Molecules in planetary nebulae

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Outline

• Introduction

• Gas-phase molecules in planetary nebulae

• Aromatic/aliphatic materials

• $C_{60}$ and fullerene-related compounds
Introduction:

**Proto-planetary nebula**

- PNe contain key information for the material recycling between the star and ISM.

Dust and various molecules are formed.

Nucleosynthesis products are dredged-up from stellar interior to surface, and are ejected into space.

Expanding into the ISM

Further processed by UV radiation.

Material lifecycle:

- PN: $10^4$ yr
- PPN: $10^3$ yr
- AGB: $10^6$ yr

PNe contain key information for the material recycling between the star and ISM.
Circumstellar chemistry (AGB)

C/O:
- 3rd dredge-up
- HBB

Chemical drivers:
- Interstellar UV radiation fields:
  - induce ion-neutral chemistry 😋
- Shocks:
  - endothermic reactions 😊
  - sputter and shatter dust 😋😊
  - dissociate molecules 😒
- Dust grains:
  - Induce grain surface reactions 😊
  - shield UV radiation field 😎

Dust formation

Low-density regions (~30K; 10^5 cm^-3)

Interstellar UV radiation

C/O:
- C/O < 1
  - CO, H_2O, SiO, OH...
- C/O < 1
  - Silicates...
- C/O > 1
  - C/O > 1
  - SiC...

Dense regions

Parent molecules

C/O > 1
- CO, C_2H, HCN, CN...

Daughter molecules

stellar wind acceleration
Circumstellar envelope at the PN stage

Dust and molecular envelope; AGB remnant

Contaminate the ISM

Hostile environments:
- Photo-dissociation (increasing radiation field);
- Dissociative recombination (abundant e⁻)

Survival of molecules:
- Optically thick clumps and central torus;
- Self- and mutual-shielding of CO and H₂

Zhang et al. 2012

- ~10³ K
- ~10⁴ cm⁻³

- ~10⁵ K
- ~10⁶ cm⁻³

- H⁺, He⁺, O²⁺...

- UV, Soft X-ray

- PDR (6eV < hv < 13.6eV)
  - Heating by e⁻ rejection from grains
  - High-density shell of shocked winds
  - Electrons are provided by
    - C⁰ UV+hν → e + C⁺
    - H⁰ X-ray → e + H⁺
Molecular line surveys at mm towards AGB, PPN and PN envelopes

Chemical evolution of C-rich circumstellar envelopes

Dynamic timescales:

- AGB
- $10^4 - 10^5$ yrs
- During the AGB-PPN transition, long C-chain molecules are enhanced. Si- and S-bearing molecules are depleted.

- PPN
- $< 10^3$ yrs
- In the PN stage, many molecules are destructed by UV radiations. Some ionized species and radicals are enhanced.

- PN
- $10^3 - 10^4$ yrs
Chemical compositions are significantly altered during the AGB-PPN-PN transitions.
Chemical models of planetary nebulae

- Black (1978,1983) predicted the presence of $H_2$, $H_2^+$, $HeH^+$non-detection; Moorhead et al. 1998; Liu et al. 1997), OH, CO$^+$, and CH$^+$.

- The models of dense globules in PNe suggest detectable $C_2H$ and CN emission, but too low HCO$^+$ abundance (Howe et al. 1994).

- The effects of shocks and soft X rays were considered in the time-dependent models of Natta & Hollenbach (1998).

- To explain the CH$^+$, OH, and CH lines observed in NGC 7027, Yan et al. (1999) and Hasegawa et al. (2000) constructed steady-state models composed of a thin-dense shell and an extended region.

- Ali et al. (2001) modeled the chemistry of cool (~15K) clumpy nebulae, and predicted high abundance of CH, CH$_2$, CH$_2^+$, HCl, OH, and H$_2$O. But the calculated CS and SiO abundances are too high.

- The clumpy models of Redman et al. (2003) can predict the survival of short-chain molecules in young PNe, but significantly underestimate molecular abundance in evolved PNe.

- Kimura et al. (2012) constructed models to study the effect of stellar and nebular properties on molecular composition. The observed HCN/HNC ratios cannot be reproduced.
### Molecules in the interstellar and circumstellar environments

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#### Molecules detected in:
- ISM (only)
- Envelopes around evolved stars
- Planetary nebulae

195 molecules are identified (or tentatively identified) in space, among which 107 are detected in circumstellar envelopes of evolved stars (VY Cma, OH231.8+4.2, IRC+10420, IRC+10216, CRL 618, CRL 2688, NGC 7027, Tc 1, etc.). More than 20 molecules are detected towards PNe.

Sensitive observations at low frequency are required to reveal the rotation transitions from complex molecules in PNe.
H$_2$ and CO

• > 70 PNe are detected in H$_2$.
  - H$_2$ emission is stronger in, but not limited to, bipolar PNe with equatorial rings (Marguez-Lugo et al. 2013, 2015 and references therein).
  - H$_2$ emission in the torus is clumpy and filamentary, but not uniform (Manchado et al. 2015).
  - Can H$_2$ be formed again on dust grains after the central star has entered the cooling track? (an observational evidence provided by Herschel; van Hoof et al. 2010).
  - H$_2$ in low-ionization structures may be excited by shocks (Akras et al. 2016).

• ~100 PNe are detected in CO (36% detection rate for young PNe, Huggins et al. 2005). Molecular mass measured from CO decreases with PN ages (1-0.01$M_{\odot}$; Bujarrabal 2006).
  - The CO/H$_2$ ratio does not significantly vary during the PN stage (Edwards et al. 2014).

Contour: CO envelope of NGC7027 (Nakashima et al.2010)
OH and H$_2$O

• OH and H$_2$O masers probably trace very young O-rich PNe ( < 100—1000 yr).
  - Confirmed sources: 5 H$_2$O-PNe (Gomez et al. 2015) and 7 OH-PNe (Uscanga et al. 2012; Qiao et al. 2016), among which only two, K3-35 and I16333 show both OH and H$_2$O masers.
  - The first “water fountain” (youngest) PN, I15103 (Gomez et al. 2015).

• Crystalline water ice has been detected in O- (Molster et al. 2001) and C-rich PNe (Cohen et al. 1999) → Transition from O- to C-rich outflow following a helium flash?

• OH and $o/p$-H$_2$O have been detected in the C- and O-rich PNe by ISO (Liu et al. 1997) and Herschel (Wesson et al. 2010; Bujarrabal et al. 2012).
  - Abundant H$_2$O in the inner shells of NGC7027 suggests an ongoing process producing water (Santander-Garcia et al. 2012).
HCO\(^+\), CO\(^+\), and OH\(^+\)

Chemistry in PDRs: 

\[
\begin{align*}
  \text{CO} & \rightarrow \text{O} \rightarrow \text{O}^+ \rightarrow \text{H}_2 \rightarrow \text{OH}^+ \rightarrow \text{H}_2\text{O}^+ \rightarrow \text{H}_3\text{O}^+ \rightarrow \text{OH} \rightarrow \text{CO}^+ \rightarrow \text{HCO}^+ \\
\end{align*}
\]

• Observations show that HCO\(^+\) is a common constituent in molecule-rich PNe, and its abundance keep constant during PN evolution (Edwards et al. 2014, Schmidt & Ziurys 2016).

• For the first time, OH\(^+\) was discovered in 5 PNe (including young and evolved PNe) by Herschel (Aleman 2014; Etxaluze et al. 2014).

• Observations show that the intensity of CO\(^+\) line in PNe is positively correlated with that of HCO\(^+\) (Bell et al. 2007).

• The routes, O\(\rightarrow\) OH\(^+\) and CO\(\rightarrow\) HCO\(^+\), can be ruled out in PDR because of high dissociative recombination of H\(_3^+\) in the presence of e\(^-\) (except in young PNe where H\(_3^+\) is enhanced by x-ray).
CH and CH⁺

- CH and CH⁺ were discovered in NGC 7027 (Liu et al. 1997; Cericharo et al. 2010; Wesson et al. 2010).
  - The excitation analysis of CH⁺ lines suggests $T_k = 300-500K$ and $n(H_2) \sim 10^7 \text{ cm}^{-3}$ (Cericharo et al. 2010).
  - A new model of CH⁺ excitation suggests $n(H_2) \sim 10^5 \text{ cm}^{-3}$ (Godard & Cernicharo 2013).

Endothermic reaction with an activation energy of 4300K:

$$0.4\text{eV} + C^+ + H_2 \rightarrow CH^+ \rightarrow CH_2^+ \rightarrow CH$$

(induced by shocks or vibrationally excited $H_2^*$).
N-bearing molecules

- HCN and CN are common in molecule-rich PNe. Photodissociation of HCN may explain the high CN/HCN.

- The chemistry HNC is similar to that of HCN. Models cannot reproduce the observed low HNC/HCN ratio in NGC 7027 (<0.06). More sensitive HNC survey in PNe is required.

- HC$_3$N was discovered only in NGC7027 with an abundance of 10 times lower than in IRC+10216 (Zhang et al. 2008).

- NH$_3$ has been detected in NGC6302 (Bujarrabal et al. 2011).

- N$_2$H$^+$ was detected only in NGC7027, but with abnormally high abundance (Josselin & Bachiller 2003; Zhang et al. 2008). → The density of H$_3^+$ is increased by X-ray from the hot center (N$_2$ $\rightarrow$ N$_2$H$^+$).

HCN/H$_2$ vs PN age

Figure from Schmidt & Ziurys (2016)

HCN abundances keep approximately constant during PN evolution, in contrast to the model prediction.
Si- and S-bearing molecules

- **CS** is abundant in C-rich AGB and PPN ($\text{CS}/\text{H}_2 \sim 10^{-6}$), but absent in PNe (Bachiller et al. 1997).

- **CS** was discovered in 5 PNe with C/O ≤ 1.→ Sulfer in grains is released into the gas phase in oxidation environments? (Edwards et al. 2014).

- **SiO, SO** and **SO$_2$** are found in a PN M2-28 (Edwards & Ziurys 2014), indicating O-rich environments.

- **HCS$^+$** was tentatively detected in NGC 7027 (Hasegawa & Kwok, 2001; Zhang et al. 2008).
C2H, c-C3H2, and H2CO

- C2H, c-C3H2, and H2CO were detected in young and evolved PNe, NGC 7027 and Helix nebula (Tenenbaum et al. 2009).

- Is C2H from AGB remnant (photodissociation of C2H2) or in situ formed in PDR?

- High c-C3H2 abundance cannot be reproduced by gas-phase chemistry model. It might be produced by photodestruction of large aromatic compounds (Fuente et al. 2003).

More sensitive line surveys continue to reveal new molecules in PNe.
Detected molecules in an evolutionary sequence

C-rich AGB: ~ 80 molecules

C-rich PPNe: ~ 40 molecules; C_{60}, complex aromatic molecules

PNe: ~ 20 simple molecules; C_{60}, C_{70}, C_{60}^+; complex aromatic molecules

Diffuse clouds: ~ 20 simple molecules; complex aromatic molecules; 5 diffuse interstellar bands from C_{60}^+

Simple molecules: atomic number < 6

See Cernicharo et al. (2011) for a review of the detected molecules during the AGB-PPN-PN transitions.

PNe have similar molecular compositions with diffuse clouds. (e.g. papers by Zijlstra's group)
The unidentified Infrared Emission (UIE)

UIE is detected in PNe. The presence of UIE is not sensitive to the excitation class of PNe.

Aromatic (sp$^2$ bonded):
- 3.3 um, 6.2 um, 7.7 um, 8.6 um, 10-15 um features

Aliphatic (sp$^3$ bonded):
- 3.4 um, 6.9um features
- 8um, 12um, and 17um plateaus
UIE carrier?

Proposed candidates: **complex carbonaceous molecules**
- Hydrogenated Amorphous Carbon (HAC)
- Quenched Carbon Composites (QCC)
- Polycyclic Aromatic Hydrocarbons (PAH)
- Nanodiamonds
- Rydberg matter

Or MAONs (Mixed aromatic-aliphatic organic nanoparticles; Kwok & Zhang 2011, *Nature*)?

PAHs:

UIE has been commonly observed in proto-PNe (Aro/Ali ratio increases during the PPN-to-PN transition).

In O-rich PNe, UIE carrier can be formed in-situ in PDRs (Guzman-Ramirez et al. 2014; Cox et al. 2016, poster p.27).
C<sub>60</sub> (Buckminsterfullerene, Buckyball)

- Fullerenes (C<sub>2n+20</sub>) are molecules composed entirely of carbon, in the form of a hollow cage.
- The most famous fullerene is C<sub>60</sub>, which is arranged as 12 pentagons (5-carbon ring) and 20 hexagons (6-carbon ring).
- C<sub>60</sub> is highly symmetric (only four IR-active modes.)
- C<sub>60</sub> is physically stable because it is the smallest cage with isolated pentagons (C<sub>70</sub> is the second smallest one).
- C<sub>60</sub> is chemically active.
The discovery of $C_{60}$ in laboratory

$C_{60}$ was discovered experimentally for the first time by Kroto et al. (1985, Nature 318, 162).

Laboratory experiments designed to simulate the gas-phase reactions in carbon star outflows.

- Krätschmer et al. (1990) developed new technique to effectively produce solid state $C_{60}$ in laboratory.

Kroto et al. (1985)
Fullerenes in the Earth and meteorites

\[ C_{60} \text{ and } C_{70} \text{ have been identified in:} \]

- Carbon-rich Pre-Cambrian rock from Russia (Buseck et al. 1992).
- Allende meteorite (Becker et al. 1994).
- Shock-produced breccias of the Sudbury impact structure in Ontario, Canada (Becker et al. 1994).
- ......

\[ C_{60} \text{ can be formed in nature.} \]

Fullerene-like structures in the Allende meteorite (Harris et al. 2000)
Search for fullerenes in space
-- failure examples

Electronic transitions of C\textsubscript{60}

• Snow & Seab (1989) did not detect C\textsubscript{60} in several reddened stars.
• Herbig (2000) did not detect C\textsubscript{60} features at 3857 and 3980Å in the spectra of O-type stars.
• Sassara et al. (2001) examined a few objects considered as possible sites of C\textsubscript{60}, but did not get positive detection.

Vibrational transitions of C\textsubscript{60}

• Uncertain detections in IRC+10216 and I07134 by Clayton (1995) and Kwok et al. (1999)
• Moutou et al. (1999) did not detect C\textsubscript{60} and C\textsubscript{60}\textsuperscript{+} in the ISO spectrum of NGC 7023 (a reflection nebula).
Search for fullerenes in space -- \(\text{C}_6\text{O}^+\) as a carrier of DIBs

- \(\text{C}_6\text{O}\) has an ionization potential of 7.6 eV, and is possibly present as \(\text{C}_6\text{O}^+\).
- The electronic transitions of \(\text{C}_6\text{O}^+\) are in the near-IR.

Foing & Ehrenfreund (1994, 1997) found that the two near-IR DIBs have wavelengths close to those of \(\text{C}_6\text{O}^+\) measured in a neon matrix.

This was recently confirmed by Campbell et al. (2015; agreements in wavelengths, intensities, and widths).

Laboratory spectra of \(\text{C}60^+\) also reveal weaker bands at 9633, 9578, and 9349 Å, which were soon detected in DIBs by Walker et al. (2015) and Campbell et al. (2016) using CFHT.

\(\text{C}60^+\) as the first identification of one of the DIB carriers (Five DIBs have been identified.)
Search for IR vibrational modes of C$_{60}$ -- The first convincing case

Vibrational transitions of C$_{60}$ and C$_{70}$ were for the first time detected in a young planetary nebula Tc1 by Spitzer Telescope (Cami et al. 2010, Science, 329, 1180).
C$_{60}$ in more objects

Circumstellar envelopes surrounding evolved stars:

- Planetary nebulae with AIBs (García-Hernández et al. 2010)
- Planetary nebulae in the Magellanic Clouds (García-Hernández et al. 2011)
- A proto-planetary nebula (Zhang & Kwok, 2011)
- Post-AGB stars (Gielen et al. 2011, Roberts et al. 2012)
- Moderately H-deficient RCB stars (García-Hernández et al. 2011)
- A peculiar binary XX Oph (Evans et al. 2012)

ISM and Pre-main sequence stars:

- Two reflection nebulae (Sellgren et al. 2010)
- Orion nebula (Rubin et al. 2011)
- Young stellar objects and a Herbig Ae/Be star (Roberts et al. 2012)

Vibrational transitions of C$_{60}^+$ are detected in some of the C$_{60}$ sources. (Berne et al. 2013; Strelnikov et al. 2012, 2015; )

C$_{60}$ in PNe

C$_{60}$ has been detected in 11 Galactic PNe, 4 LMC PNe and 7 SMC PNe. The detection rate increases with decreasing metallicity (5% in the Milky way, 20% in the LMC, and 44% in the SMC). (García-Hernández et al. 2012; Otsuka et al. 2016)
$C_60$ in a proto-planetary nebula
-- Producer of DIB carrier?

$C_60$ can be efficiently in circumstellar envelopes with a timescale of about 1000 years.

$C_60^+$ is enhanced in IRAS 01005+7910 (Iglesias-Groth & Esposito, 2013). → Circumstellar envelopes can produce DIB carrier.

Two optical DIBs are enhanced in $C_60$-containing PNe (Diaz-Luis et al. 2015). → $C_60$ derivatives might be DIB carrier.
Search for fullerene-related compounds in PNe

\[ C_{60}H_m & C_{60}H_m^+ \]

Cataldo et al.

\[ \text{Na@C}_{60} \]

(Dunk et al. 2013)

\[ \text{CO@C}_{60} \]

\[ \text{H}_2@C_{60} \]

Interstellar fullerene compounds & DIBs (Omont, 2016)

Fullerene compounds as DIB carrier?

<table>
<thead>
<tr>
<th>fullerene compounds</th>
<th>DIBs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physically stable</td>
<td>ubiquitous</td>
</tr>
<tr>
<td>Chemically active</td>
<td>various</td>
</tr>
</tbody>
</table>
Fullerane (C$_{60}$H$_m$)

C$_{60}$ can be readily hydrogenated when mixed with H atoms.

Intensities of the 4 IR transitions decrease with increasing hydrogenations. → When C60 is heavily hydrogenated, the 4 IR transitions are hardly discovered.

Fullerane was tentatively discovered in a PPN. (Zhang & Kwok 2013)

However, Diaz-Luis et al. (2016) did not detect the CH stretching mode from fullerane in two strong C$_{60}$-PNe, TC1 and M1-20.
Excitation of C$_{60}$ IR bands: models vs. observations

Possible causes for the discrepancy:
- Uncertain intrinsic strengths
- Uncertain measurements
- Other excitation mechanisms

Or hydrogenation of C$_{60}$?

The observed intensity ratios of C$_{60}$ cannot be reproduced by fluorescence and thermal models (also see Bernard-Salas et al. 2012; Zhang & Kwok 2013).
Excitation of $\text{C}_6\text{O}$ IR bands: models vs. observations

The observed intensity ratios of $\text{C}_6\text{O}$ cannot be reproduced by fluorescence and thermal models (also see Bernard-Salas et al. 2012; Zhang & Kwok 2013).

$\text{C}_6\text{O} \xrightarrow{\text{H}} \text{C}_6\text{O}_\text{m} \xrightarrow{\text{hv}} \text{C}_6\text{O} + \text{H}_2$

Hydrogenation can affect the intensity ratios of the $\text{C}_6\text{O}$-cage vibrational bands.
Formation of circumstellar $\text{C}_60$: bottom-up vs. top-down

- **Collisions of small carbon clusters (bottom-up):**
  - Hydrogen-poor environments at normal temperature.
  - Hydrogen-rich at high-temperature (> 3500K).

- **Dehydrogenation of HAC or PAH (top-down):**
  - UV photon-induced.

(Berne & Tielens 2012)

(García-Hernández et al. 2010; Micelotta et al. 2012)
Aliphatic/aromatic organics as the precursor of fullerene?

Most of the C60 sources exhibit plateau emission. (García-Hernández et al. 2012; Zhang & Kwok 2013; Otsuka et al. 2013)

Strong plateaus at 8 and 12 um from aliphatic components

A similar route with that presented by Micelota et al. (2012)

Carrier of the extinction bump at 2175A (Iglesias-Groth et al. 2003)?
Summary

• Molecular component is important in PNe.
• Large molecules can survive or form during the PN evolution.
• The chemistry in the PN stage is still far from well understood.
• The compounds blown from PNe are dispersed into the ISM, and are possibly related to the DIB phenomenon (e.g. C\textsubscript{60} & C\textsubscript{60}\textsuperscript{+}).
• C\textsubscript{60} and C\textsubscript{70} have been detected in PNe, but their excitation and formation mechanisms are unclear.

Future:

• Sensitive surveys of molecules in PNe are required to investigate circumstellar chemistry and compare with the molecules observed in diffuse ISM.
• It is worth Search for fullerene-related compounds (e.g. C\textsubscript{60}H\textsubscript{m}) to study the DIB phenomenon.