The Origins and Evolution of Molecules in Icy Solids

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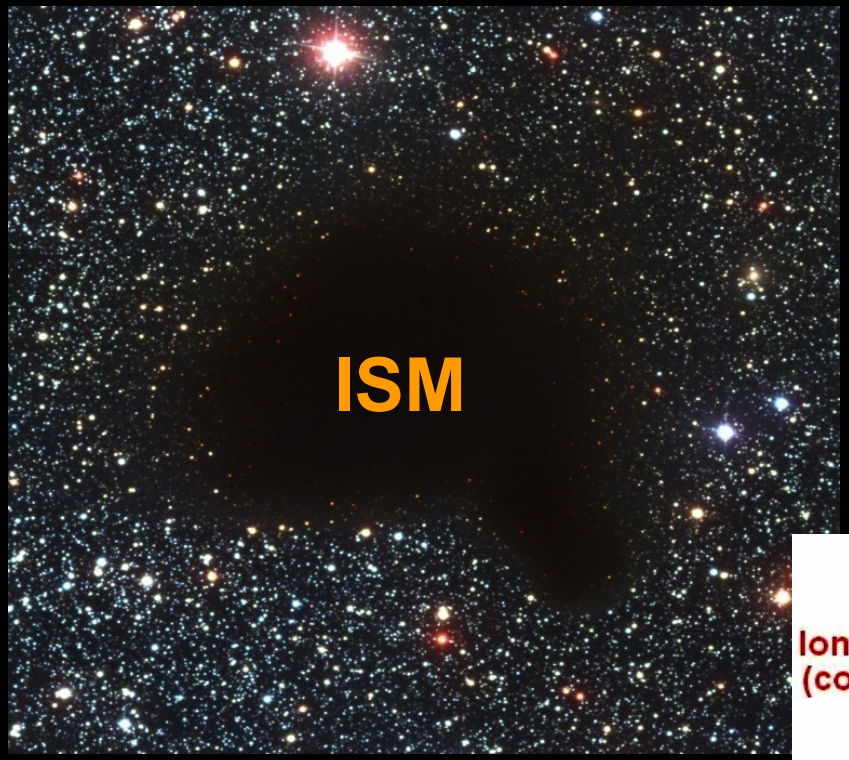
October 27, 2010

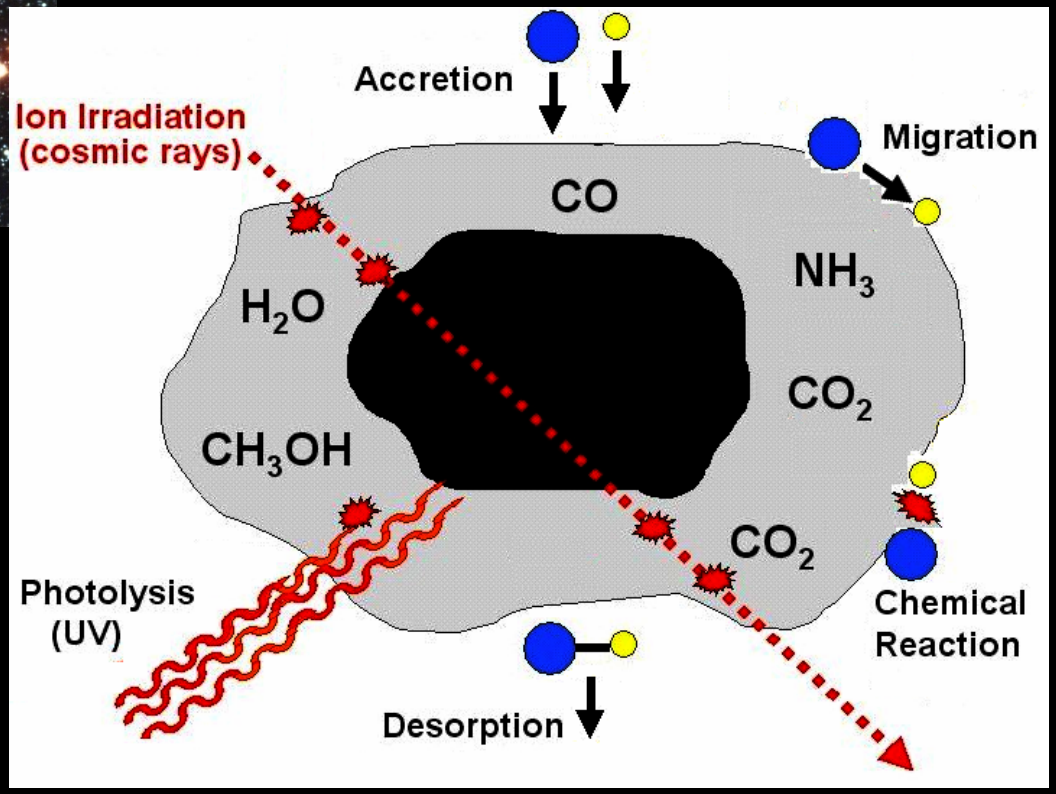
Molecular Ices … Grain Mantles



0.1 μm T ~ 10 K

H_2O	CO	CO_2
OCN^-	NH_3	OCS
CH_3OH	CH_4	SO_2

… and others

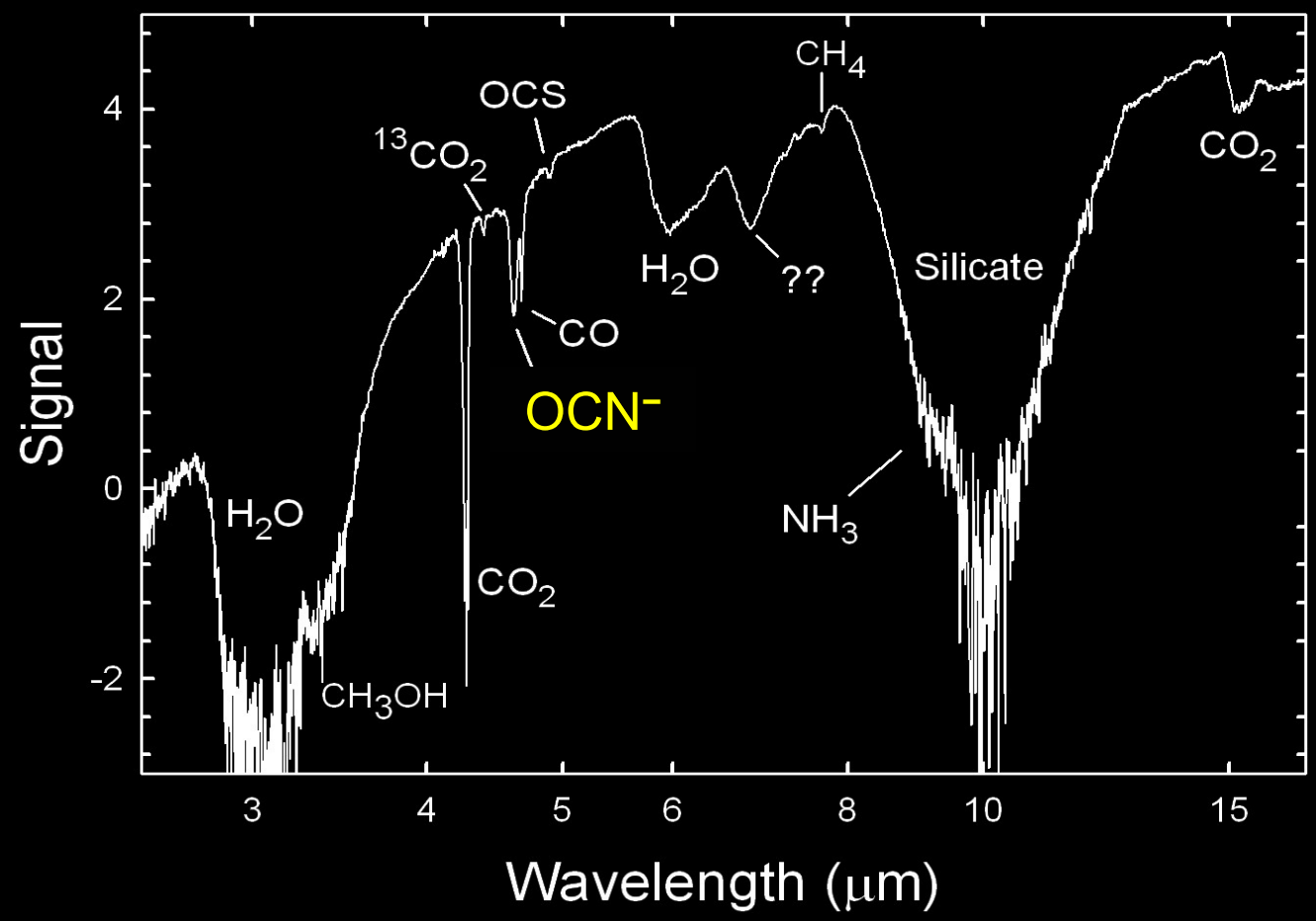


Some Molecular Abundances

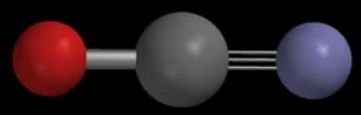
Molecule	IRS 9 Ices	Comet Coma Hale-Bopp
H_2O	= 100	= 100
CO	16	20
CO_2	22	6 -20
CH_3OH	5	2.4
H_2CO	~4	1.1
CH_4	2	1.5
C_2H_2	---	~0.2
C_2H_6	---	~0.6
NH_3	13	0.7 - 1.8

An Interstellar Ice Spectrum
(and a 20-Year Controversy)

W33A Infrared Space Observatory (ISO)



RNCO
ROCN
RNC
RCN
and more



OCN^-
cyanate
anion

ApJ, 2001, Hudson et al.

Some Lab Tasks – Ice Chemistry

Reaction pathways ⟶ **Observed molecules** ⟶ **Unobserved molecules**

Explanation **Prediction**

Reaction products and reaction pathways

Formation rates and yields

Destruction rates in ices

Some Tools and Approaches

Spectra: IR (etc.) Mass Spectrometry

Chromatography

Computational Chemistry

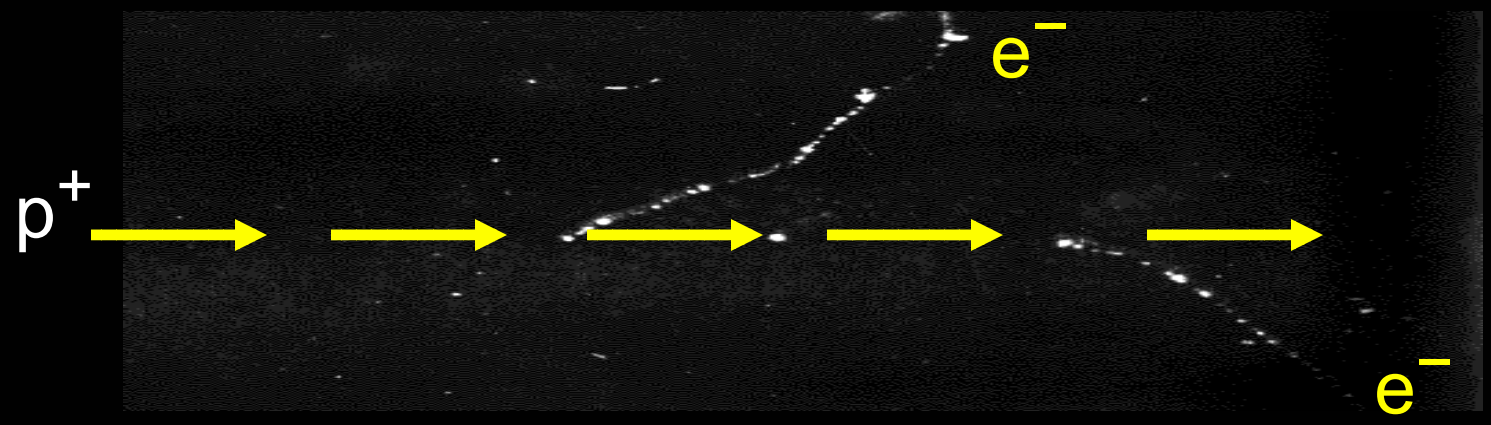
Thermal Chemistry

Radiation Chemistry vs. Photochemistry

Radiation Chemistry of Ice

$$H_2O \xrightarrow{cr} H_2O^+ + e^-$$

$$H_2O^+ + H_2O \longrightarrow OH + H_3O^+$$



~10^4

~10 eV

$$H_3O^+ + e^- \longrightarrow H + H_2O$$

Overall	$H_2O \longrightarrow H + OH$

Radiation Chemistry

Generates reactive species

Generates secondary electrons (~ 10 eV)

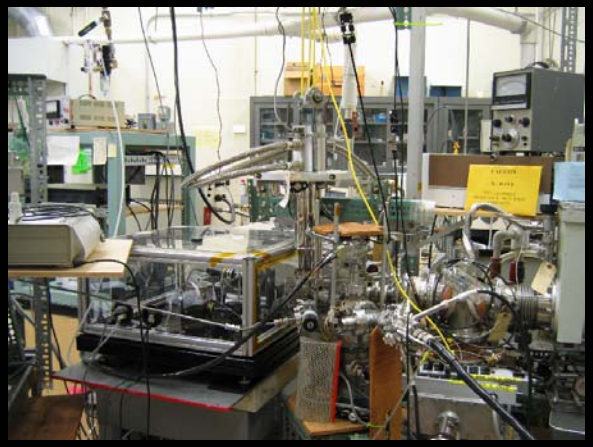
Far-UV Photochemistry

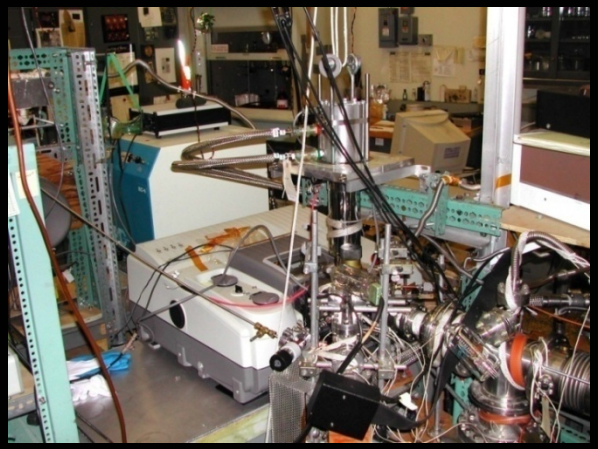
Lowering of ioniz. energy

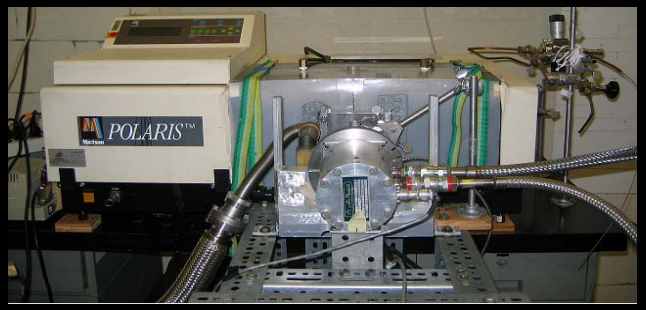
$$\mathrm{PAH} \xrightarrow{H_2O} \mathrm{PAH}^+ + e^-$$

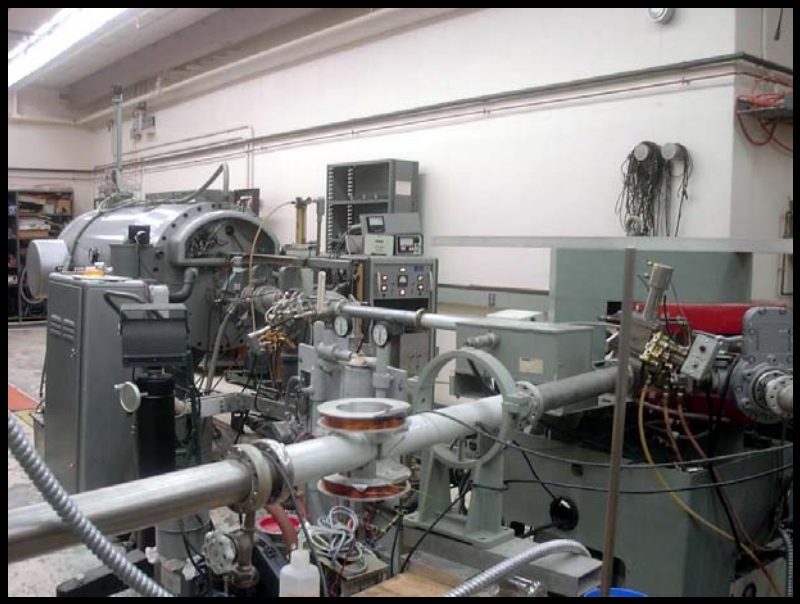
Gudipati and Allamandola, *Ap. J.*, 2003, 2004, 2006

We're equipment intensive!

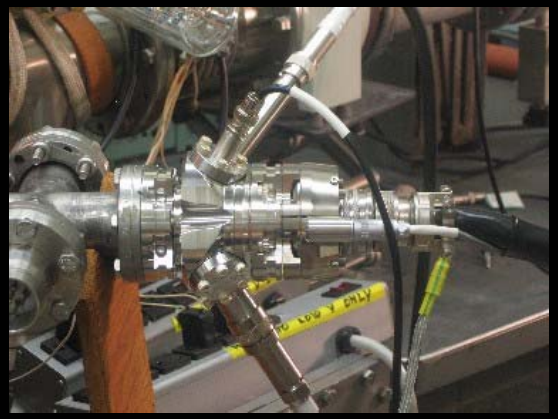


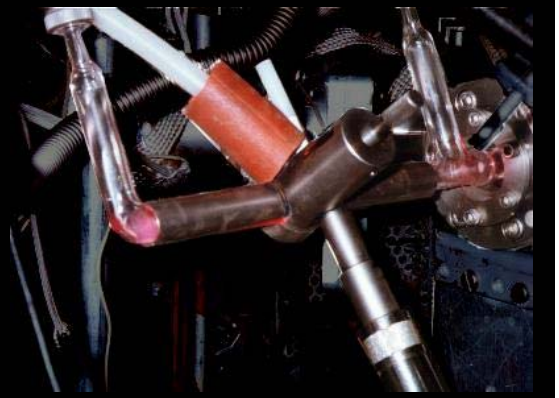






1 MeV
p^+





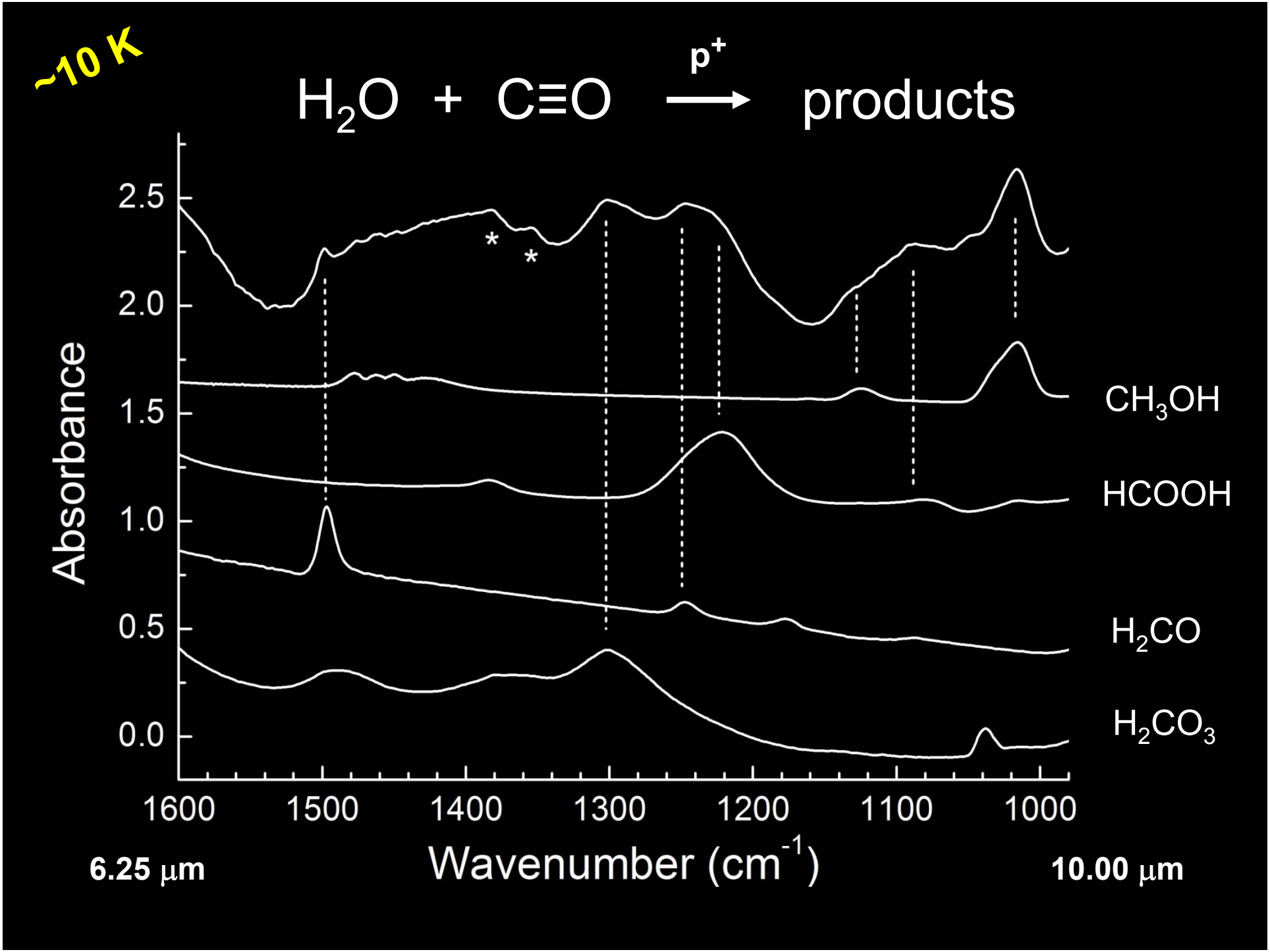
An Example: C≡X Bonds are Reduced in Irradiated H_2O-Rich Ices

$$C{\equiv}O \rightarrow H_2C{=}O \rightarrow H_3C\text{-}OH$$

$$HC{\equiv}CH \rightarrow H_2C{=}CH_2 \rightarrow H_3C\text{-}CH_3$$

$$CH_3\text{-}C{\equiv}N \rightarrow CH_3\text{-}CH{=}NH \rightarrow CH_3\text{-}CH_2\text{-}NH_2$$

Hudson & Moore, *Icarus*, 1997 through
Hudson et al., *Astrobiology*, 2008 and Hudson et al., *IAU Proc*., 2009


~10 K
H_2O + C≡O $\xrightarrow{p^+}$ products
Absorbance
2.5
2.0
1.5
1.0
0.5
0.0
*
*
CH_3OH
HCOOH
H_2CO
H_2CO_3
1600
1500
1400
1300
1200
1100
1000
6.25 μm
Wavenumber (cm^{-1})
10.00 μm

~10 K

Reactions in Irradiated H_2O + CO Ices

$$H_2O \xrightarrow[\sim 10\ K]{p^+} H + OH$$

$$C{\equiv}O \xrightarrow[\sim 10\ K]{H} HCO \xrightarrow{H} H_2CO \xrightarrow{H} [H_3CO] \xrightarrow{H} CH_3OH$$

Methanol

$$HCO \xrightarrow{OH} HCOOH$$

Formic Acid

$$HCOOH \rightarrow H_3O^+ + HCOO^-$$

Formate anion

$$C{\equiv}O \xrightarrow{OH} CO_2 \xrightarrow[\sim 10\ K]{p^+} H_2CO_3$$

Carbonic Acid

See ISO spectrum of W33A

~10 K

Reactions in Irradiated $H_2O + C_2H_2$ Ices

$$H_2O \xrightarrow[\sim 10\ K]{p^+} H + OH$$

$$HC{\equiv}CH \xrightarrow[\sim 10\ K]{H} [C_2H_3] \xrightarrow{H} C_2H_4 \xrightarrow{H} [C_2H_5] \xrightarrow{H} C_2H_6$$

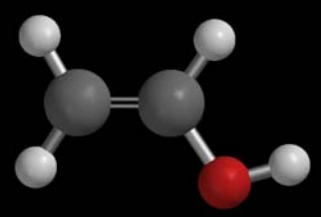
$$[C_2H_3] \xrightarrow{OH} CH_2CH(OH)$$

$$CH_2CH(OH) \rightarrow CH_3C(O)H$$

Acetaldehyde

$$[C_2H_5] \xrightarrow{OH} CH_3CH_2OH$$

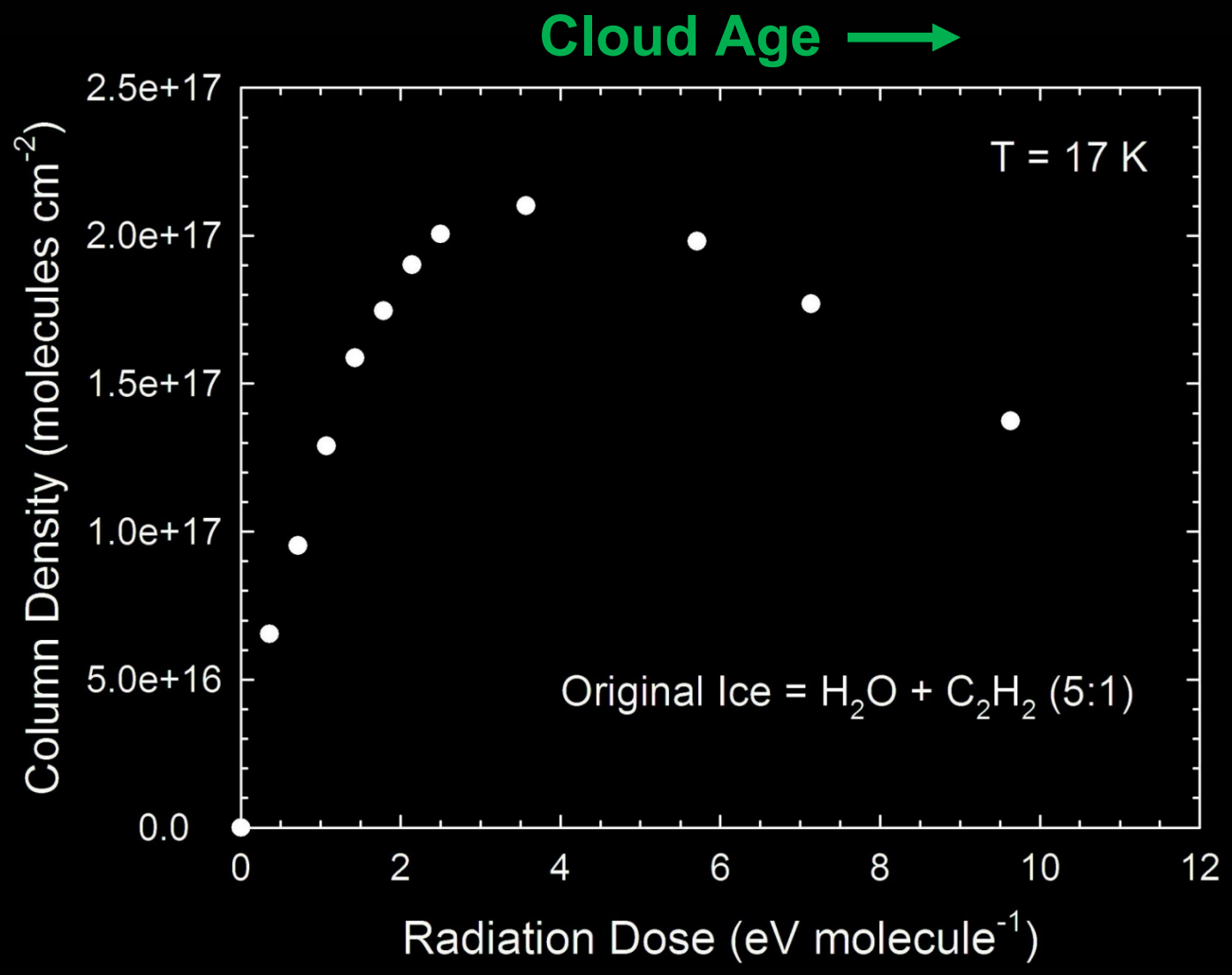
Ethanol



Vinyl Alcohol

For photochemistry see Wu et al. Icarus (2002)

Vinyl Alcohol – Formation and Destruction



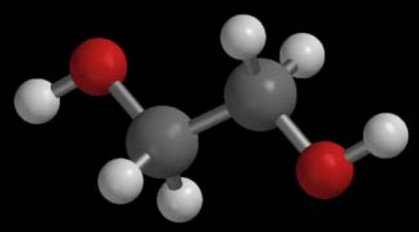
Hudson & Moore, *ApJL*, 2003

A Different Reaction: Dimerization

$$H_2O \xrightarrow{p^+} H + \bullet OH \qquad H_2O_2$$

$$CH_3OH \xrightarrow{p^+} H + \bullet CH_2OH$$

Methanol



$$C_2H_4(OH)_2$$

Ethylene Glycol

Prediction

Hudson & Moore, *Icarus*, 2000

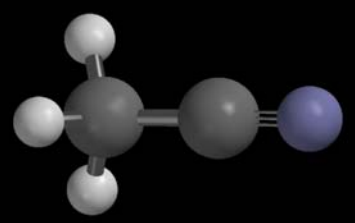
Confirmation

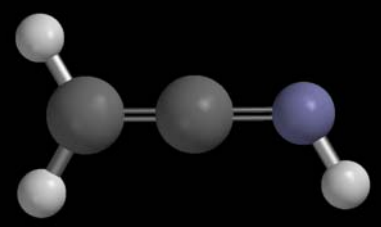
2002 - ISM in 2002
2004 - Hale-Bopp

A Third Example – Isomerization

$$H_3C\text{-}C{\equiv}N \xrightarrow{p^+} H_2C{=}C{=}NH$$

ketenimine





Prediction

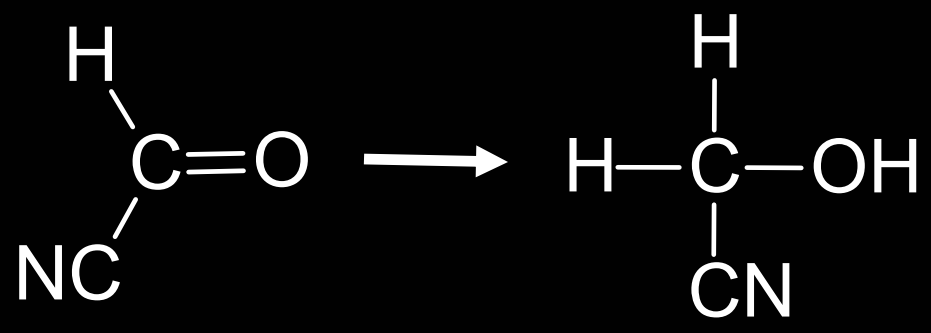
Hudson & Moore, *Icarus*, 2004

Confirmation

2006 - ISM

Can Make New Lab-Based Predictions

Reduction

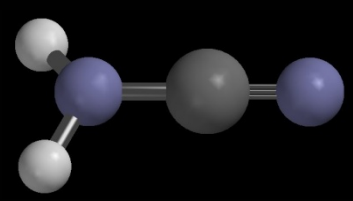


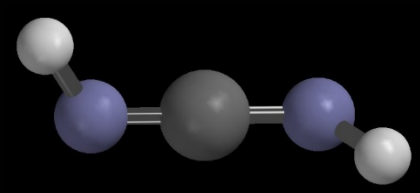
Dimerization

$CH_3CN \longrightarrow (CN)H_2C\text{-}CH_2(CN)$

Isomerization

$H_2N\text{-}C{\equiv}N \longrightarrow HN{=}C{=}NH$



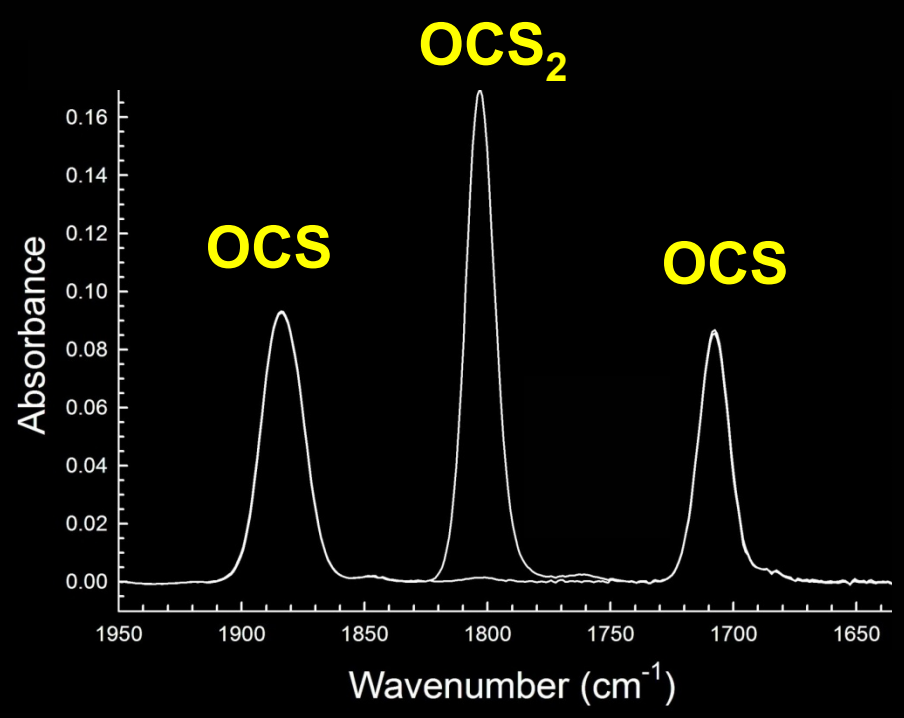


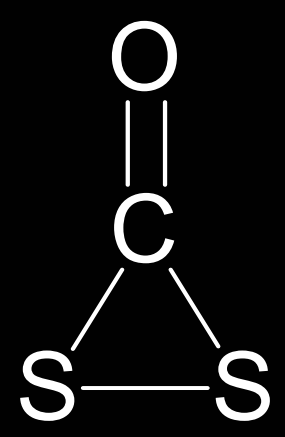
Atom Capture – An Icy Path to "Dark Matter"

$$CO \xrightarrow{S} OCS \xrightarrow{S} OCS_2 \longrightarrow O + CS_2$$

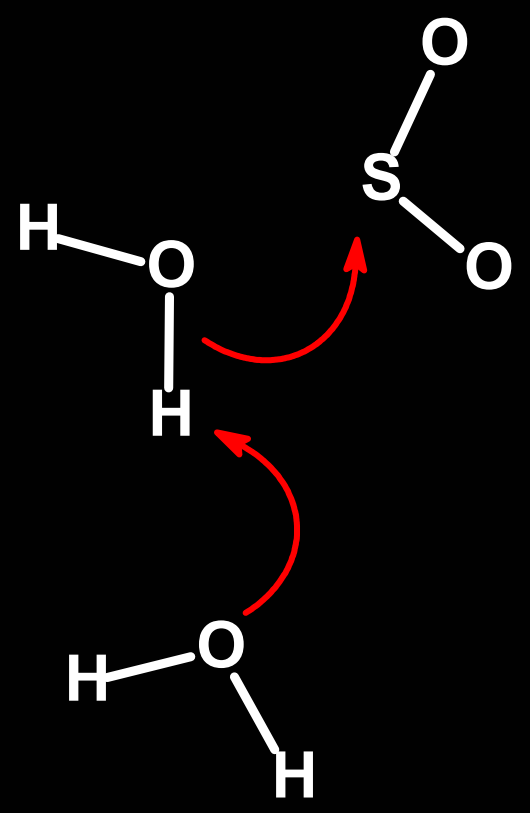
dithiiranone

~ 6%





Ferrante et al., *ApJ*, 2008



Thermal Chemistry

$H_2O + SO_2$ at 50 K

$$H_3O^+ + HOSO_2^-$$

hydronium bisulfite

Loeffler & Hudson
Geophys. Res. Lett., 2010

Solid-phase sulfurous thermal chemistry …

… that can destroy interstellar SO_2 ice !

Many Reaction Types Occur in Ices!

Reductions and oxidations

Dimerizations and isomerizations

Atom capture

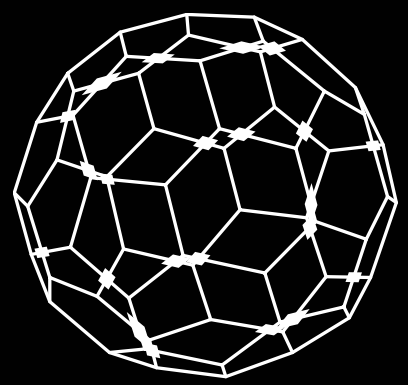
Molecular elimination

Radical-radical couplings

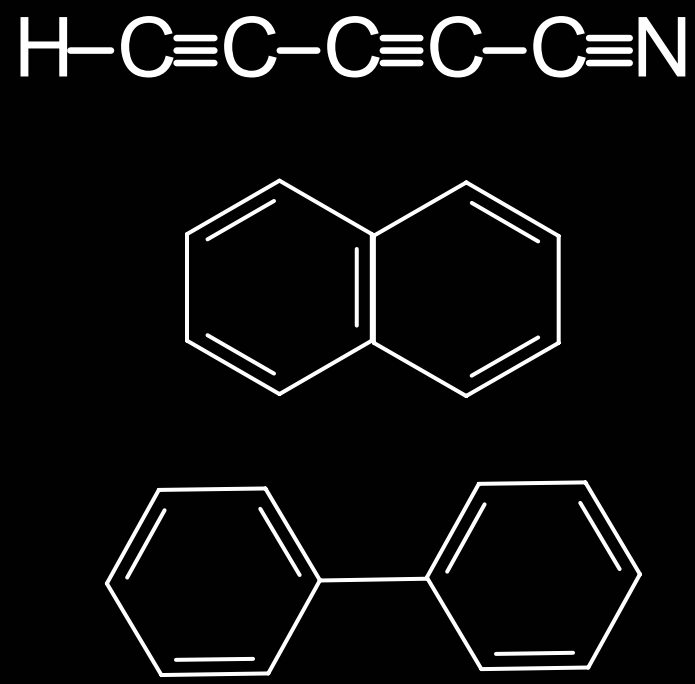
Proton transfer (acid-base)

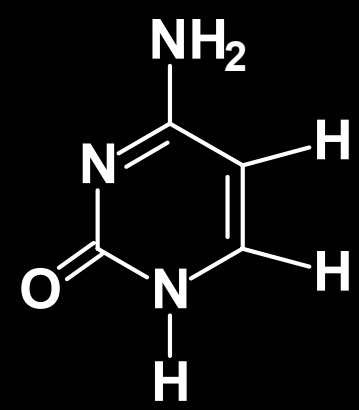
A Persistent Difficulty – Big Molecules

Hard to make in realistic ice analogs



C_{60}





… but fairly easy to modify … Nuevo et al. (2009)

Some Lab Needs for Ice Astrochemistry

Better quantification … reaction rates & yields

Competition studies … multi-component ices

Quantitative comparisons (p^+, UV, e^-, atoms)

Ejection mechanisms from ices (comparisons)

Explicit waters in comp. models (DFT, etc.)

Isotopic enrichments / depletions / exchanges possible ?

New analyical methods: ESR? Raman? Fluorescence

Some Benefits for Astrophysics

Chemistry happens in ices (but now always as desired)

The field is reasonably mature (as are some practitioners)

Can help reveal conditions along a line of sight

Can suggest some molecules for searches

Electronic databases (a few)

Solar system and astrobiological connections

Acknowledgments and Thanks

Financial support from NASA programs

- Planetary Geology and Geophysics
- Planetary Atmospheres
- Outer Planets Research
- Cassini Data Analysis
- Mars Fundamental Research
- NASA Astrobiology Institute
- Exobiology
- APRA (of course)