂]/[H₂] = 10/70)
Grain surface chemistry

surface-C + O → surface-CO

CO + O → CO₂

CO + H → HCO + H → H₂CO

CO + H + H → H₂CO
Grain surface chemistry

- surface-C + O $\rightarrow$ surface-CO
- CO + O $\rightarrow$ CO$_2$
- CO + H $\rightarrow$ HCO + H $\rightarrow$ H$_2$CO
- CO + H + H $\rightarrow$ H$_2$CO

Not detected
Grain surface chemistry

A new route of molecules formation in the ISM: grain surface processes

Atom bombardment (H + O)
The next steps (two examples)

Methanol

H₂CO – H₃CO – CH₃OH

Methylamine

HCN – CH₂N – CH₃N – CH₃NH – CH₃NH₂

Glycine
Outlook: erosion of grains in cold environments through formation of volatile molecules

Conversion factors of C atoms of the grains:

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>CO₂</th>
<th>H₂CO</th>
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<tbody>
<tr>
<td>0.009</td>
<td>0.005</td>
<td>0.003</td>
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In total about 2% of grain C was converted into volatile species
Outlook: erosion of grains in cold environments

Molecular clouds

Debris disks

Surface chemistry (can be important)

UV photodesorption (typically considered)
Thank you very much for your attention