

Introduction to Astrochemistry **Part 3**: Interstellar Dust and Evolved Stars

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Observatory (NRAO)

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National
 Radio
 Astronomy
 Observatory



Astrochemistry is an interdisciplinary field! Including, chemistry, physics, astronomy, biology, etc.,

242.0



Submillimeter and Millimeter Radio Telescopes Identify Molecules via <u>Rotational Spectroscopy</u>!



1) ELECTRONIC STATES

- electrons change levels
- energies in visible, UV

2) VIBRATIONAL STATES

- normal modes of nuclear motions
- occur in infrared region

3) ROTATIONAL STATES

- end-on-end motion of nuclei
- energies in microwave/millimeter-wave regions
- Electronic states have vibrational/rotational structure
- Vibrational states have rotational structure









Molecule Formation (in Molecular Clouds)



- Typical Conditions in molecular gas:
 - low Densities (10 10^7 cm^{-3} ; < 10^{-12} torr)
 - compared to Earth atmosphere ($\sim 10^{19}$ cm⁻³)
 - low Temperatures: T ~ 10 100 K
- \rightarrow Severely restricts allowed chemical processes!
 - only two body collisions
 - reactions must be **exothermic!**

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Basic Chemical Scheme:

1) H_2 formed on grain surfaces: $H + H + \text{grain} \rightarrow H_2 + \text{grain}$

2) Gas-phase reactions initiated by cosmic rays (photons, γ) and proceed via ion-molecule reactions

```
\begin{array}{l} H_2 + \gamma \rightarrow H_2^+ + e + \gamma' \\ H_2^+ + H_2 \rightarrow H_3^+ + H \\ H_3^+ + CO \rightarrow HCO^+ + H \\ H_3^+ + N_2 \rightarrow N_2H^+ + H \\ etc. \end{array}
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Starless core L1498 → CO frozen out on grains thus less HCO⁺



Tafalla 2006



11

- Organic chemistry on interstellar grains resulting from cold H addition reactions to CO

- Broken arrows indicate reactions with activation energy barriers

- Where 2H is shown, a barrier penetration reaction followed by exothermic addition

 Molecules in blue detected in star-forming molecular clouds!







Evolved Stars - the end stage of star formation



Evolved Stars - the end stage of star formation

- **IMPORTANT** in astrochemistry because material is cycled back to the ISM!
- Mass loss from evolved stars

 \Rightarrow Supplies 85% of material in ISM

Material cycled in

circumstellar shells of low-mass giants

- Remainder from Supernoave and Wolf-Rayet Stars
- Material ends up in diffuse clouds
- Collapse to form dense clouds
- Important in evaluating
 - \Rightarrow Composition of ISM
 - \Rightarrow Galactic Chemical Evolution





Evolved Stars - the end stage of star formation!

+ Dust Formation!

• **IMPORTANT** in astrochemistry because material is cycled back to the ISM!

- Mass loss from evolved stars
 - \Rightarrow Supplies 85% of material in ISM
- Material cycled in

• Shell is COOL; *Dust grains form*

circumstellar shells





* Universe 99% gas (mostly hydrogen), 1% dust (by mass)

Evolved Stars - the end stage of star formation!



+ Dust Formation!





Pristine presolar SiC grains from the Murchison meteorite (Bernatowicz et al. 2003)

Evolved Stars - the end stage of star formation! + Dust Formation!

Oxide dust Carbonaceous dust Other amorphous silicates (I,C,S) PAHs (I,C,S) silicon nitride Si_3N_4 (S) Fullerene, C_{60} (C,I) crystalline forsterite, Mg_2SiO_4 (C,S) magnesium sulfide, MgS (C) crystalline enstatite ($MgSiO_3$) (C,S) Amorphous Carbon (C,I,S) Carbonate (C,I) Ice (C,I)Silica, SiO_2 (C) Graphite (C,I,S)Diamond (C,S) aluminum oxide, Al_2O_3 (C,S) spinel, $MgAl_2O_4$ (C,S) silicon carbide, SiC (C,I ?,S) titanium oxide, TiO_2 (S) other carbides (C?, S) hibonite, $CaAl_{12}O_{19}$ (S) Magnesium iron oxide, $Mg_{0.1}Fe_{0.9}O$ (C)

 Table 1. Inventory of dust in space





Legend: I: Spectroscopic evidence for presence in interstellar dust. C: Spectroscopic evidence for presence in circumstellar dust. S: Present as stardust in meteoritic or cometary material (For a a discussion, see Tielens 2001, Zinner 2003).

Tielens 2011

Dust grains in meteorites directly linked to the dust grains created during stellar deaths!



Evolved Stars - the end stage of star formation!



Dust grains in meteorites directly linked to the dust grains created during stellar deaths!

Evolved Stars provide the material that enrich the later stages of star and planet formation!



Chemistry in Evolved Stars - lifecycle and mass loss is key!

- **Mass loss** starts due to convection, shock waves
- Radiation pressure on grains
- Usually associated with **helium-burning phases** in evolved (old) stars
- Stars with highest mass loss
 (M ~ 10⁻⁶ 10⁻⁴ M_☉/yr)
 ⇒ Asymptotic Giant Branch
 - (AGB) Stars (low mass)
- ⇒ Red Supergiants (RSG) and Yellow Hypergiants (high mass; rare!)



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AGB (1 - 8 M_{\odot})

- H, He-burning shells around a carbon core
- He-shell creates instabilities
- Convective mixing or dredge-up
- can undergo "third dredge-up"
 ⇒ mixes carbon form CNO cycle
- to surface such that C > O



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 to surface such that C > O
- Nucleosynthesis: makes star and envelope:

O > C or C > O

Carbon-rich or oxygen-rich

- Stars start with O ~ 0.5 C (ISM ratio)
- Third-dredge up on the AGB: ${}^{4}\text{He} \rightarrow {}^{12}\text{C}$
- Creates a carbon star with C \sim 0.5 O





Dust Grains born from material ejected in stars!



Credit: Hope Ishii, University of Hawai'i.

Olofsson 2011



Olofsson 2011

What does this mean for molecule formation? We know that where there is dust, molecules are likely form!!

"Famous" case: Carbon-rich star IRC+10216 !

(Also known as CW Leonis)



Source Source # # $\mathbf{2}$ Sgr B2 69 L1527 TMC-1 57L1544 $\mathbf{2}$ IRC+10216 NGC 2024 55 $\mathbf{2}$ LOS Cloud 42NGC 7023 $\mathbf{2}$ Orion NGC 7027 24 $\mathbf{2}$ L483TC 1 $\mathbf{2}$ 9 W518 W49 $\mathbf{2}$ VY Ca Maj CRL 2688 6 B1-b Crab Nebula 4 DR 21 DR 21(OH) 4 **IRAS 16293** Galactic Center 4 NGC 6334 IC 443G 4 Sgr A 4 K3-50 CRL 618 L134 3 G+0.693-0.0273 L183 NGC 2264 3 Lupus-1A W3(OH)3 M17SW rho Oph A 3 NGC 7538 Orion Bar Horsehead PDR $\mathbf{2}$

of molecule discoveries per source

"Famous" case: Carbon-rich star IRC+10216 !



Outer Shell Circumstellar Chemistry!

- Neutral-neutral reactions with free radicals
- \bullet n ${\sim}10^5~\text{cm}^{\text{-3}}$ and lower with T ${\sim}~25~\text{K}$
- Penetration of UV photons from ambient star light
- Formation of radicals and some ions
- Photodissociation "long carbon-chain formation"

$$\label{eq:hcn} \begin{split} \mathsf{HCN} + \mathsf{hv} &\to \mathsf{CN} + \mathsf{H} \\ \mathsf{HCCH} + \mathsf{hv} &\to \mathsf{CCH} + \mathsf{H} \end{split}$$

CN and CCH then react with other neutral species building multi-carbon chains!

 $\mathsf{CN} + \mathsf{HCCH} \to \mathbf{HC_3N} + \mathsf{H}$

Credit: L. Ziurys $_{_{29}}$



CO J=2-1





IRAM 30m Radio Telescope, Granada, Spain



ALMA interferometer

'Zooming in' with higher resolution and more sensitive telescope → Many 'U' lines, which are 'unidentified' !

Cernicharo et al., 2013

"Famous" case: Carbon-rich star IRC+10216 !

Molecular Maps:

Freeze-out and Photochemistry in action

- Maps of "parent" and "daughter"
 molecules in envelope of IRC+10216 →
- **HCN** the parent
- Photodissociation produces **CN**
- CN reacts to form C_3N , HC_3N , etc.
 - e.g., $HCN + hv \rightarrow CN + H$ $HCCH + hv \rightarrow CCH + H$ $CN + HCCH \rightarrow HC_3N + H$



More recent observations show other carbon-rich stars show similar structure!



Unnikrishnan 2023

"Famous" case: Carbon-rich star IRC+10216 !

But! Warm HC₃N shows a more compact distribution!

- Implication: photochemistry is occurring more rapidly in warmer layers
- A solar-like companion (binary) emitting UV photons in the inner wind is likely driving the photochemistry

Contours: $HC_3N J = 28-27$ Colormap: ¹³CO J=3-2



Known Binary: Carbon-rich star V Hydrae



- V Hydrae has been caught in the process of shedding its atmosphere in a series of expanding and outflowing rings
- First time these outflowing rings are seen during this end stage of stellar evolution!
- V Hydrae also is known to produce high-speed, intermittent jets of material!
- These extreme-scale plasma eruptions happen roughly every 8.5 years and the presence of a nearly invisible companion star





Siebert et al., 2024 (in review)



Known Binary: Carbon-rich star V Hydrae



Compact emission of CCH and the complex organic molecule (COM) CH₃CN - increased photochemistry from the binary?



Siebert et al., 2024 (in review)

Red Supergiant Phase (M ~ 10 - 30 $M_{\odot})$

- Similar to Red Giants, but larger
- Ignite helium in core-burning
- So massive, can ignite other elements
- Multiple burning shells in C, O, etc
- evolve to **supernova**



Red Supergiant Phase (M ~ 10 - 30 $M_{\odot})$

- Similar to Red Giants, but larger
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- Multiple burning shells in C, O, etc
- evolve to **supernova**

Massive Supergiant stars (~ 40 $M_{\odot})$

- Undergo *more violent mass loss*
- Create huge circumstellar envelopes
- Shocks, convective cells bursting through atmosphere
- Supergiant stars: oxygen-rich!



Oxygen-rich Supergiant star VY Canis Majoris



of molecule discoveries per source

Source	#	Source	#
Sgr B2	69	L1527	2
TMC-1	57	L1544	2
$\operatorname{IRC}+10216$	55	NGC 2024	2
LOS Cloud	42	NGC 7023	2
Orion	24	NGC 7027	2
L483	9	TC 1	2
W51	8	W49	2
VY Ca Maj	6	CRL 2688	1
B1-b	4	Crab Nebula	1
DR 21	4	DR 21(OH)	1
IRAS 16293	4	Galactic Center	1
NGC 6334	4	IC 443G	1
Sgr A	4	K3-50	1
CRL 618	3	L134	1
G + 0.693 - 0.027	3	L183	1
NGC 2264	3	Lupus-1A	1
W3(OH)	3	M17SW	1
rho Oph A	3	NGC 7538	1
Horsehead PDR	2	Orion Bar	1



Oxygen-rich Supergiant star VY Canis Majoris





C-rich vs. O-rich



• IRC+10216 Spectrum dominated by C₄H, HCN

C-rich vs. O-rich

Both objects overall **very** line rich!









Phosphorous in Evolved Stars

Metals in Evolved Stars

- Metals typically found in molecular form:
 Al, Mg, Na, K, Fe
- In C-rich envelopes
 - \Rightarrow Cyanides, Halides
- Now in O-rich Envelopes

 \Rightarrow Oxides, Hydroxides

- First definitive detections
- of **Fe and Ti –bearing** species
 - \Rightarrow MgCN species most common



Detection of TiO and TiO₂! VY CMa -40 -20 20 -60 0 40 60 80 100 PdBI TiO 0.8 SMA 0.6 -0.2 PdBI TiO₂ 0.8 SMA 0.6 0.4

NaCl

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SO₂

-40

-20

0

20

 $V_{LSR} (km s^{-1})$

40

60

0.8 0.6

0.4 0.2

-0.2

0.8 0.6 0.4 0.2

-0.2

-60



Kaminski et al., 2013



100

80

- Final stage in life cycle of most stars (~1-8 M_☉)
- Follows (AGB) phase w/ molecule-rich circumstellar shells
- Mass Loss continues into PNe phase!
- Nucleosynthesis ceases
- Central Star exposed: Hot UV-emitting white dwarf with mass ~ 0.5 $\,\,\text{M}_{\odot}$
- Remnant AGB shell flows far from star
 ⇒ becomes highly ionized
- T_{star} ~ 100,000 K.
- Timescales: 10,000 12,000 yrs



- Material cycled through PNe phase
 - \Rightarrow 83% of interstellar material
- Material ends up in diffuse clouds
- Collapse to form dense clouds
- Evaluating PNe ejecta crucial
 - \Rightarrow Composition of ISM
 - \Rightarrow Galactic Chemical Evolution
- PNe traced by highly excited atomic lines
 - \bullet [O III], [OII], CII, Ne II, He II, and [N II]
- Can molecules exist here?



Yes, there should be MOLECULES!

- UV radiation from central star intense
- Some photochemistry occurs
- Theory/Models predicts overall molecular content
 - \Rightarrow steadily decreases with time
 - \Rightarrow early increase due to photochemistry
- By 10,000 years, molecular abundance drops



Figure 3. Clump (solid lines) and interclump (dashed lines) abundances for C_2H_2 (uppermost solid line) and C_4H_2 . The time is measured in years and the fractional abundance is with respect to the total number of hydrogen atoms.



Young PN: **~ 700 years old** T_{star} ~ 200,000 K

Molecular Content: CO, CN, HCN, HCO⁺, N₂H⁺, CCH, C₃H₂, HC₃N, OH, CH, CH⁺







• Age: 12,000 yrs

- Extended spatial distribution > 1,000"
- Highly ionized atomic gas (e.g. O'Dell et al. 2004, Meaburn et al. 2005)
- Lines of H I, [S II], [N II], C I, and [O I]
- H₂ and CO also detected
- Coincident with ionized gas
- One position: rich molecular content:
- Bachiller et al. (1997): HCN, HNC, HCO⁺, CN
- Tenenbaum et al. (2009): C₂H, c-C₃H₂, H₂CO
- Look at the molecular content globally....

Oldest Known Planetary Nebula: The Helix





 $n(H_2) \sim 0.3 - 8 \times 10^5 \text{ cm}^{-3}$

- $T_{K} \sim 20 45 \text{ K}$
- Mapped $J = 1 \rightarrow 0$ transition of HCO⁺

across entire nebula

- First time for old PNe
- Found at most positions
- HCO⁺ emission follows optical atomic image
- $HCO^+/H_2 \sim 10^{-8}$



Dec Offset (Arcsec)

Oldest Known Planetary Nebula: The Helix



R. A. Offset (arcsec)

Zeigler et al., 2013

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Bublitz et al., 2022

Oldest Known Planetary Nebula: The Helix

• HCO⁺ across Helix \rightarrow X-ray

irradiation in outer regions where
photodissociation is limited and cold
gas and ionized molecules abundant
increase of HNC/HCN ratio with
radial distance – indicate dependence
not only on UV irradiation but gas
pressure and density

Chemistry depends on environment and physical properties of the gas!

Chemistry in **Planetary Nebula** – Observations vs. Models



Molecule

abundances stay

constant with age

Not destroyed by

Photodissociation

• Survive in dense clumps! with $n(H_2) \sim 10^6 \text{ cm}^{-3}$

 Molecular clumps ejected into diffuse ISM

• Preserve C-enrichment

Planetary Nebula connection to **Diffuse Clouds**

• Planetary Nebulae disperse into

diffuse ISM

• Molecular gas entering diffuse ISM in

clumps

• Evidence from Observations of

Diffuse Clouds

• Diffuse Clouds and Planetary

Nebulae similar set of **molecules**



Diffuse Clouds

H₂CO HCN







	Molecule	Older PNe	Diffuse Clouds ^{a)}	
	H ₂ CO	0.3 -1 x10 ⁻⁷	4 x 10 ⁻⁹	
	C ₂ H	1 x10 ⁻⁶	3 x10 ⁻⁸	
	$c-C_3H_2$	1 x 10 ⁻⁸	1 x10 ⁻⁹	
	CO	0.5 - 9 x 10 ⁻⁴	3 x10 ⁻⁶	
	CN	3 x 10 ⁻⁶	2 x10 ⁻⁸	
	HCN	5 x 10 ⁻⁷	3 x10 ⁻⁹	
	HNC	3 x10 ⁻⁷	6 x10 ⁻¹⁰	
\rightarrow	HCO+	0.1 - 5 x10 ⁻⁸	2 x10 ⁻⁹	
	SO	0.2 – 2 x 10 ⁻⁷	8 x 10 ⁻¹⁰	
	CS	2.8 x 10 ⁻⁸	1 x 10 ⁻⁹	

Molecular Abundances -

Credit: L. Ziurys

a) Liszt et al. 2006

Diffuse Clouds – Definition and Chemical Makeup

- Lack a Definite Morphology
- Semi-transparent in the visible (A $_v \sim 1$)
- Total hydrogen column density: N ~ 10^{21} cm⁻²
- Readily penetrated by UV radiation



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- Lack a Definite Morphology
- Semi-transparent in the visible (A $_{\rm v}\sim$ 1)
- Total hydrogen column density: N ~ 10^{21} cm⁻²
- Readily penetrated by UV radiation

- Best traced by **21 cm H I line**
- T_k ~ 100 K
 - n ~ 1 100 particles/cm³ ($H^0 + H_2$)
 - $x_e \sim 10^{-3}$ (Fractional ionization)



Reminder! Typical Conditions of Molecular Clouds: T ~ 10 – 50 K; n ~ 10³ – 10⁶ cm⁻³

F = 1

Diffuse Clouds – Definition and Chemical Makeup

- Densities low: No radio/mm emission lines
- Not sufficient density for collisional excitation
- Molecules observed in ABSORPTION
- Common molecules observed

OH, H_2 (HD), CH, C_2 , CH⁺, NH, CO, H_3^+



*line of sight to the blazar/radio-continuum source







SUMMARY:

- Reminder! Submillimeter and millimeter radio telescopes are powerful instruments that let observational astrochemists (like myself) study the rotational spectra of interstellar molecules in high detail!
- Cold molecular clouds are the birthplaces of stars and planets. Within molecular clouds, H₂ forms on the surfaces of interstellar dust grains and is released into the gas – this is the start of chemistry in the interstellar medium!



- Dust grains are formed in the circumstellar shells of evolved stars, specifically AGBs! Dust and molecular gas
 is transported outward in winds, enriching the interstellar medium! Mass loss from Evolved stars supplies
 ~85% of the material in the ISM!
- **Evolved stars show a rich chemistry** in the submillimeter and millimeter spectrum, which is regulated by photochemistry (photon chemistry) from the central star.
- In the **planetary nebula phase molecule abundances stay consistent with age**, and thus are not destroyed by photodissociation! These molecules enrich the surrounding **diffuse** gas and eventually the dense gas that goes on to form stars and planets!





