Nitrogen Isotopic Ratios in Cometary Ammonia

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in collaboration with:
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Emmanuël Jehin (Univ. de Liège),
and many colleagues
1. Background

What is comet?

- Comet: one of the most pristine icy small bodies in the solar system
- Component of the cometary nucleus
  - Volatiles (Ice): H$_2$O, CO, CO$_2$, NH$_3$, HCN, etc.
  - Dust: Silicate, Graphite, other minerals, etc.

† Comet: one of the most pristine icy small bodies in the solar system

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  - Volatiles (Ice): H$_2$O, CO, CO$_2$, NH$_3$, HCN, etc.
  - Dust: Silicate, Graphite, other minerals, etc.
1. Background

Pristine properties of volatiles

1. Chemical composition ([X]/[H$_2$O]; X = HCN, C$_2$H$_2$, CH$_4$, …)
   → gives the limitation of temperature and chemical network in formation environment of the nucleus

2. Isotopic ratio (D/H ratio, $^{14}$N/$^{15}$N ratio, etc.)
   例） H$_3^+$ + HD → H$_2$D$^+$ + H$_2$ + 220K
   → D-fractionation occur by low-temp.
   gas-phase chemistry (depending on temperature?)

3. Nuclear spin isomers ratio (ortho/para ratio: OPR)
   例） ortho–H$_2$O
       para–H$_2$O
   → Is OPR depending on molecular formation environment?
1. Background

**Pristine properties of volatiles**

1. Chemical composition \([X]/[H_2O]; X = \text{HCN, C}_2\text{H}_2, \text{CH}_4\, \cdots\)  
   \(\rightarrow\) gives the limitation of temperature and chemical network in formation environment of the nucleus

2. Isotopic ratio \((\text{D/H ratio, } ^{14}\text{N}/^{15}\text{N ratio, etc.})\)
   
   例） \(\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 + 220\text{K}\)  
   
   \(\rightarrow\) D-fractionation occur by low-temp. gas-phase chemistry (depending on temperature?)

3. Nuclear spin isomers ratio \((\text{ortho/para ratio: OPR})\)
   
   例） ortho-\(\text{H}_2\text{O}\) \(\uparrow\uparrow\uparrow\) \((l = 1)\)
   
   para-\(\text{H}_2\text{O}\) \(\uparrow\downarrow\downarrow\) \((l = 0)\)  
   
   \(\rightarrow\) Is OPR depending on molecular formation environment?
1. Background

Isotopic ratios in comets and ISMs

Relationship between observational object and obtained stage

Gas-phase

- determined by Obs. of ISM
- determined by Obs. of ISM
- determined by Obs. of YSO

Solid-phase

- N/A
- determined? by Obs. of Comet
- determined by Obs. of Comet

Early in the molecular cloud
Late
Disk

Comet is the important clue to obtain $^{14}\text{N}/^{15}\text{N}$ ratios of volatiles in/on solid-phase
1. Background

**D/H ratio in Water**

**LEFT:** D/H ratios in H$_2$O in solar system objects (Altwegg et al. 2014).

**RIGHT:** Relationship between D/H ratio and formation temperature, assuming H$_2$O form in gas-phase chemistry (Millar et al. 1989)
1. Background

D/H ratio in Water

![Graph showing D/H ratios in water in solar system objects and relationship between D/H ratio and formation temperature.]

- ** Formation temperature that reproduces D/H ratios in H₂O in comet is **30 – 40 K**, if H₂O captured in comet formed in gas-phase**
1. Background

\[ \frac{^{14}N}{^{15}N} \text{ ratio in comets} \]

- Determined from HCN and CN (a major photodissociation product of HCN)
  \[ \Rightarrow \frac{^{14}N}{^{15}N} \text{ clusters } \sim 150 \text{ (No large variation)} \]

- Cometary HCN fractionated of \(^{15}N\) than elemental abundances in nitrogen of Sun (441±5; Marty et al. 2011)

- However, there is no report for NH\(_3\)
  \[ \Rightarrow \text{the most abundant and the most stable N-bearing volatile in comet} \]

\[ \begin{array}{c}
\text{Protosolar value (441±/5; Marty et al. 2011)} \\
\text{Oort Cloud Comets} \\
\text{Jupiter Family Comets} \\
\end{array} \]

- References:
1. Background

Comparison with $^{14}\text{N}/^{15}\text{N}$ ratio in ISMs

Obs. of three Class 0 YSOs

$^{14}\text{N}/^{15}\text{N} = 441$ in solar value (Marty et al. 2011)

$^{14}\text{N}/^{15}\text{N} = 150$ in comets (Manfroid et al. 2009)

Wampfler et al. 2014 (astro-ph.)

$^{14}\text{N}/^{15}\text{N}$ ratio in HCN probably depends on gas temperature
1. Background

Comparison with $^{14}\text{N}/^{15}\text{N}$ ratio in ISMs

- $^{14}\text{N}/^{15}\text{N}$ ratio in HCN probably depends on gas temperature
- High $^{15}\text{N}$-fractionation of HCN can reproduce by theory
  - Cometary HCN might form in the molecular cloud at $\sim10$ K
  - We check the $^{14}\text{N}/^{15}\text{N}$ ratio in cometary $\text{NH}_3$
2. Observations

Observations of NH$_3$ in comets

However, there are few samples to detect an ammonia (NH$_3$) in comet cause 1) Band strength of NH$_3$ is weak cause 2) NH$_3$ can exist in the small area of the inner coma because,

\[ \text{Ammonia (NH}_3\text{)} \leftrightarrow \text{H atom} \]

Example of detection of cometary ammonia in very bright comet (Hale-Bopp) taken by 100-m Effelsberg Radio telescope (Bird et al. 1997)
2. Observations

Observations of NH$_3$ in comets

† However, there are few samples to detect an ammonia (NH$_3$) in comet cause 1) Band strength of NH$_3$ is weak cause 2) NH$_3$ can exist in the small area of the inner coma because,

→ We focus on NH$_2$ as a proxy of NH$_3$!!

† Most NH$_3$ become NH$_2$ by photodissociation (B.R. ~95 %; Huebner 1992)

† NH$_2$ can be observed easily in the optical wavelength region

Example of detection of cometary ammonia in very bright comet (Hale-Bopp) taken by 100-m Effelsberg Radio telescope (Bird et al. 1997)

Subaru UM 2014, 2015 Jan. 13 – 15, Mitaka, Japan
2. Observations

Observations of two OC comets

C/2012 S1 (ISON)
- sungrazing comet from the Oort cloud
- broke during its approach to the Sun

C/2013 R1 (Lovejoy)
- originates from the Oort cloud

<table>
<thead>
<tr>
<th>Items</th>
<th>C/2012 S1 (ISON)</th>
<th>C/2013 R1 (Lovejoy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observational Data</td>
<td>UT 2013 November 15 (S13B-089; PI: Y. Shinnaka)</td>
<td></td>
</tr>
<tr>
<td>Instruments (Spectral resolution)</td>
<td>HDS ((\lambda/\Delta \lambda =72,000))</td>
<td></td>
</tr>
<tr>
<td>Heliocentric distance (relative velocity)</td>
<td>0.601 AU (~53.8 km/s)</td>
<td>1.066 AU (~19.9 km/s)</td>
</tr>
<tr>
<td>Geocentric distance (relative velocity)</td>
<td>0.898 AU (~24.4 km/s)</td>
<td>0.412 AU (~12.4 km/s)</td>
</tr>
<tr>
<td>Magnitude in V-band</td>
<td>~5.0 mag.</td>
<td>~5.6 mag.</td>
</tr>
<tr>
<td>Total exposure time</td>
<td>20 min</td>
<td>130 min</td>
</tr>
<tr>
<td>Wavelength coverage</td>
<td>550 – 830 nm</td>
<td>360 – 830 nm</td>
</tr>
</tbody>
</table>

Subaru UM 2014, 2015 Jan. 13 – 15, Mitaka, Japan
2. Observations

Example of cometary spectrum

Optical Spectrum of Comet C/2012 S1 (ISON) with Subaru/HDS on 2013 November 15.6

And there are many weak and unidentified lines

Subaru UM 2014, 2015 Jan. 13 – 15, Mitaka, Japan
2. Observations

Example of cometary spectrum

Method

\[
\frac{^{14}\text{NH}_2}{^{15}\text{NH}_2} = \frac{A}{A'} = \frac{B}{B'} \rightarrow \text{Weighted mean value}
\]

Assumption:

branching ratios of NH\textsubscript{3} by photodissociation and transition rates of NH\textsubscript{2} are equal in cases of \textsuperscript{14}N and \textsuperscript{15}N.

\[

\rightarrow \frac{^{14}\text{NH}_2}{^{15}\text{NH}_2} = \frac{^{14}\text{N}}{^{15}\text{N}}\text{ in NH}_3
\]
3. Results & Discussion

Summary of $^{14}$N/$^{15}$N ratios in comets

<table>
<thead>
<tr>
<th>Objects</th>
<th>Species</th>
<th>$^{14}$N/$^{15}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean of 2 Comets</td>
<td>HCN</td>
<td>113 – 205*1</td>
</tr>
<tr>
<td>Mean of 19 Comets</td>
<td>CN</td>
<td>148 ± 6*2</td>
</tr>
<tr>
<td>Mean of 12 Comets</td>
<td>NH$_3$ (from NH$_2$)</td>
<td>127 ± 32*3</td>
</tr>
<tr>
<td>ISON</td>
<td>NH$_3$ (from NH$_2$)</td>
<td>139 ± 38*4</td>
</tr>
<tr>
<td>Lovejoy</td>
<td>NH$_3$ (from NH$_2$)</td>
<td>161 ± 41*5</td>
</tr>
</tbody>
</table>

References
*1 Bockelée-Morvan et al. 2008
*2 Manfroid et al. 2009
*3 Rousselot et al. 2014
*4 Shinnaka et al. 2014
*5 Shinnaka et al. 2015, in prep.
3. Results & Discussion

Comparison among cometary NH$_3$

+ High $^{15}$N-fractionation
→ These values cannot be reproduced by current chemical evolution model (Wiström et al. 2012)

![Graph showing the comparison among cometary NH$_3$ with high $^{15}$N-fractionation.](image)
3. Results & Discussion

Comparison among cometary NH$_3$

**High $^{15}$N-fractionation**
- These values cannot be reproduced by current chemical evolution model (Wiström et al. 2012)

**Small variation(?)**
- YES: Similar temp. conditions → the molecular cloud
- NO: Various temp. condition → the solar nebula

We need to
(1) increase samples with
(2) the small measurement error of each comet
3. Results & Discussion

**Comparison among cometary volatiles**

- **Similar** $^{15}$N-fractionation between **nitriles** (HCN and CN) and **amines** (NH$_3$)
  - NH$_3$ also formed at low-temperature condition
  - In general, fractionation of heavy element to volatiles occur at low-temperature environment by chemical reactions
  - However, current theoretical model **cannot be reproduced**
  - Request to theoreticians to update the chemical evolution model!
Summary & Future works

- Comet is the most pristine icy small bodies in the solar system
- We determined the $^{14}\text{N}/^{15}\text{N}$ ratios in $\text{NH}_3$ from high-S/N spectra of $\text{NH}_2$ in two single comets, C/2012 S1 (ISON) and C/2013 R1 (Lovejoy), using the Subaru / HDS on 2013 Nov. 15
- We determined the $^{14}\text{N}/^{15}\text{N}$ ratios in $\text{NH}_3$ from that of $\text{NH}_2$
  - High $^{15}\text{N}$-fractionations
    - Cometary $\text{NH}_3$ may form at very low-temperature condition
    - However, this result cannot be reproduced by the recent chemical evolution scenario (Wirström et al. 2012)
  - Small variation?
    - We can estimate a formation environment of cometary $\text{NH}_3$
      YES: cometary $\text{NH}_3$ may form in the molecular cloud
      NO: cometary $\text{NH}_3$ may form in the solar nebula
    - We need to more samples with small error of each comet to update a theoretical chemical evolution model