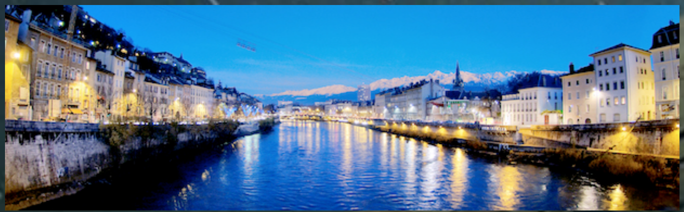
Nuclear Spin Isomers in Cometary Molecules: Survey for Ortho-to-Para Ratios of Ammonia in Comets

Hideyo KAWAKITA

Koyama Astronomical Observatory
Kyoto Sangyo Univ.



Nuclear spin effects in astrochemistry
2-4 May 2017 Grenoble (France)

In collaboration with …

Yoshiharu Shinnaka (Kyoto Sangyo Univ.)

Emmanuël Jehin (Université de Liège)

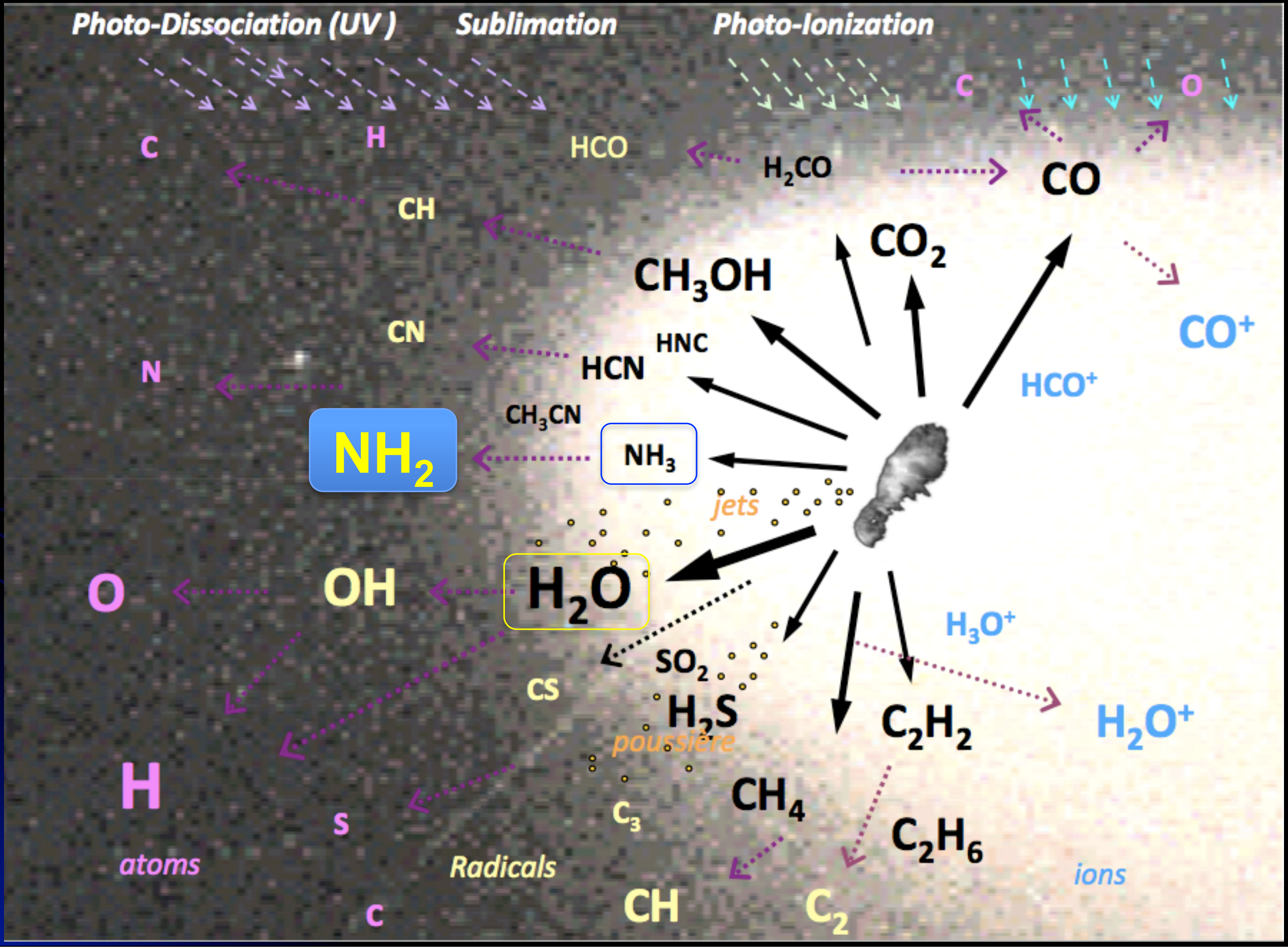
Alice Decock (Université de Liège)

Jean Manfroid (Université de Liège)

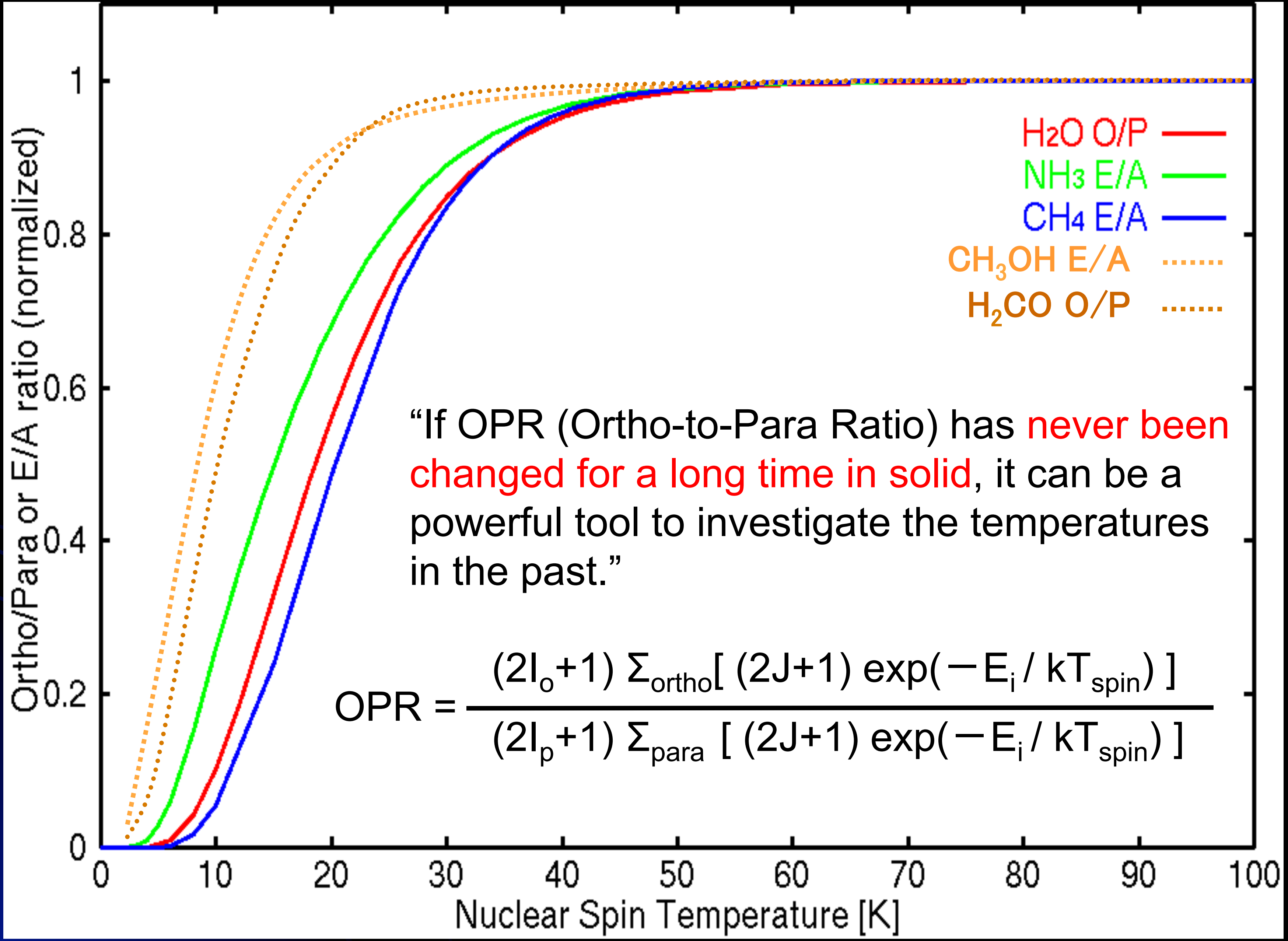
Damien Hutsemékers (Université de Liège)

- And many collaborators with their help

Molecules & Atoms in Coma



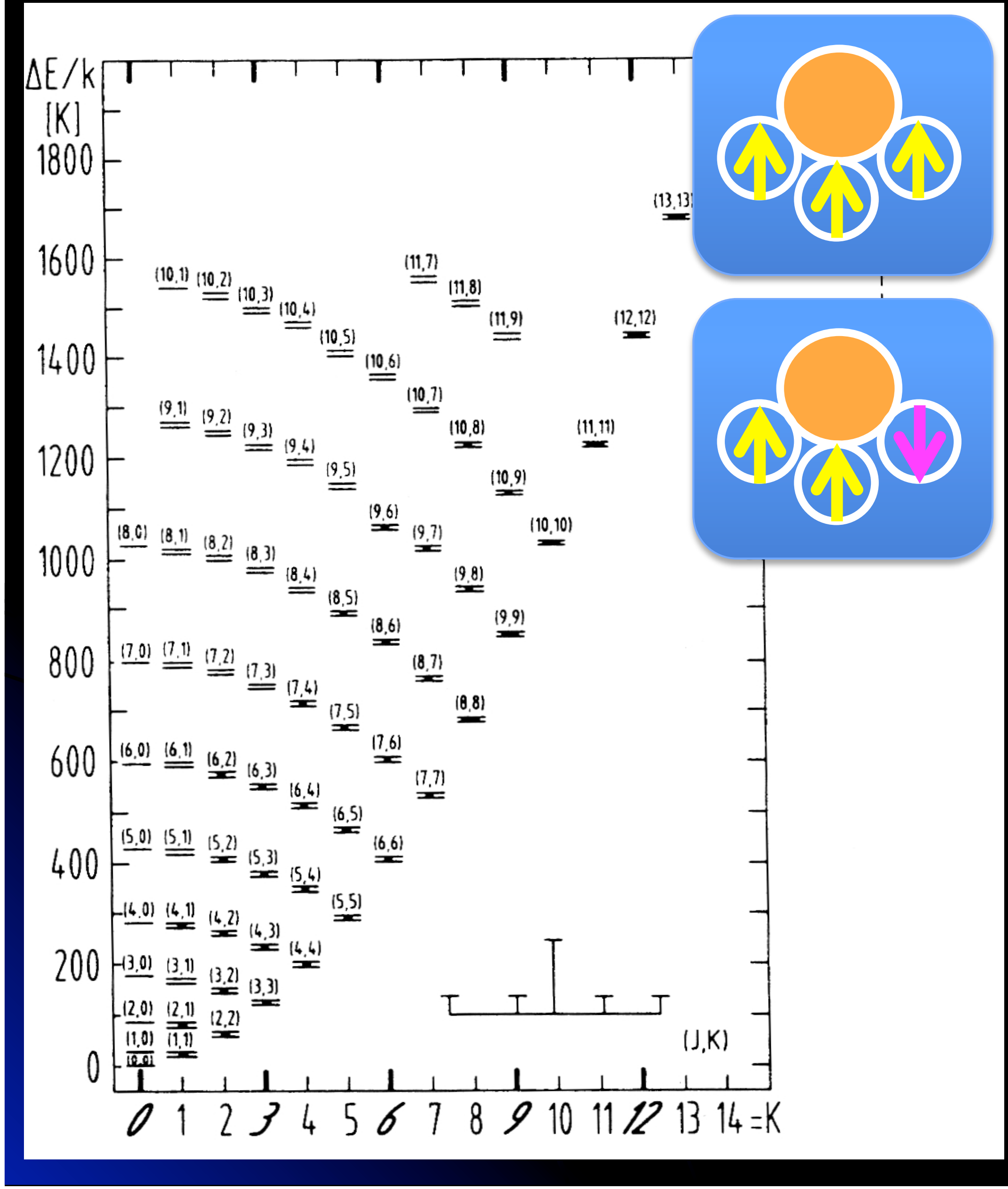
“Spin Temperature” of Cometary Molecules



“If OPR (Ortho-to-Para Ratio) has never been changed for a long time in solid, it can be a powerful tool to investigate the temperatures in the past.”

$$OPR = \frac{(2I_o+1)\,\Sigma_{ortho}[\,(2J+1)\,\exp(-E_i\,/\,kT_{spin})\,]}{(2I_p+1)\,\Sigma_{para}\,[\,(2J+1)\,\exp(-E_i\,/\,kT_{spin})\,]}$$

Ortho- and Para-NH_3



Ortho-NH_3 → $K = 0, 3, 6, \ldots$
($I = 3/2$)

Para-NH_3 → $K = 1, 2, 4, 5, \ldots$
($I = 1/2$)

where K is a projection of total angular momentum J to the molecular axis.

Selection rules:

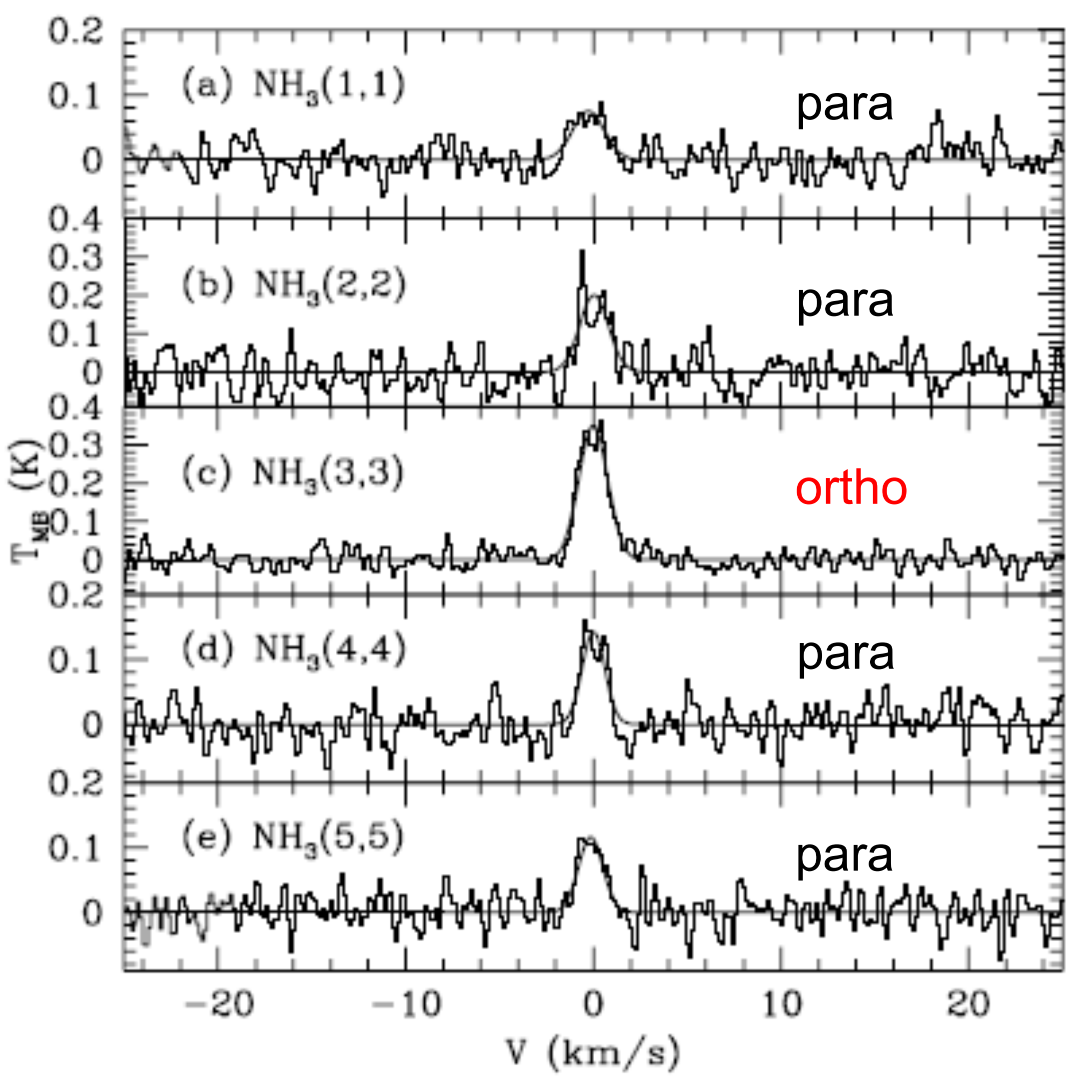
$\Delta K = 0$
for electric dipole transition.

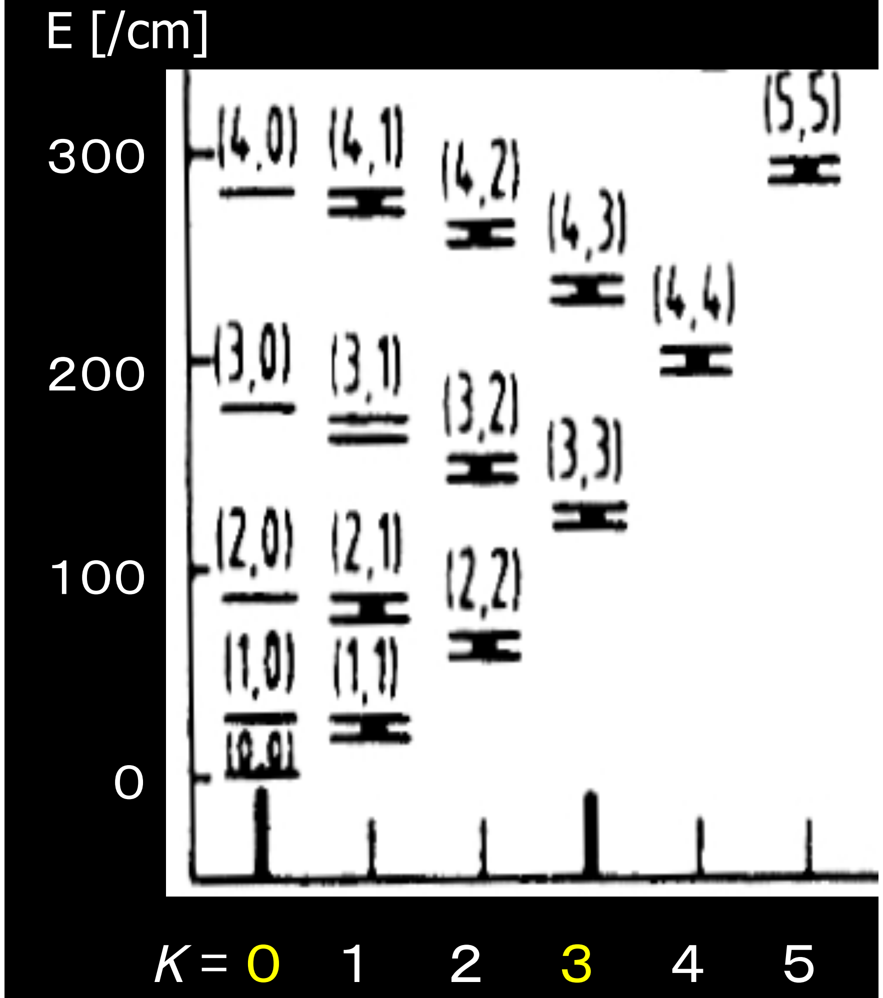
$\Delta K = \pm 3$
for collisional transitoin.

i.e., ortho $\nleftrightarrow$ para

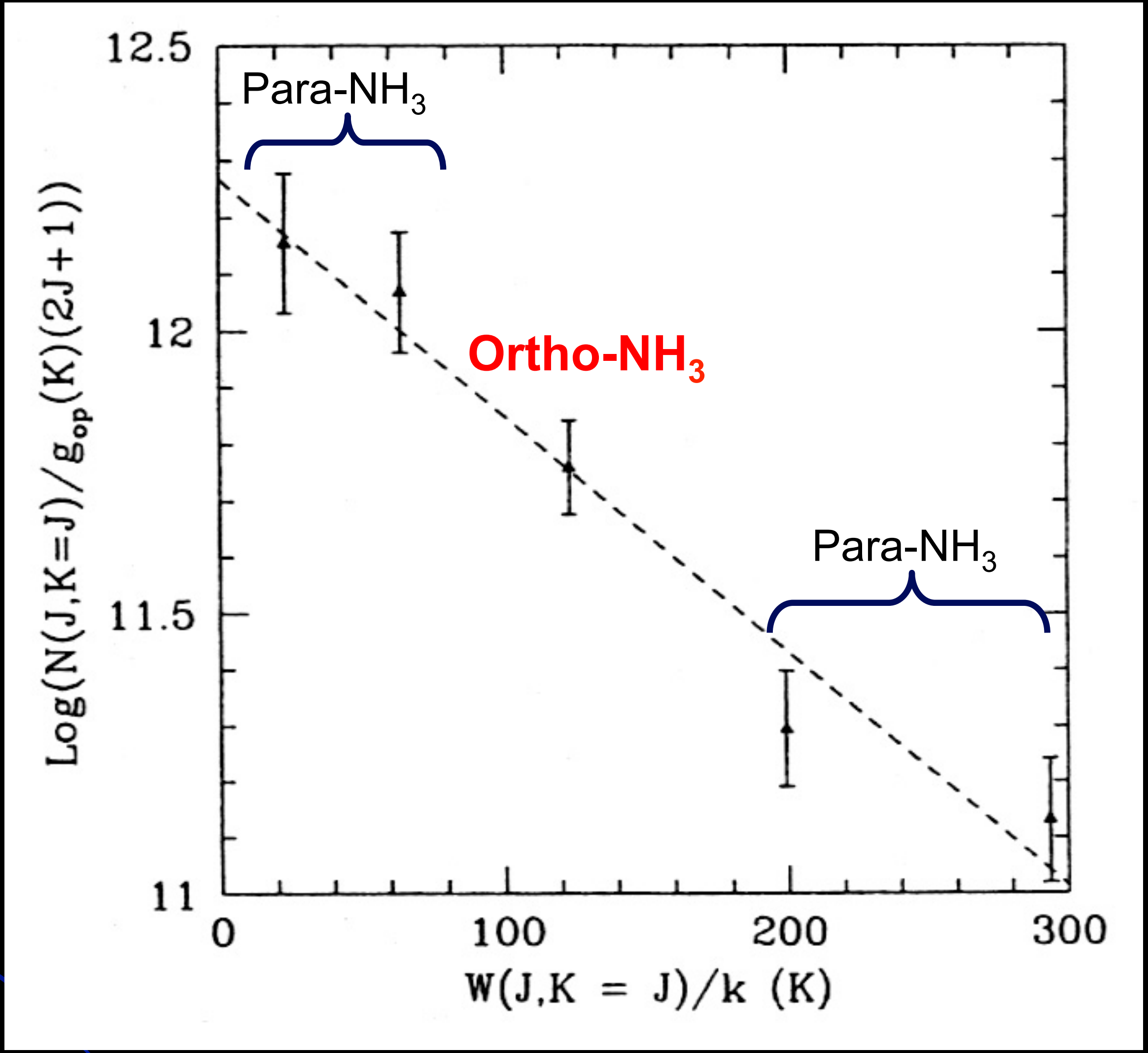
NH_3 Observation in C/Hale-Bopp by the 100m Radio Telescope

Inversion transitions of NH_3 ~ 23GHz (Bird et al. 1997)





ortho : K=0,3,…; para: K=others

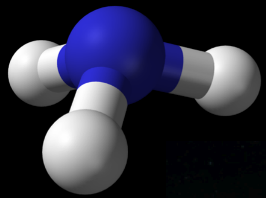


(Bird et al. 1997)

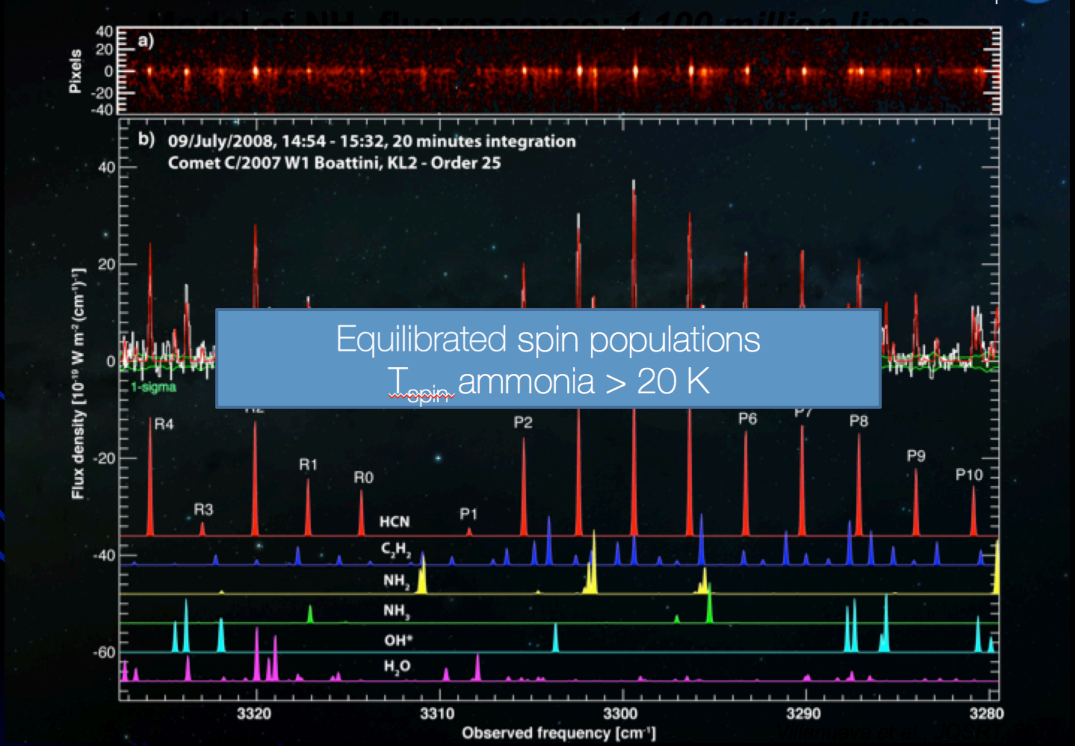
$1.79 > \mathrm{OPR}(\mathrm{NH_3}) > 0.55$

→ It is very difficult to obtain the reliable OPR of NH_3 even for the very bright comet like C/Hale-Bopp

It is difficult to measure multiple lines of NH_3 in comet very accurately …



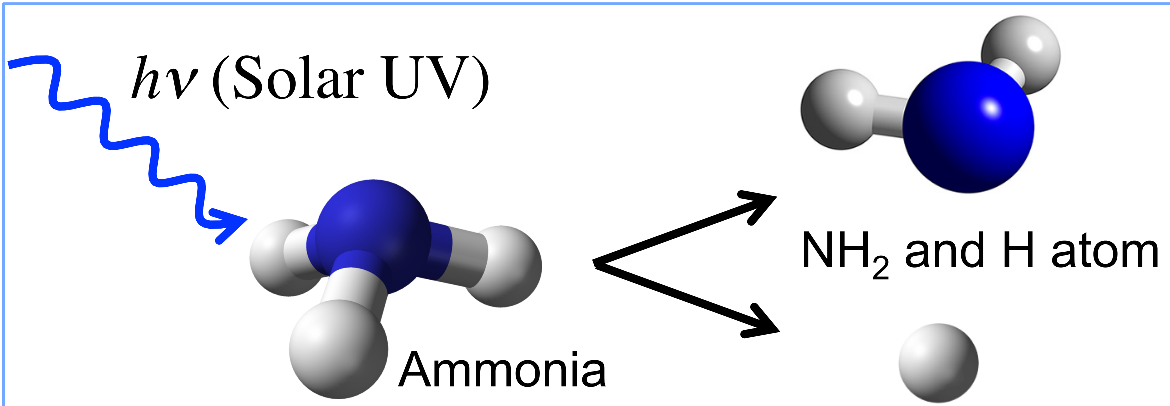
Spin Temperatures in comets: Cosmogonic?
Villanueva – Goddard Space Flight Center



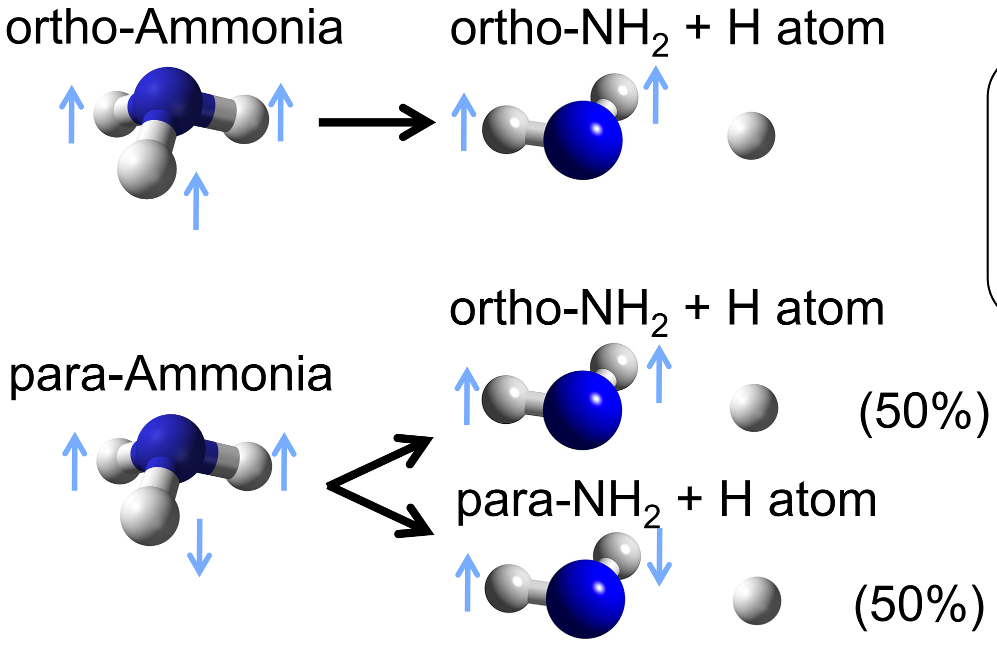
Equilibrated spin populations
T_{spin} ammonia > 20 K

Villanueva's talk, yesterday

Why we focused on NH_2



Branching ratio of NH_3 to NH_2 ~ 95%


ortho-Ammonia

ortho-NH_2 + H atom

para-Ammonia

ortho-NH_2 + H atom (50%)

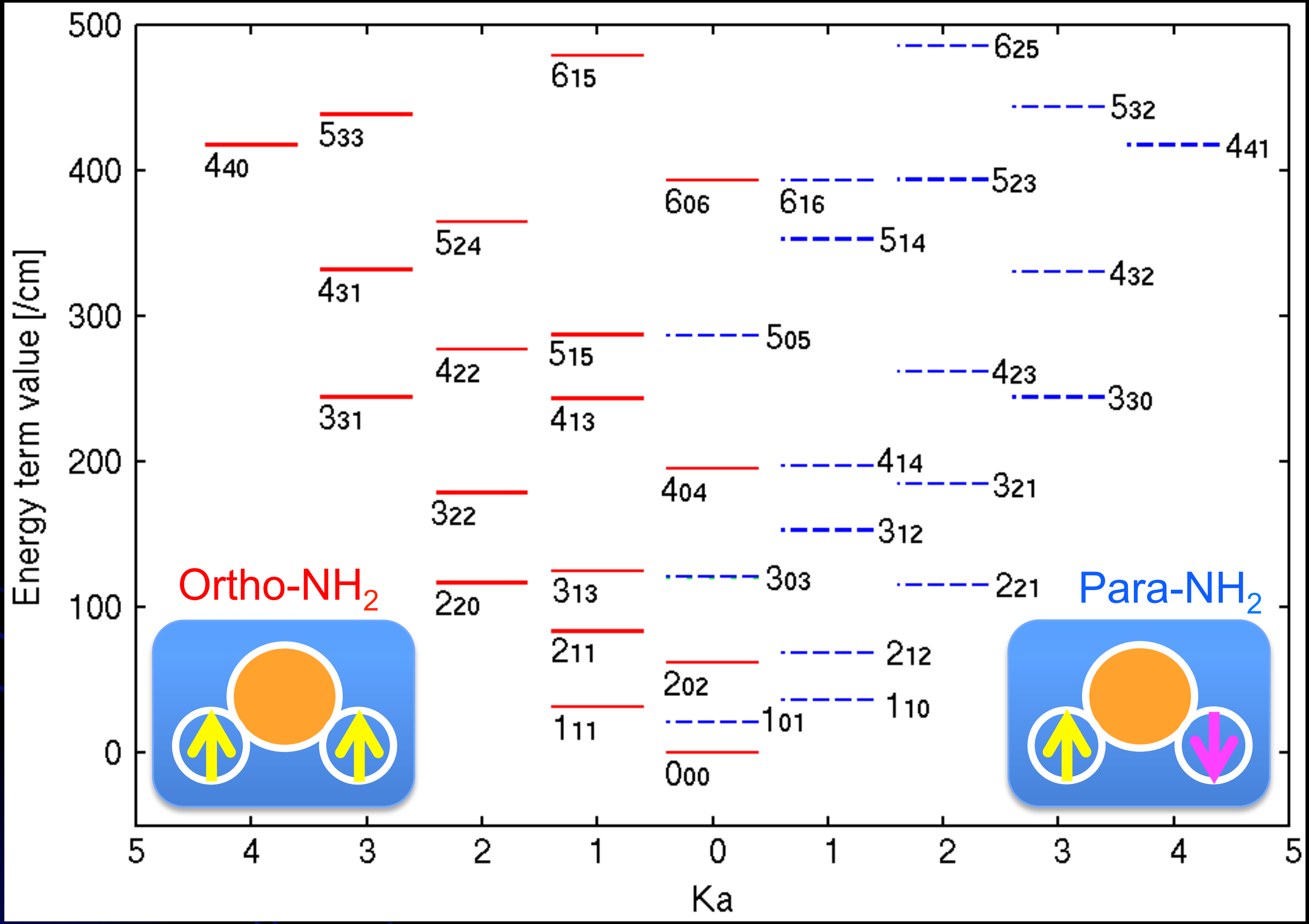
para-NH_2 + H atom (50%)

(based on Quack 1977; Oka 2004)

Ammonia is a major source of NH_2 in cometary coma. (Kawakita & Mumma 2011)

OPR of ammonia can be inferred from that of NH_2.

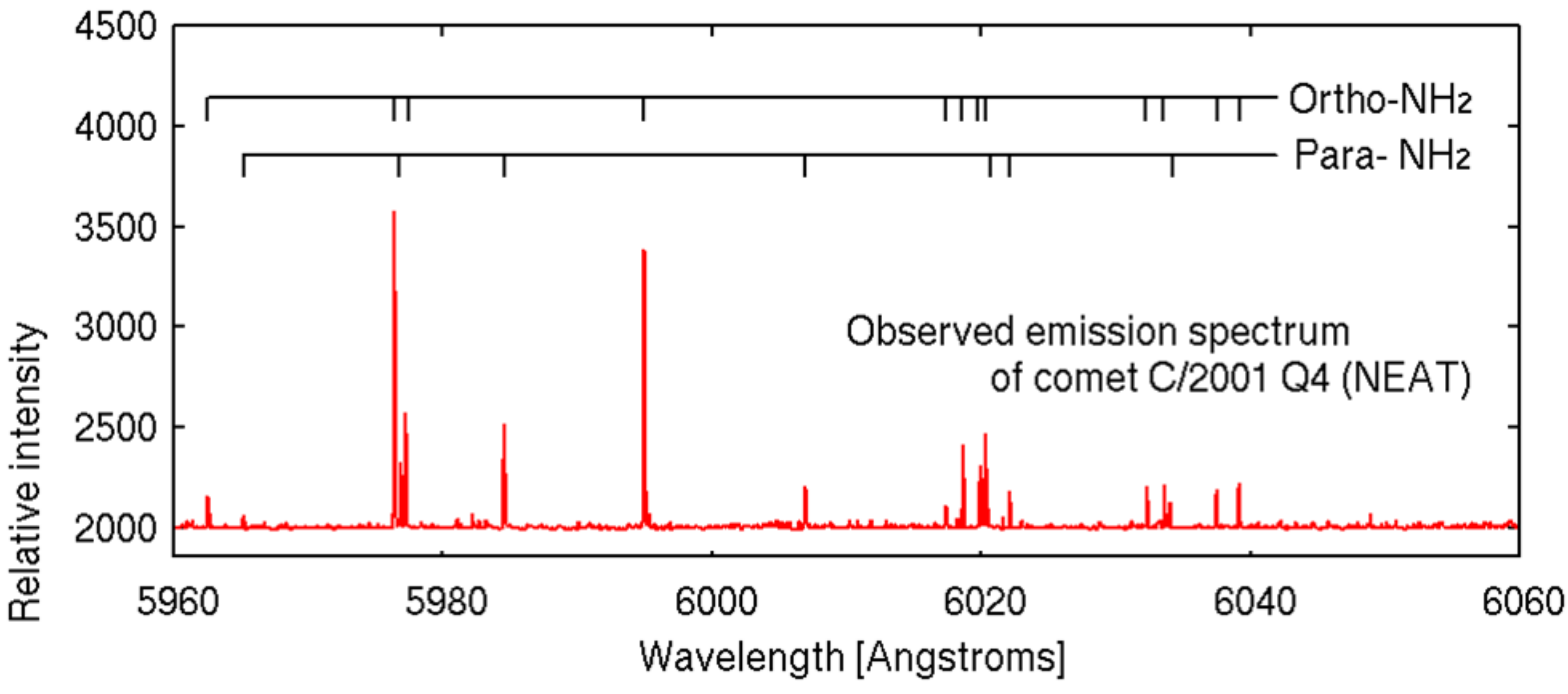
Ortho- and Para-NH_2

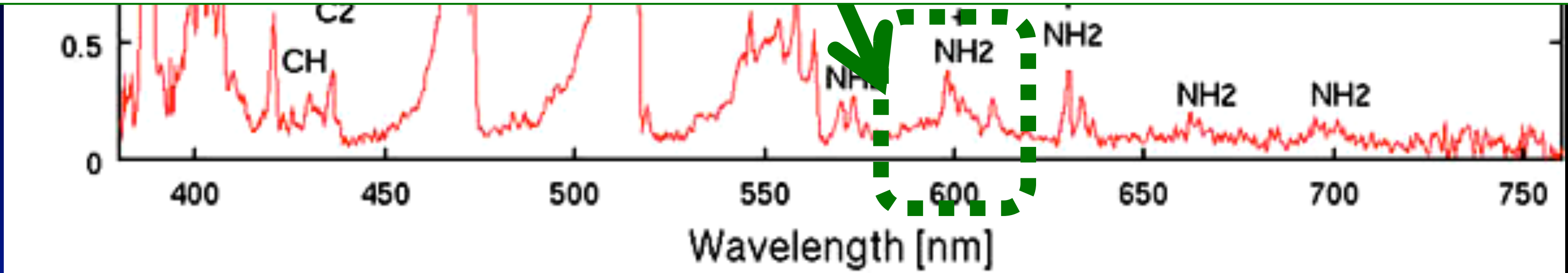


NH_3 + hv (UV) → NH_2 + H (in cometary coma)

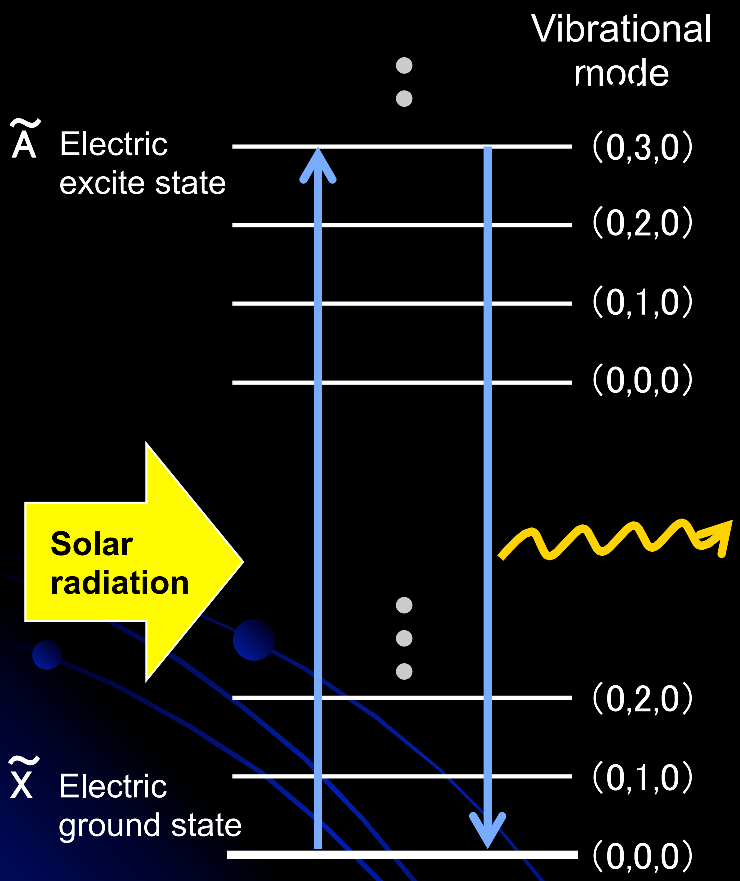
Electronic transition → Multiple lines representing spin distribution could be obtained simultaneously.

Optical wavelength → No serious telluric absorption and easy to observe comets.





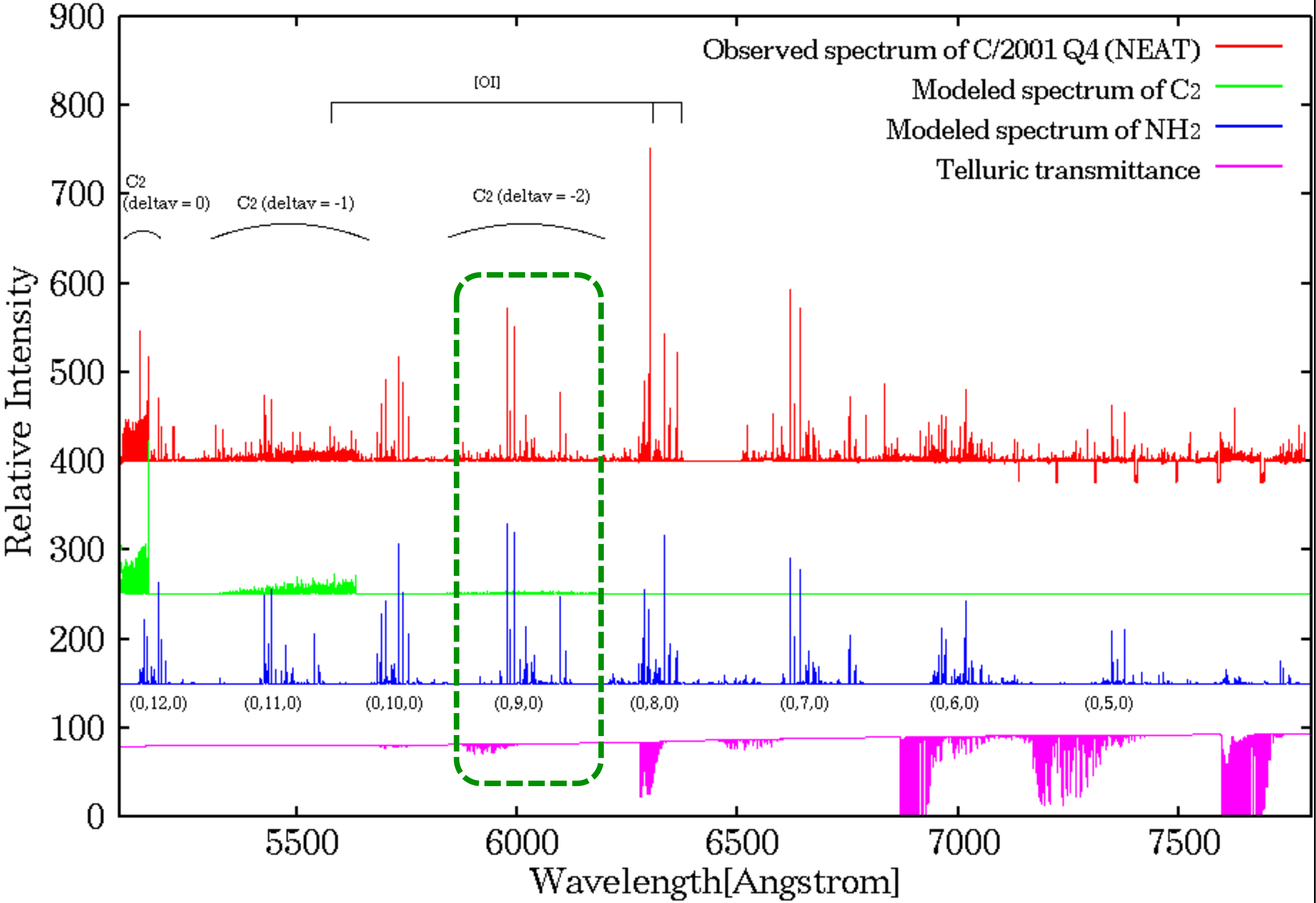
Fluorescence Excitation Model



Outline of our emission model (NH_2):

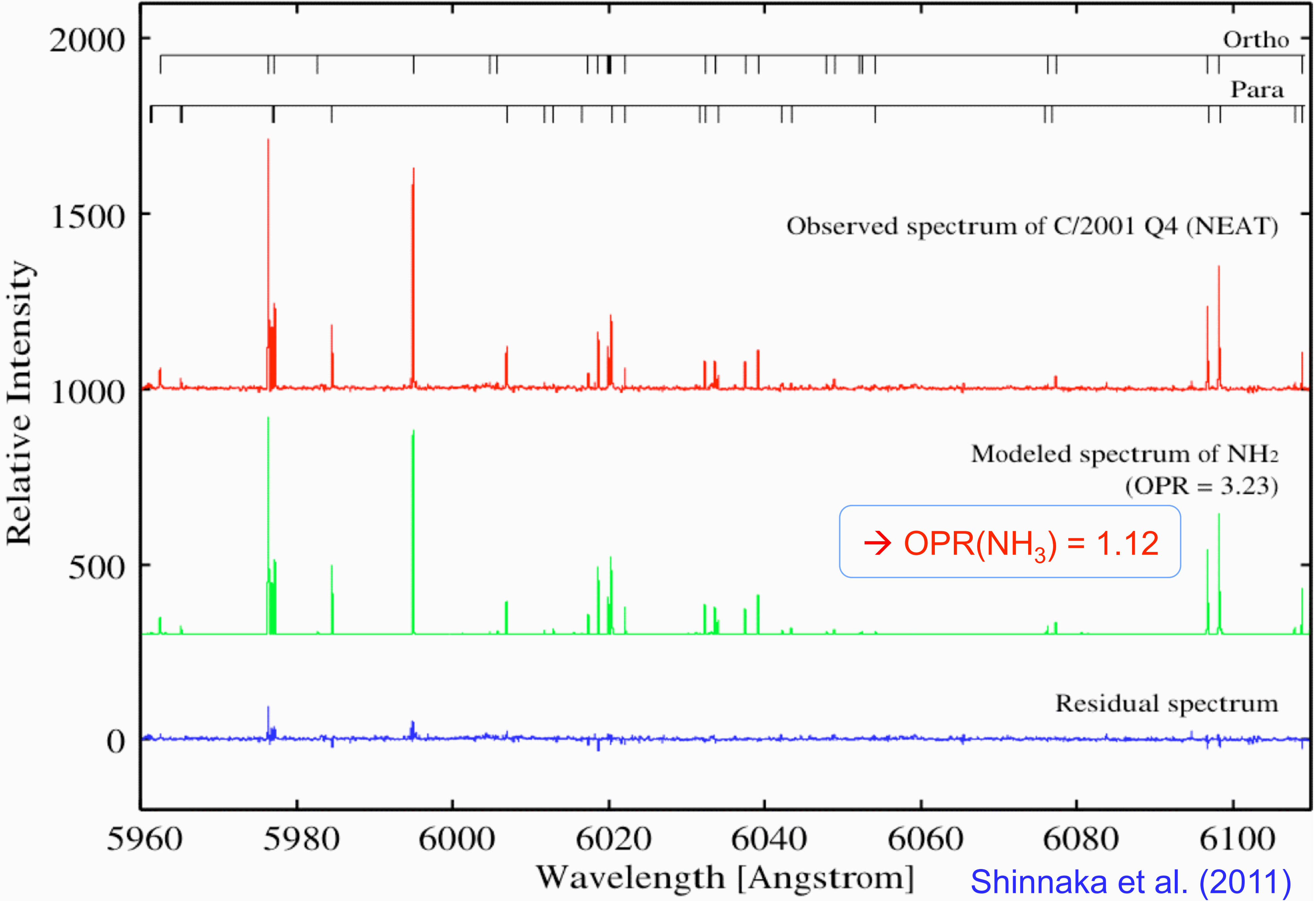
1. The fluorescence excitation in coma by the solar irradiation (assuming the fluorescence equilibrium).
2. Coma is assumed to be optically thin.
3. Considering the rovibronic transitions.
4. Considering the fine structure of energy levels (split into F1 and F2 levels).
5. High resolution solar spectrum was used to take the Swings effect into account.
6. A free parameter is OPR only.

We had great help from Jensen et al. (2003) for the *ab initio* calculation of vibronic transition moments of NH_2.



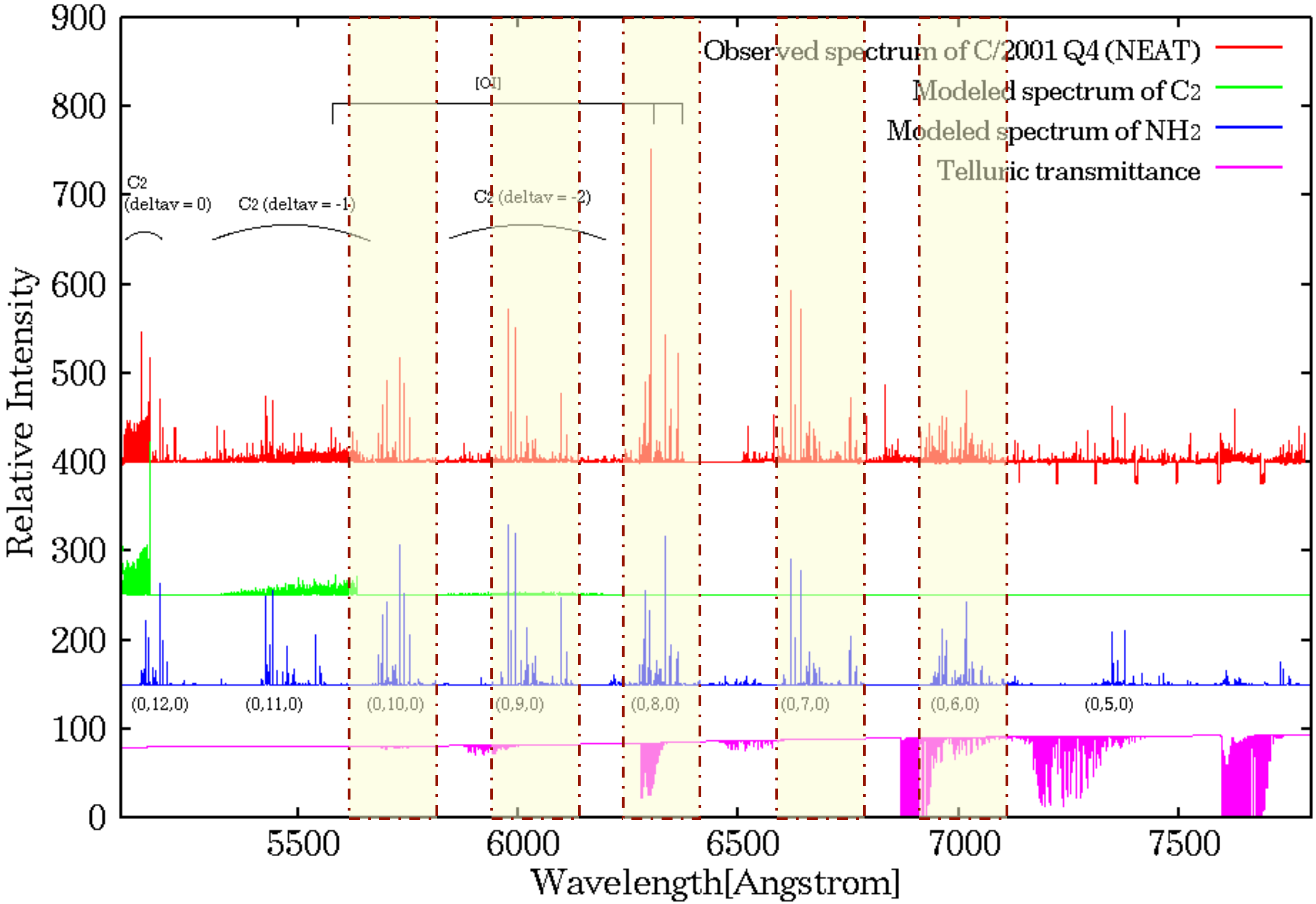
Shinnaka et al. (2010)

Example: C/2001 Q4 (NEAT)



→ OPR(NH_3) = 1.12

Shinnaka et al. (2011)


Observed spectrum of C/2001 Q4 (NEAT)
Modeled spectrum of C_2
Modeled spectrum of NH_2
Telluric transmittance
[OI]
C_2 (deltav = 0)
C_2 (deltav = -1)
C_2 (deltav = -2)
(0,12,0)
(0,11,0)
(0,10,0)
(0,9,0)
(0,8,0)
(0,7,0)
(0,6,0)
(0,5,0)
Relative Intensity
0
100
200
300
400
500
600
700
800
900
Wavelength[Angstrom]
5500
6000
6500
7000
7500

Multiple Determinations at Different Bands

Vibronic band	OPR of NH_2
(0,10,0)	2.94 ± 0.38
(0,9,0)	3.24 ± 0.06
(0,8,0)	3.20 ± 0.06
(0,7,0)	3.31 ± 0.05
(0,6,0)	3.16 ± 0.06
Weighted mean	3.23 ± 0.03

(Shinnaka et al. 2010)

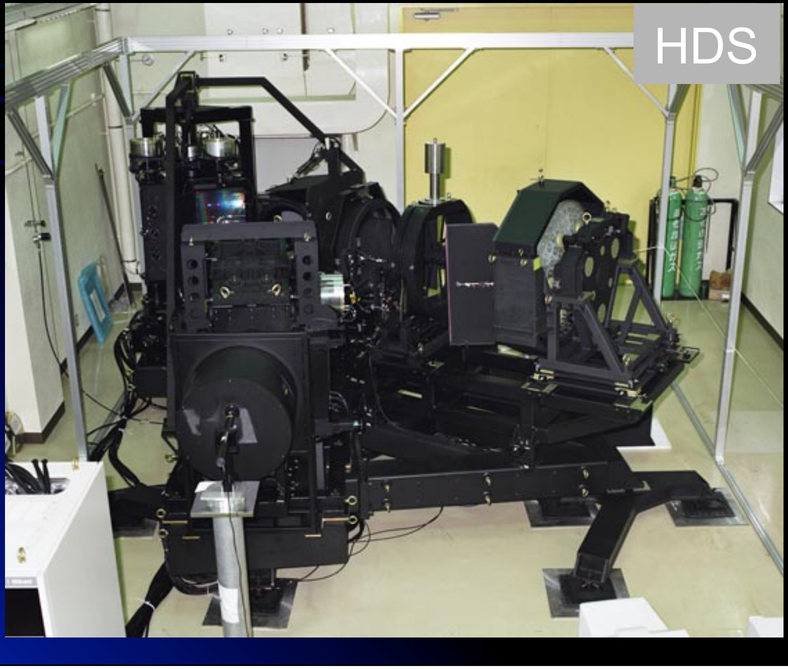
The OPR determined from the (0,9,0) band is accurate enough (since less contamination and good transmittance at this band).

Summary of our survey for OPRs of cometary ammonia (2001 – 2016)

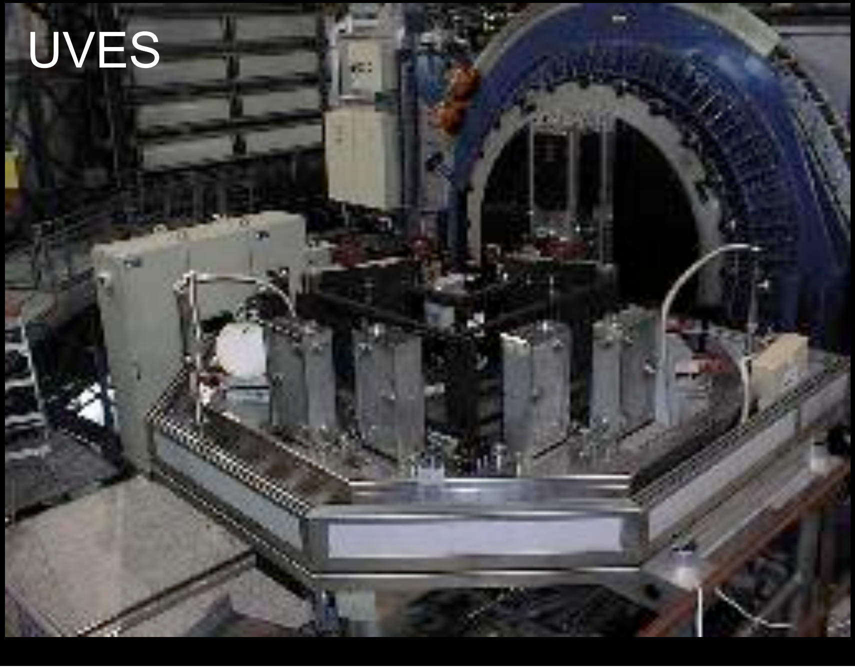
Observations were mainly made by 8-m telescopes: VLT & Subaru

Subaru Telescope

VLT



HDS



UVES

26 Comets in Our Survey


C/1995 O1


C/1999 S4


C/2001 A2


153P/Ikeya-Zhang


C/2000 WM1


C/2002 V1


C/2002 X5


C/2002 Y1


88P/Howell


C/2001 Q4


C/2002 T7

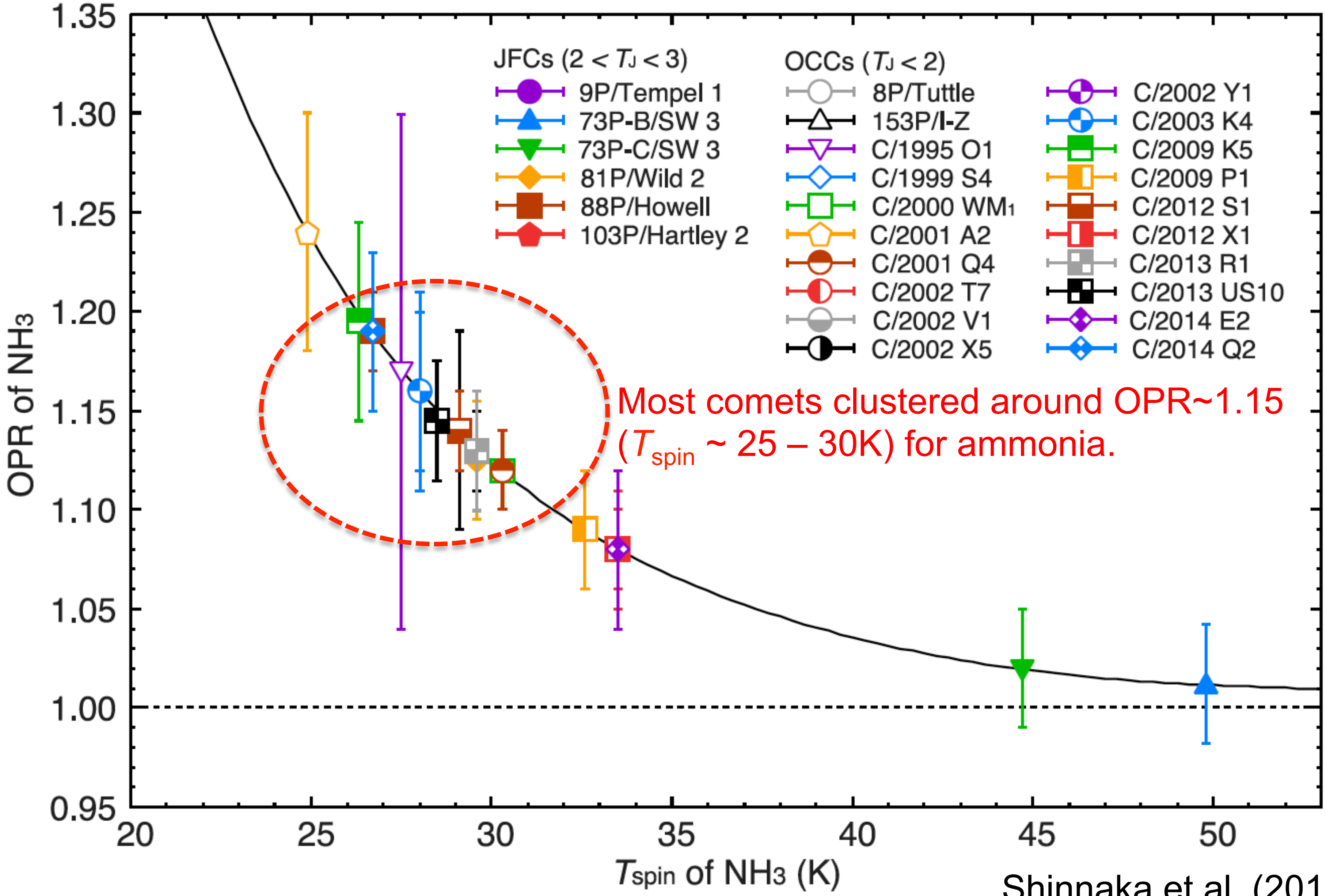

C/2003 K4


9P/Tempel 1


73P-B and -C/SW3


8P/Tuttle

OPRs of Ammonia in 26 Comets

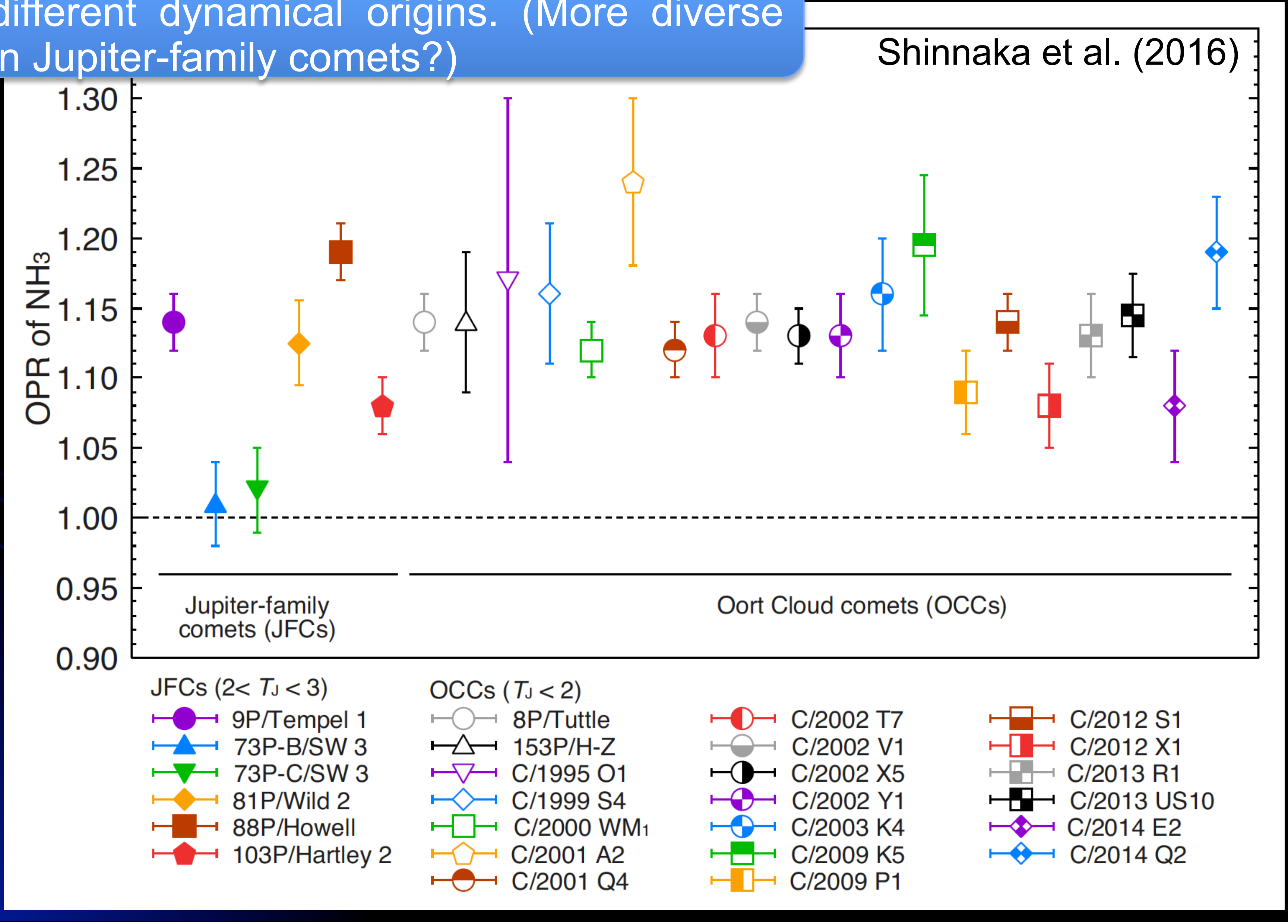


Most comets clustered around OPR~1.15 (T_{spin} ~ 25 – 30K) for ammonia.

Shinnaka et al. (2016)

OPRs of Ammonia in 26 Comets

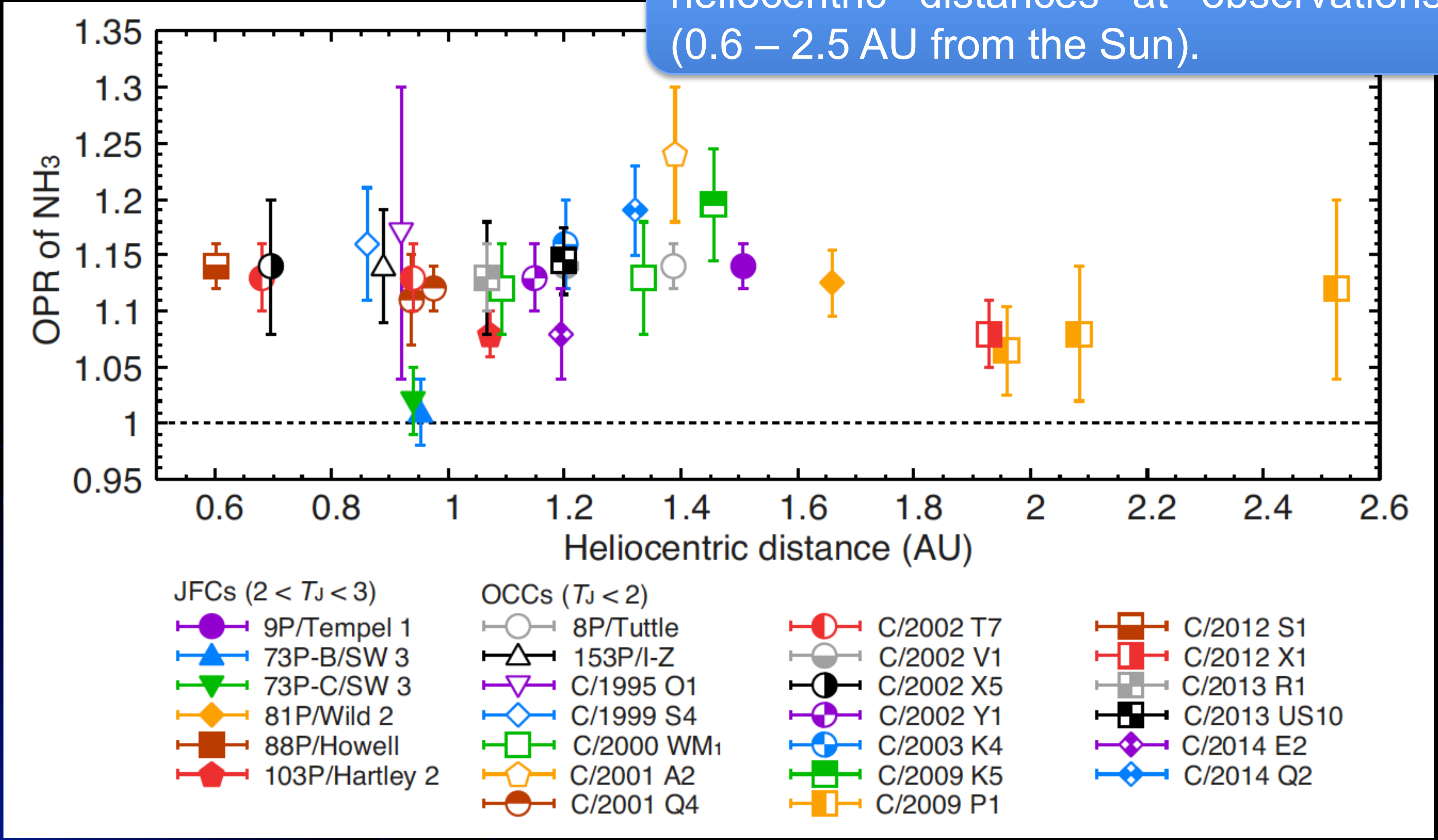
No clear difference in OPRs of NH_3 for different dynamical origins. (More diverse in Jupiter-family comets?)



Shinnaka et al. (2016)

OPRs of Ammonia in 26 Comets

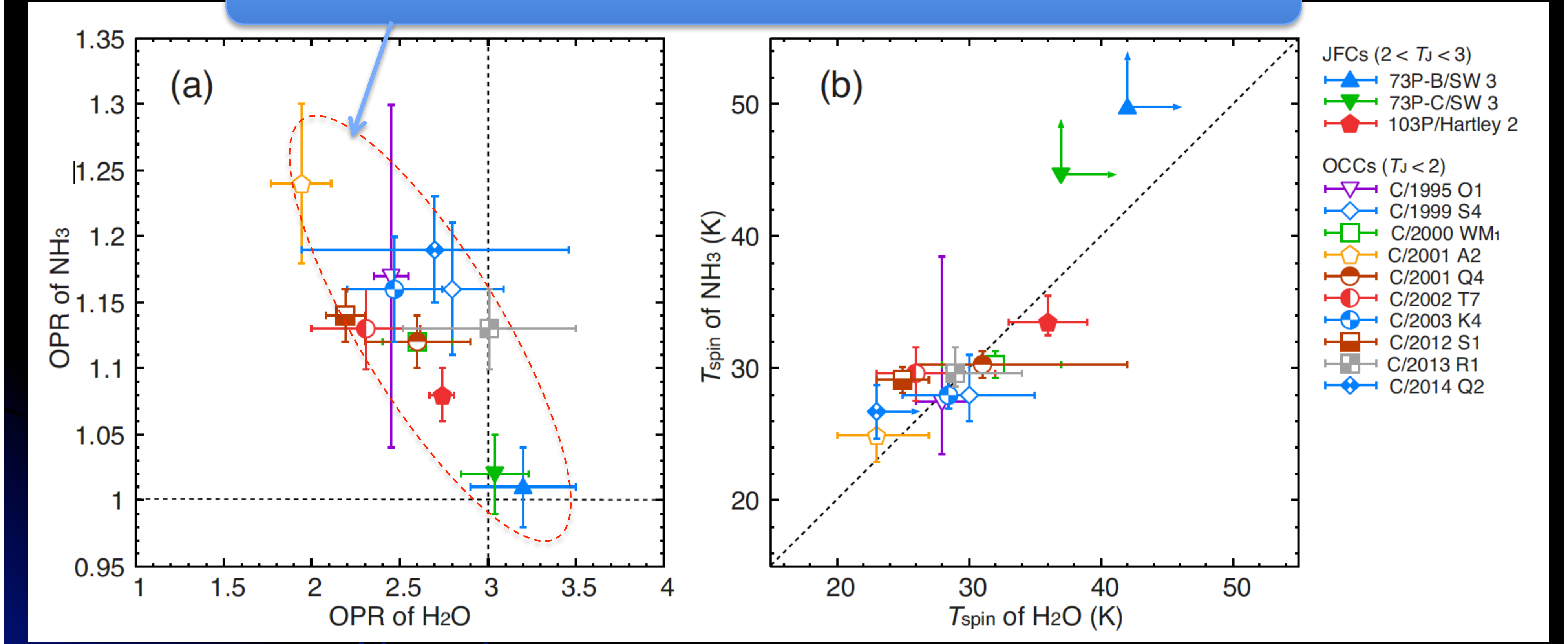
No clear trend in OPRs with respect to heliocentric distances at observations (0.6 – 2.5 AU from the Sun).



Shinnaka et al. (2016)

OPRs of Ammonia in 26 Comets

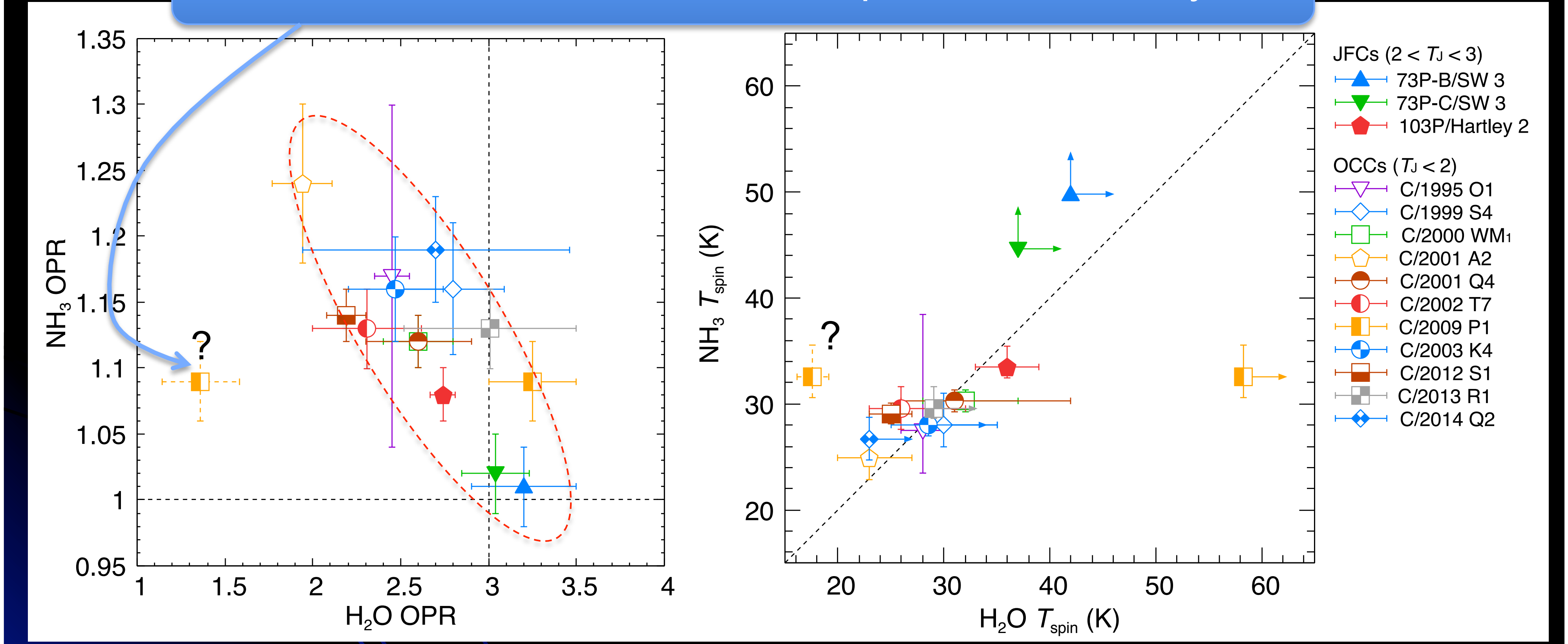
There is a trend in the plot of OPR_{H2O} and OPR_{NH3}.



Shinnaka et al. (2016)

OPRs of Ammonia in 26 Comets

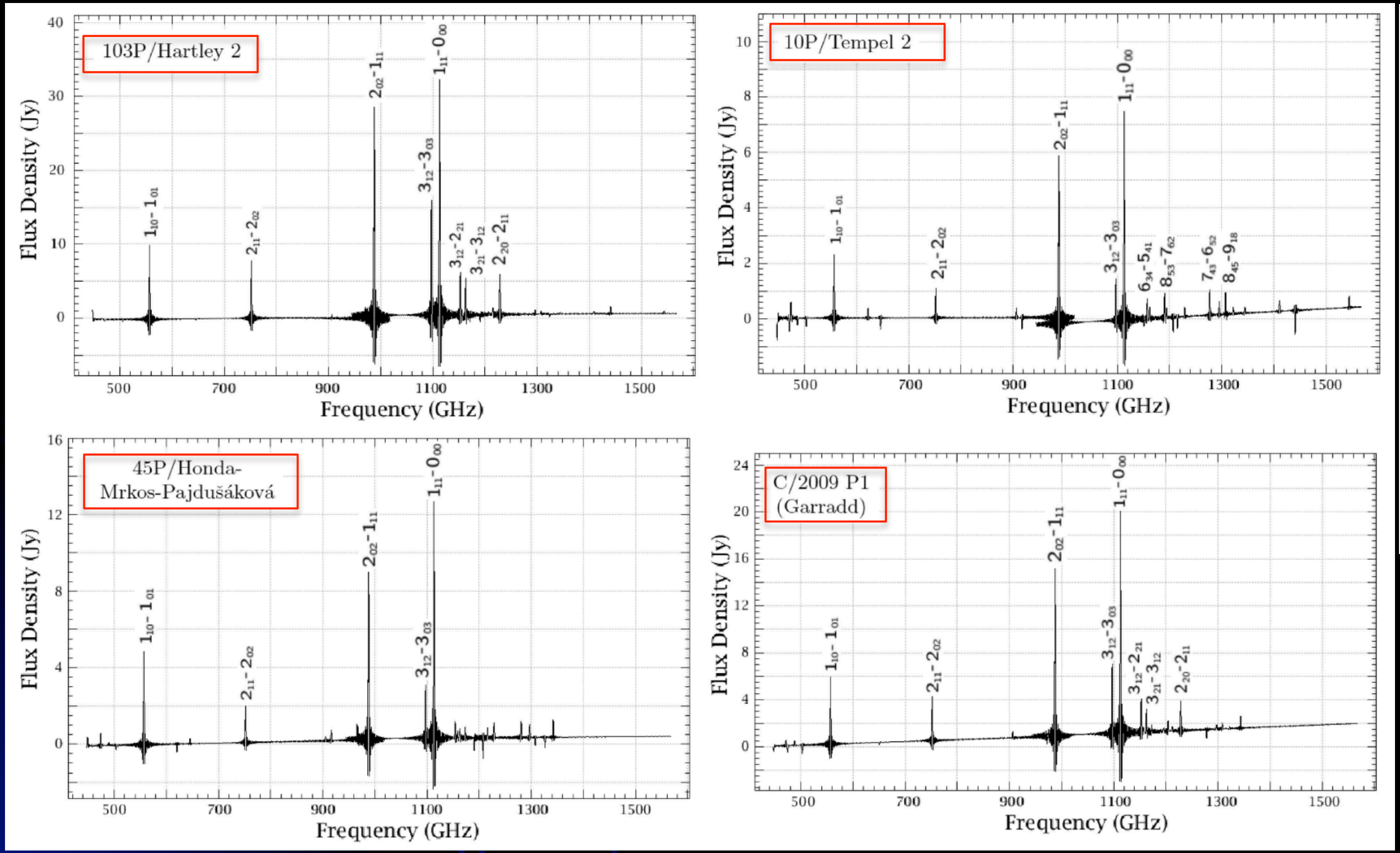
However, if we add the new data published recently …



Recent reports of OPR (H_2O) by Herschel/SPIRE observations

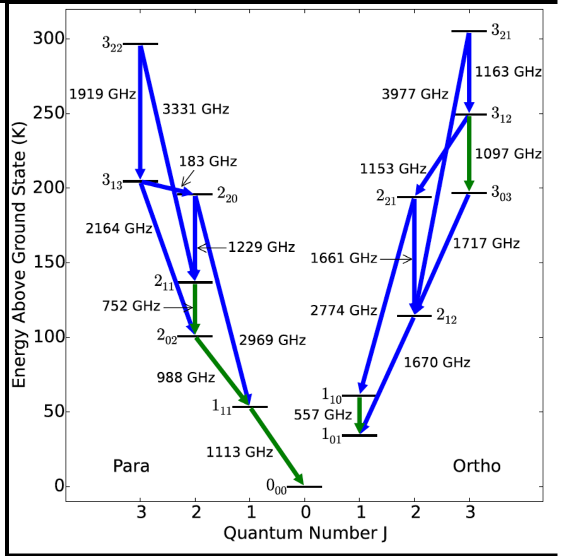
OPR(H_2O)=2.44±0.71

OPR(H_2O)=1.59±0.23



OPR(H_2O)=2.00±0.30

OPR(H_2O)=1.36±0.22

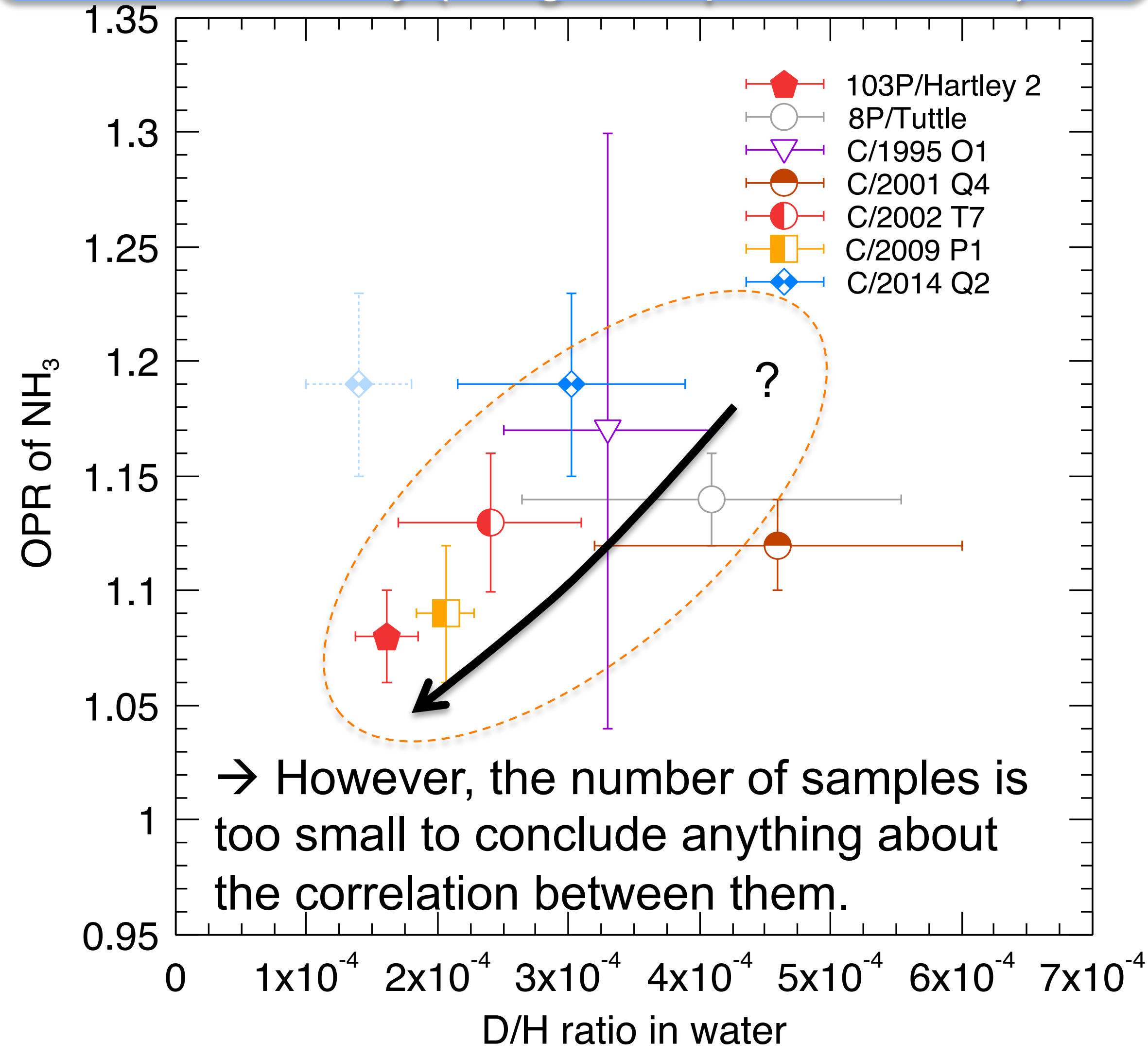


Observations of pure rotational lines of water.

→ Lower values for 4 comets observed by Herschell / SPIRE

OPRs of Ammonia in 26 Comets

Smaller D/H ratios of water for NH_3 OPRs closer to unity (a high-temperature limit)?

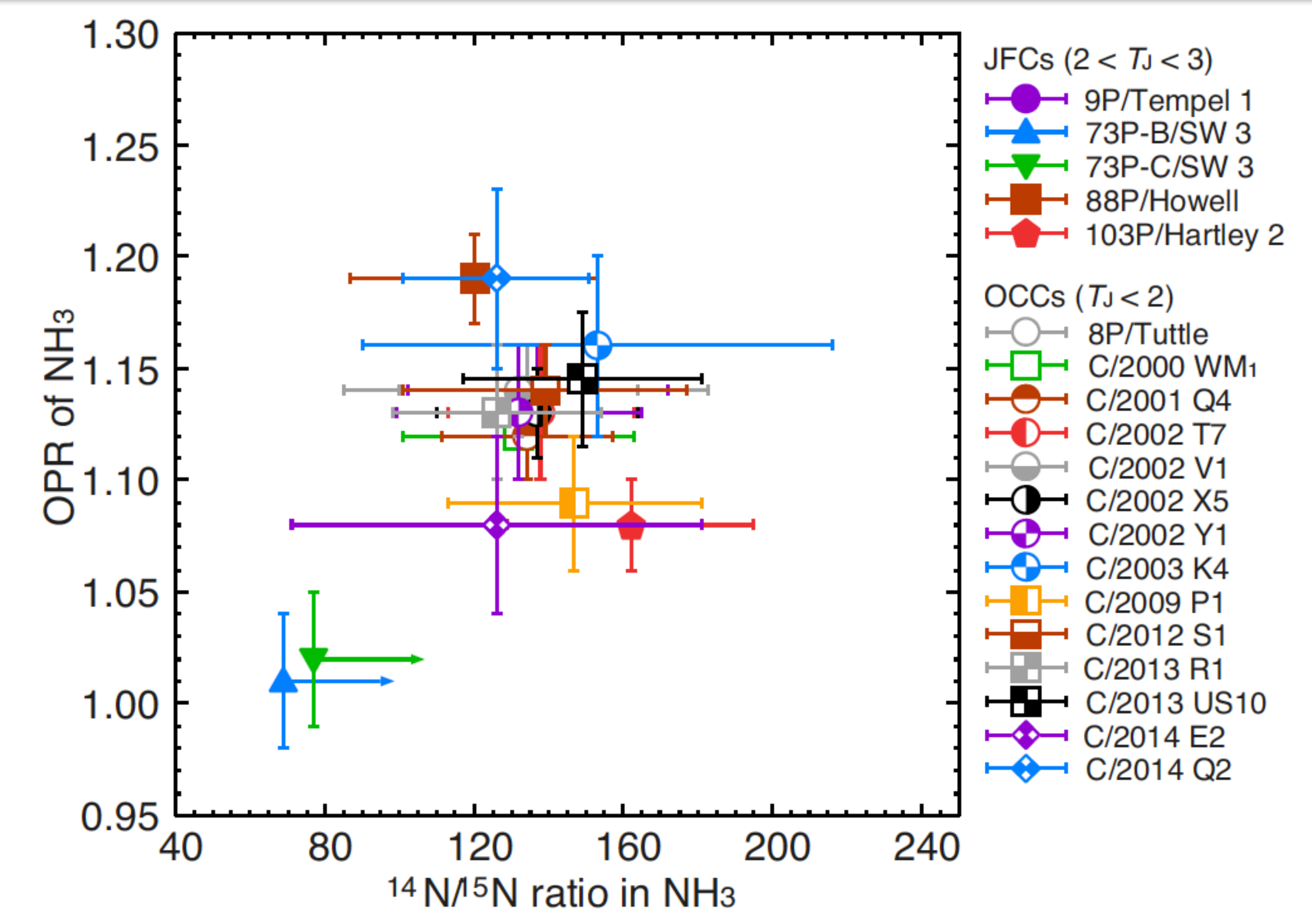


→ However, the number of samples is too small to conclude anything about the correlation between them.

Shinnaka et al. (2016)

OPRs of Ammonia in 26 Comets

No clear trends between OPRs and $^{14}N/^{15}N$ ratios in NH_3.

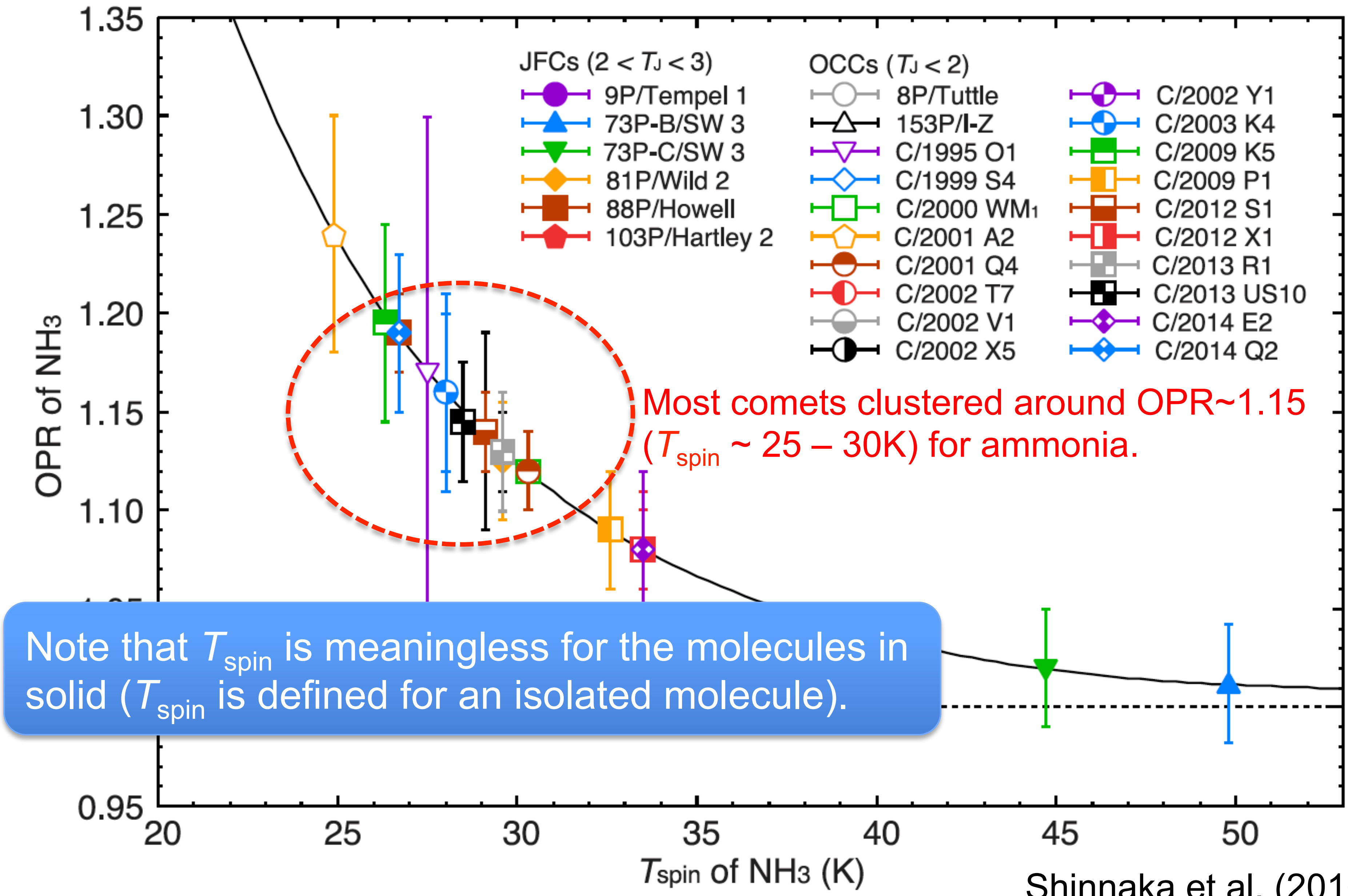


^{15}N-fractionation in cometary NH_3 is ~3 compared to the solar value (441±5).

Shinnaka et al. (2016)

Discussions
– the meaning of OPRs –

T_{spin} is old memory?

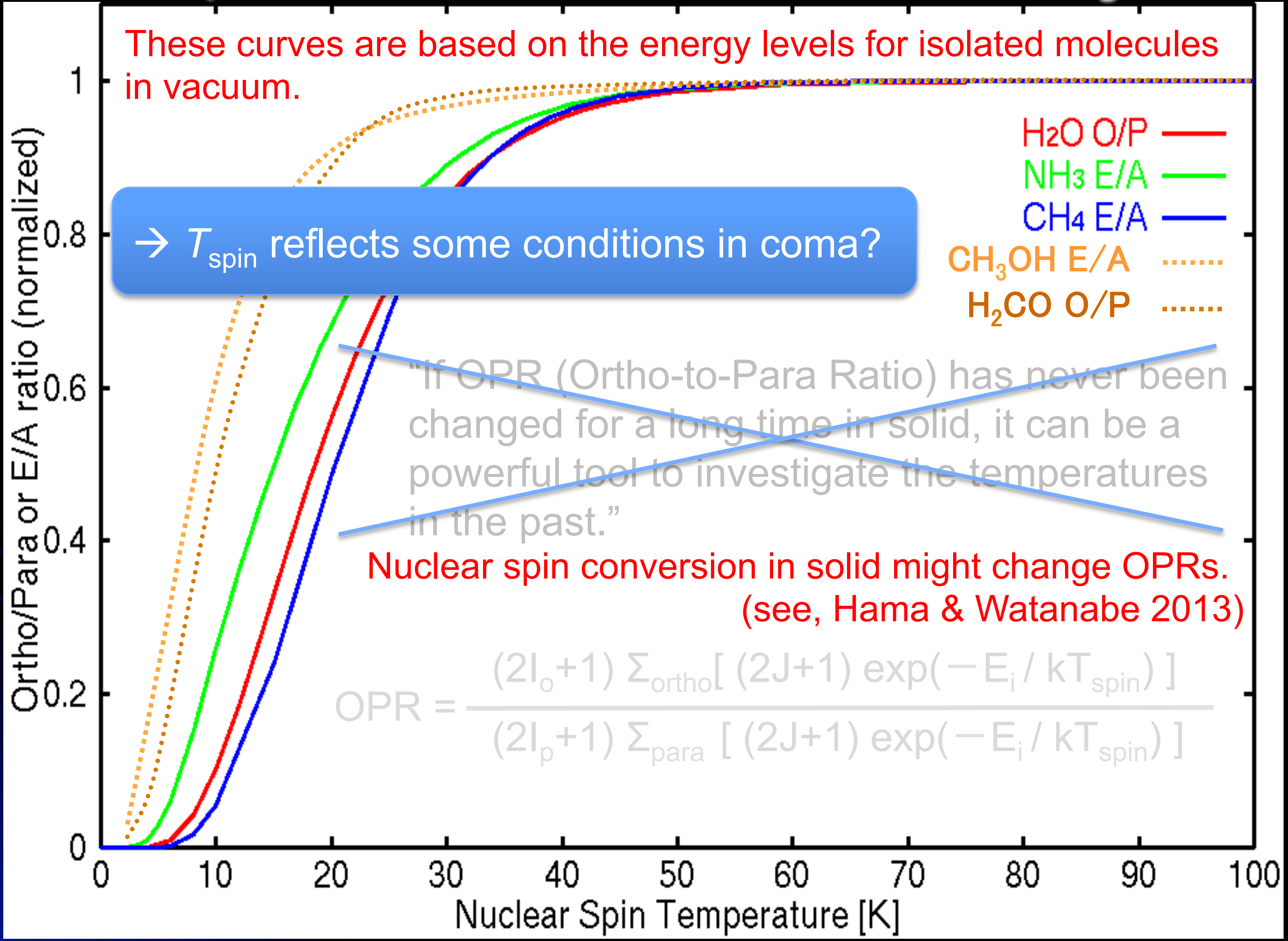


Most comets clustered around OPR~1.15 (T_{spin} ~ 25 – 30K) for ammonia.

Note that T_{spin} is meaningless for the molecules in solid (T_{spin} is defined for an isolated molecule).

Shinnaka et al. (2016)

T_{spin} is not old memory!?



These curves are based on the energy levels for isolated molecules in vacuum.

→ T_{spin} reflects some conditions in coma?

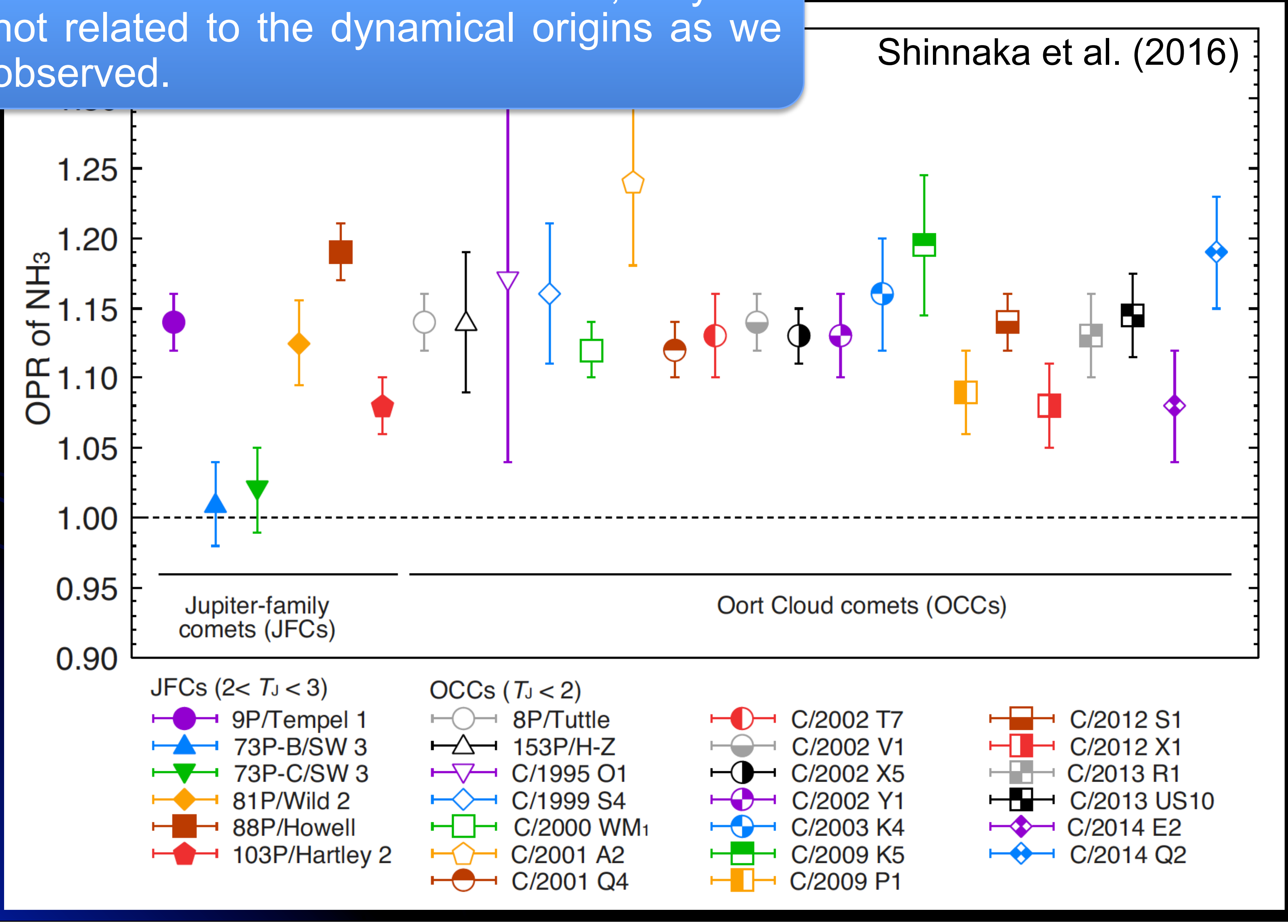
~~"If OPR (Ortho-to-Para Ratio) has never been changed for a long time in solid, it can be a powerful tool to investigate the temperatures in the past."~~

Nuclear spin conversion in solid might change OPRs.
(see, Hama & Watanabe 2013)

$$\mathrm{OPR} = \frac{(2I_o+1)\,\Sigma_{ortho}[\,(2J+1)\exp(-E_i/kT_{spin})\,]}{(2I_p+1)\,\Sigma_{para}\,[\,(2J+1)\exp(-E_i/kT_{spin})\,]}$$

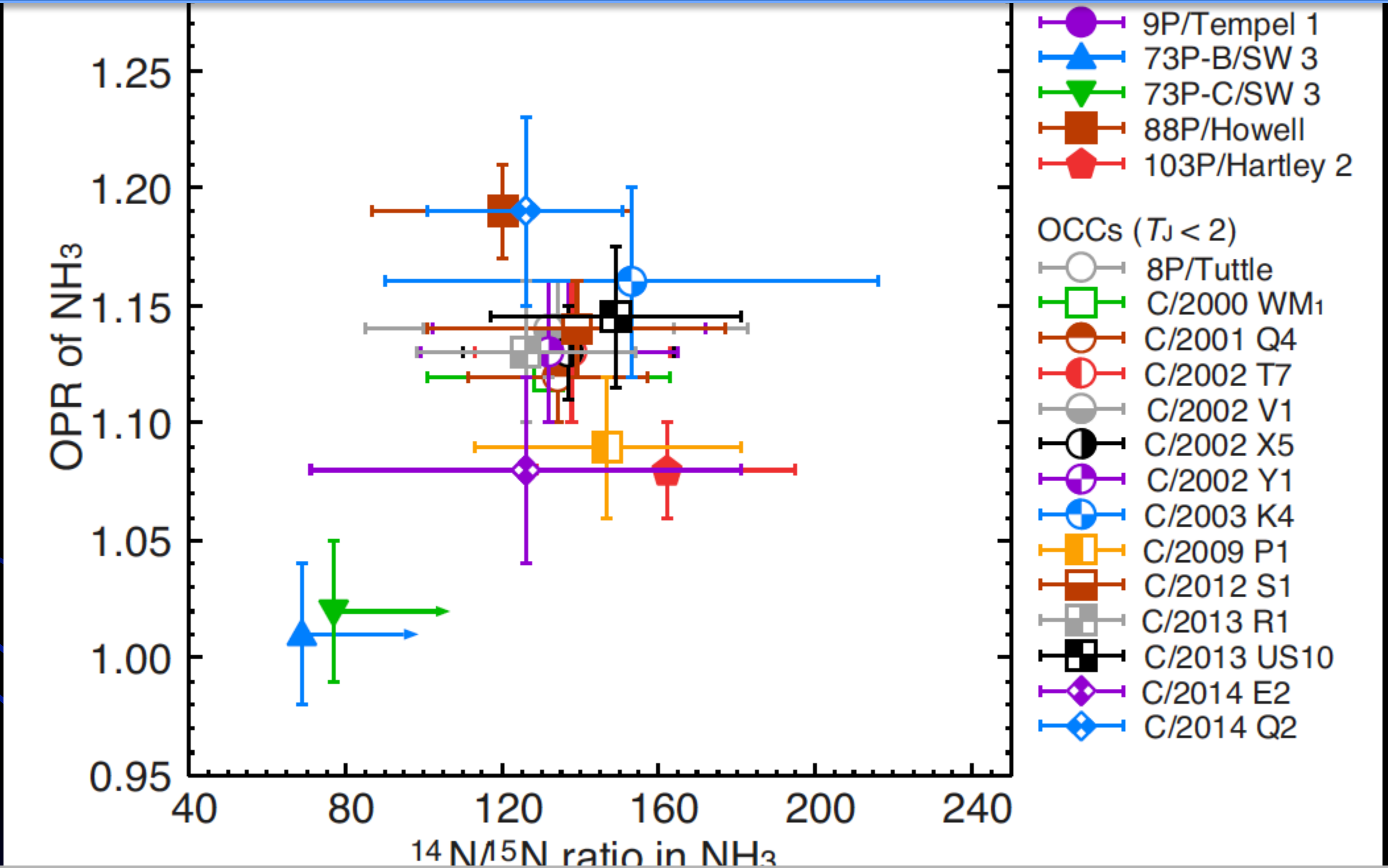
OPRs of Ammonia in 26 Comets

If OPRs were determined in coma, they are not related to the dynamical origins as we observed.


Shinnaka et al. (2016)

Ammonia formation at ~10K?

The observed ^{15}N-fractionation of NH_3 in comet ($^{14}N/^{15}N$ ~ 135 compared to the solar value 441±5) suggesting the formation of NH_3 by the low-temperature chemistry at ~10 K (e.g., Rodgers & Charnley 2008).



However, we cannot ruled out the possibility for the NH_3 formation in warm conditions. The ^{15}N-fractionation of NH_3 might be caused by selective photo-dissociation of N_2 (Furi & Marty 2015) even at higher temperatures than ~10 K.

OPR is not a indicator for conditions at molecular formation

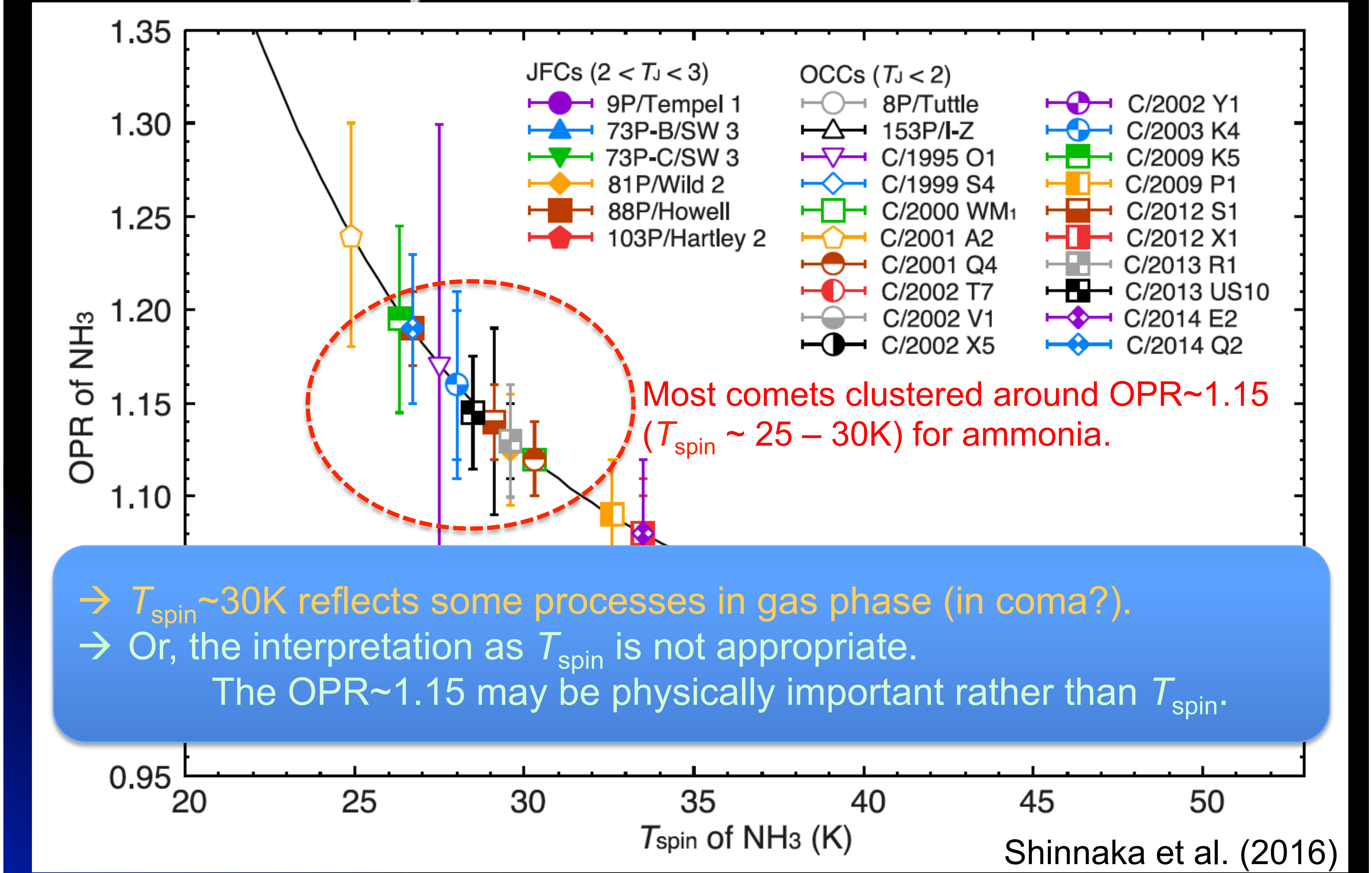
- ✓ Recent laboratory works for OPRs of water (e.g., Hama & Watanabe 2013; Hama et al. 2016) demonstrated OPR~3 for water molecules just after desorption from ice.
  → Those laboratory studies suggest the existence of 'nuclear spin conversion' processes in cometary coma, at least for water molecules (OPR_{H2O}~2.5 – 3).

- ✓ NH_3 molecules in comets could have OPR~1 just after their desorption (the rotational motion is also inhibited in cometary ices as water, and nuclear-spin conversion could occur due to small energy differences between ortho and para energy levels of NH_3 in solid).

- ✓ Cometary NH_3 might form at ~10K (not ~30K as indicated by T_{spin}) based on the measurements of $^{14}N/^{15}N$ ratios in NH_3. If so, the OPRs are not old memories.

→ "Is the nuclear spin conversion for ammonia possible in cometary coma?"
→ "Is the interpretation as T_{spin} appropriate?"
The OPR~1.15 may be physically important rather than T_{spin}.

T_{spin} is old memory?



Most comets clustered around OPR~1.15 (T_{spin} ~ 25 – 30K) for ammonia.

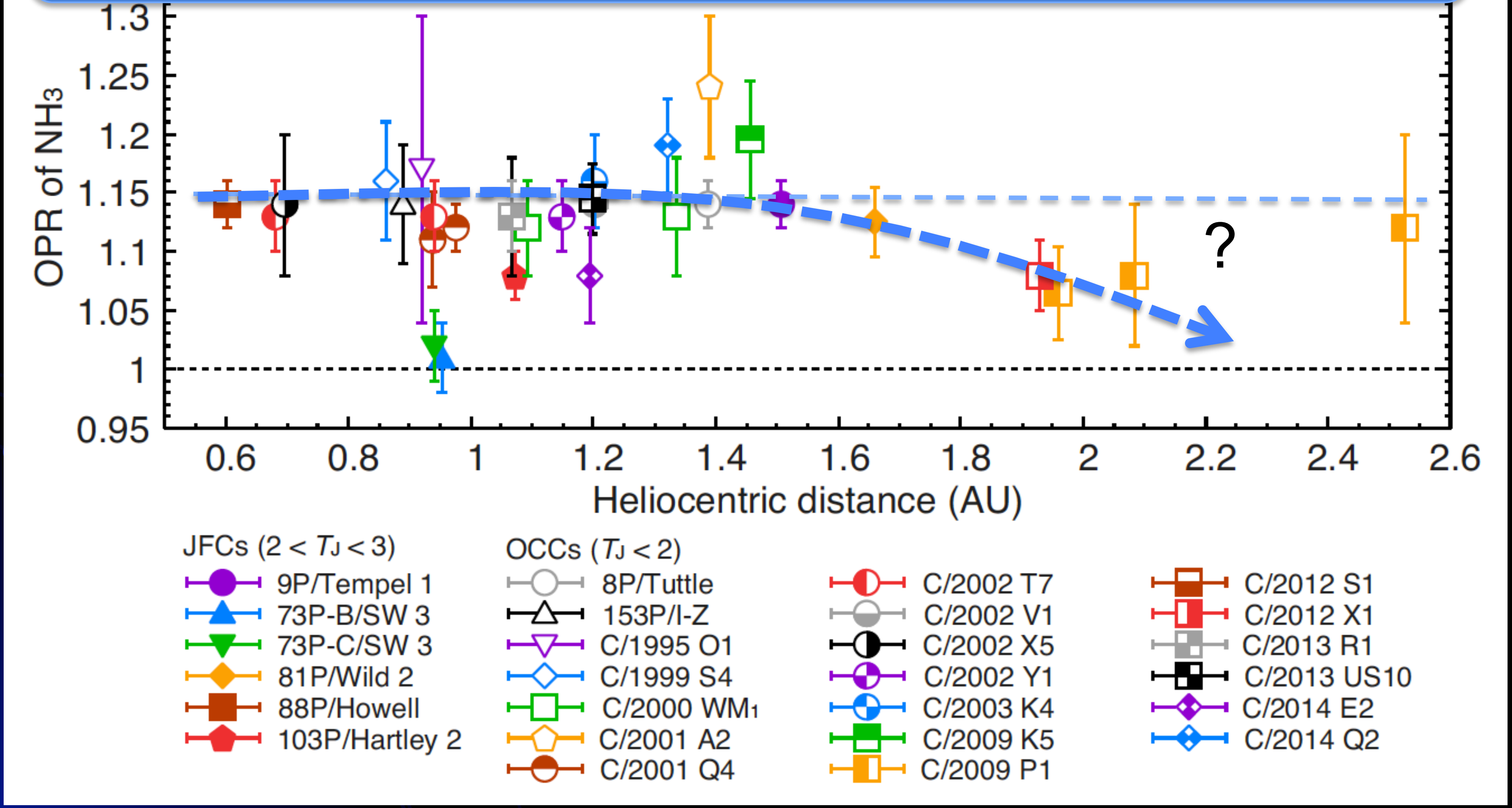
Shinnaka et al. (2016)

→ T_{spin}~30K reflects some processes in gas phase (in coma?).

→ Or, the interpretation as T_{spin} is not appropriate.
The OPR~1.15 may be physically important rather than T_{spin}.

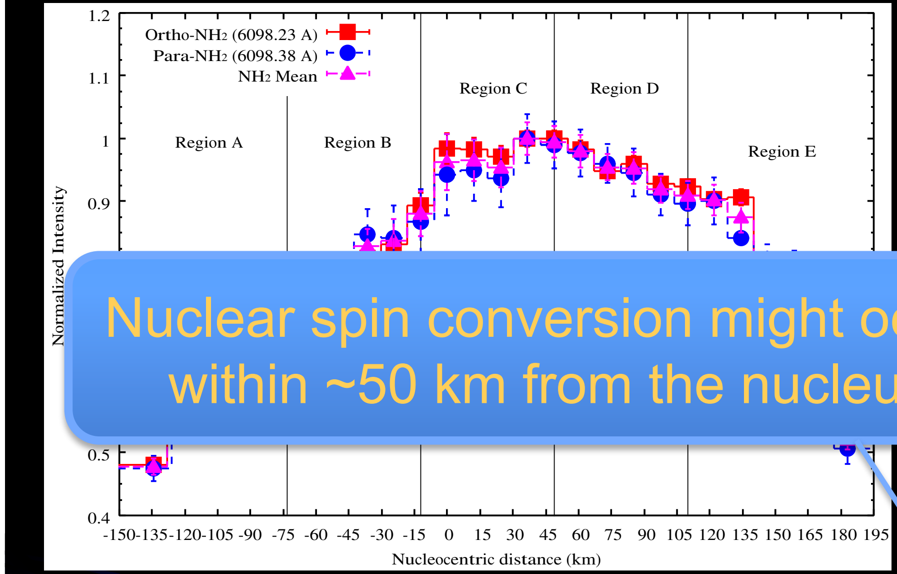
Nuclear spin conversion in comets

Nuclear spin conversions might occur through the processes not sensitive to the distances from the Sun (at least, 0.6 – 1.5 AU)



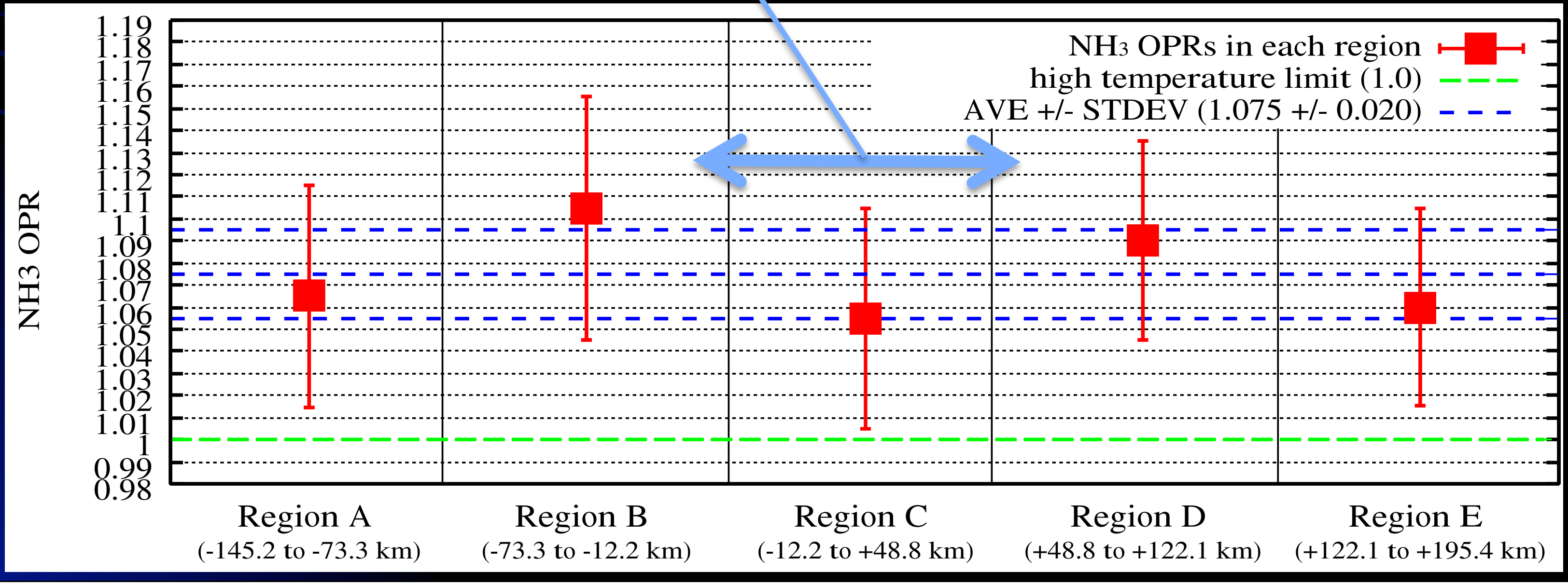
Shinnaka et al. (2016)

Nuclear Spin Conversion of NH_3 in the inner coma (103P/Hartley 2)

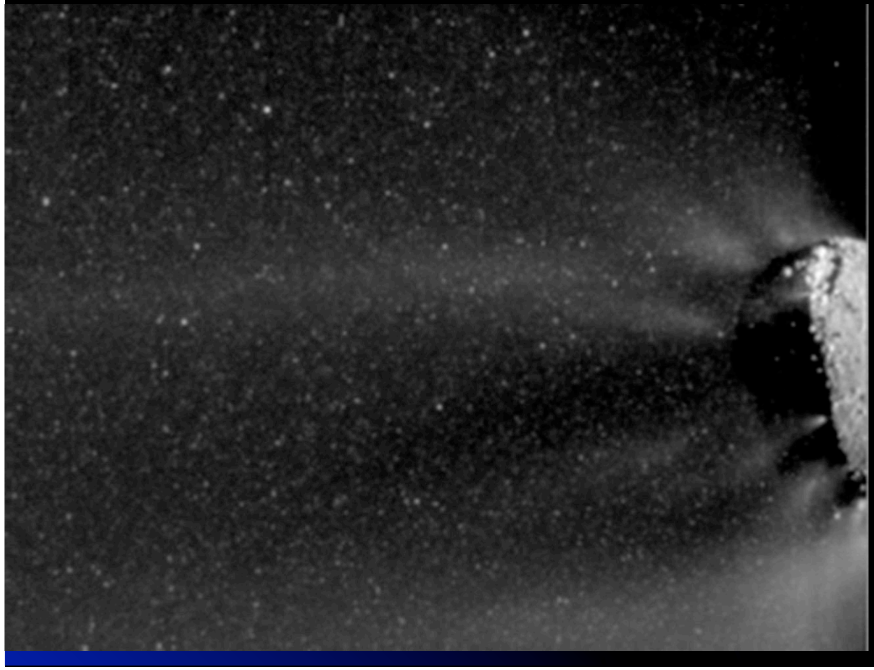


Nuclear spin conversion might occur within ~50 km from the nucleus

Region	NH_3 OPR
A (–145.2 to –73.3 km)	1.07 ± 0.05
B (–73.3 to –12.2 km)	1.11 +0.05/–0.06
-12.2 to +48.8 km)	1.055 ± 0.05
+48.8 to +122.1 km)	1.09 ± 0.05
E (+122.1 to +195.4 km)	1.06 ± 0.05
Sum of all regions	1.065±0.03 (38+6/-4)

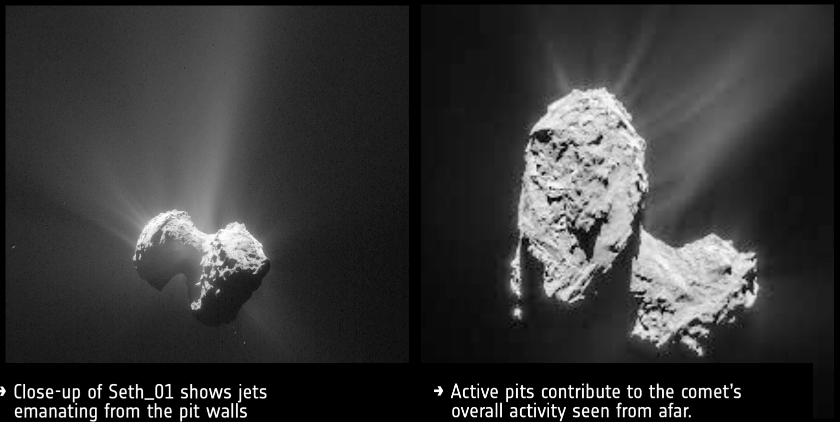


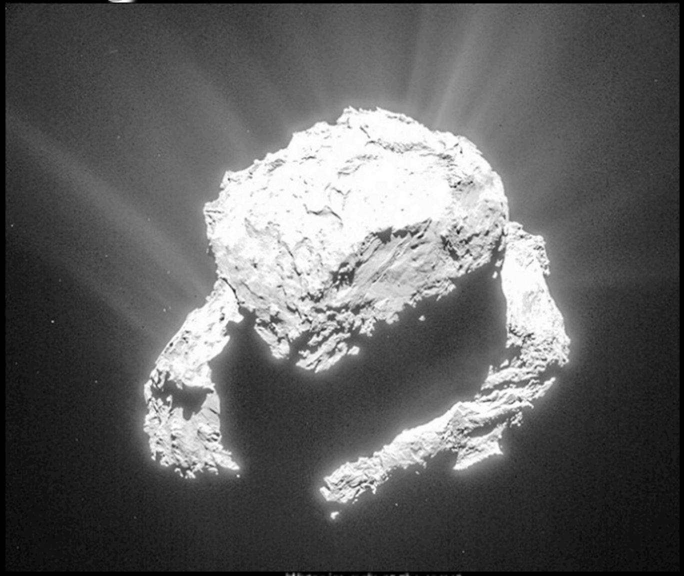
Icy grains near the nucleus of 103P/Hartley 2 seen by EPOXI



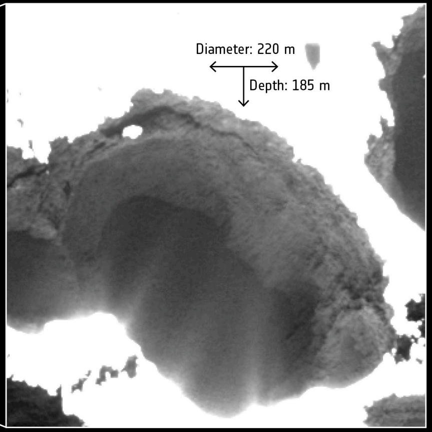
Most water sublimated from icy grains (chunks) in comet 103P/Hartley 2 as observed by EPOXI spacecraft.

Quite different for 67P/C-G and other cometary nuclei

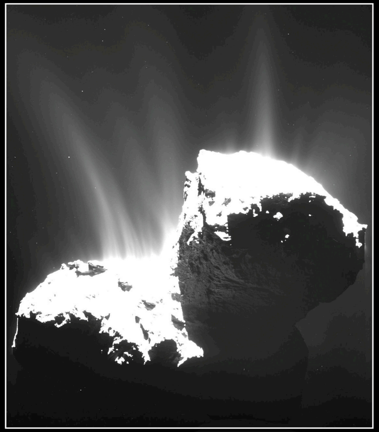




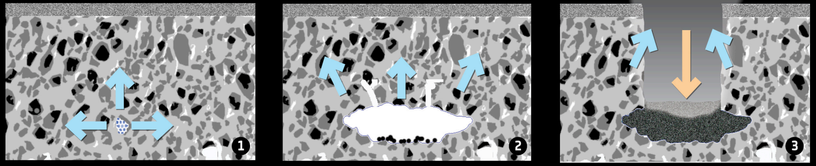
→ Close-up of Seth_01 shows jets emanating from the pit walls



→ Active pits contribute to the comet's overall activity seen from afar.

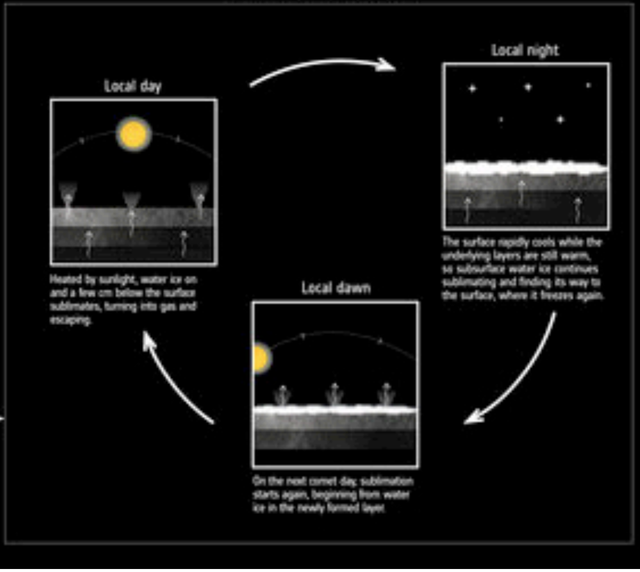


→ Pit formation via sinkhole collapse



1. Heat causes subsurface ices to sublimate (blue arrows), forming a cavity (2). When the ceiling becomes too weak to support its own weight, it collapses, creating a deep, circular pit (3, orange arrow). Newly exposed material in the pit walls sublimates, accounting for the observed activity (3, blue arrows).

Water ice cycle at the comet



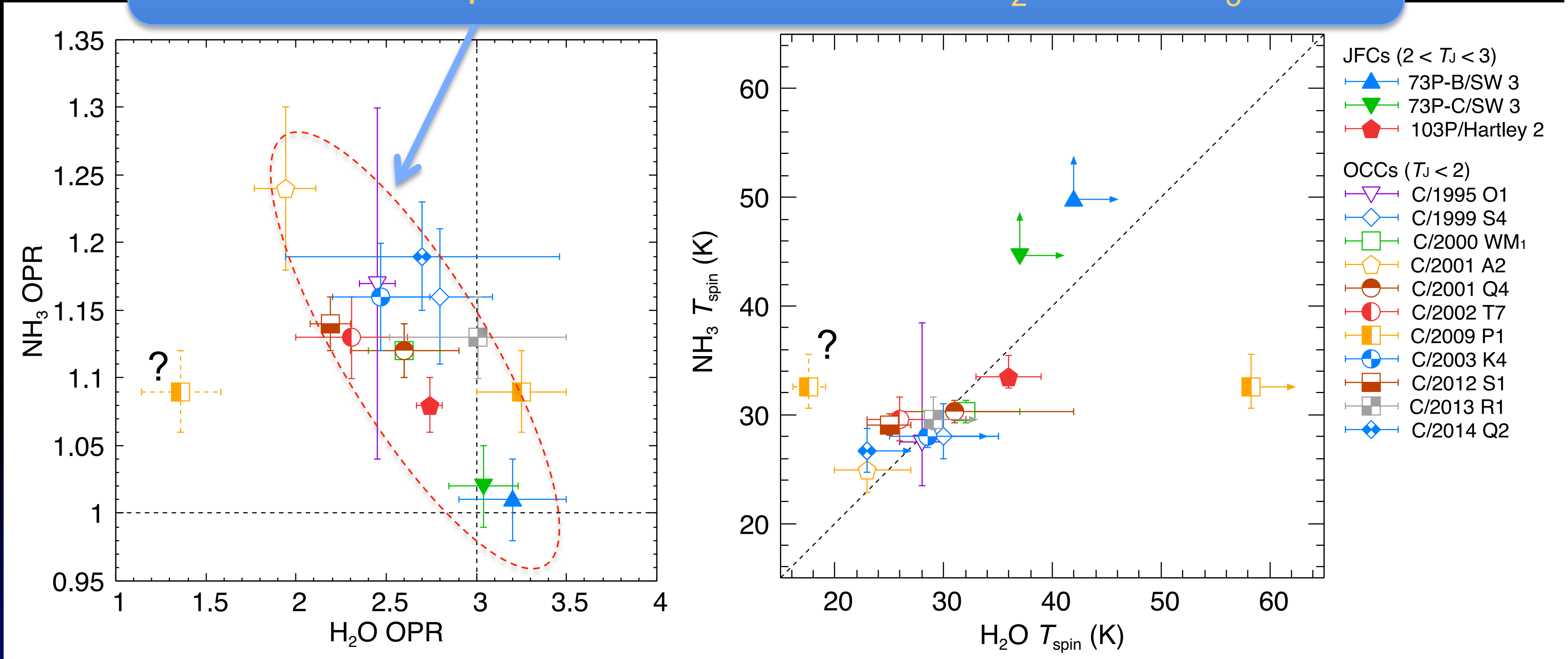
Heated by sunlight, water ice on and a few cm below the surface sublimates, turning into gas and escaping.

The surface rapidly cools while the underlying layers are still warm, so subsurface water ice continues sublimating and finding its way to the surface, where it freezes again.

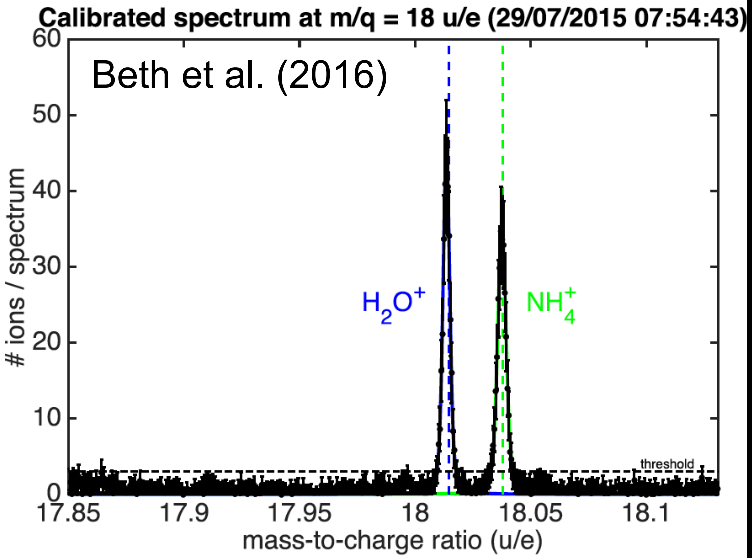
On the next comet day, sublimation starts again, beginning from water ice in the newly formed layer.

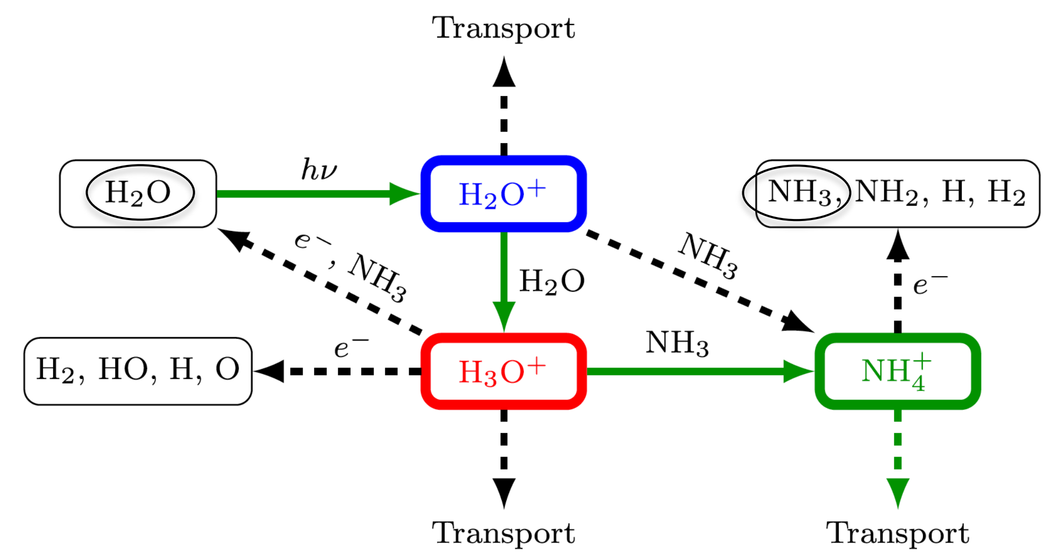
Correlation between OPRs of H_2O and NH_3

This trend for OPR_{H2O} and OPR_{NH3} may suggest some chemical processes related to both H_2O and NH_3.



First *in situ* detection of NH_4^+ in 67P/C-G by Rosetta/ROSINA

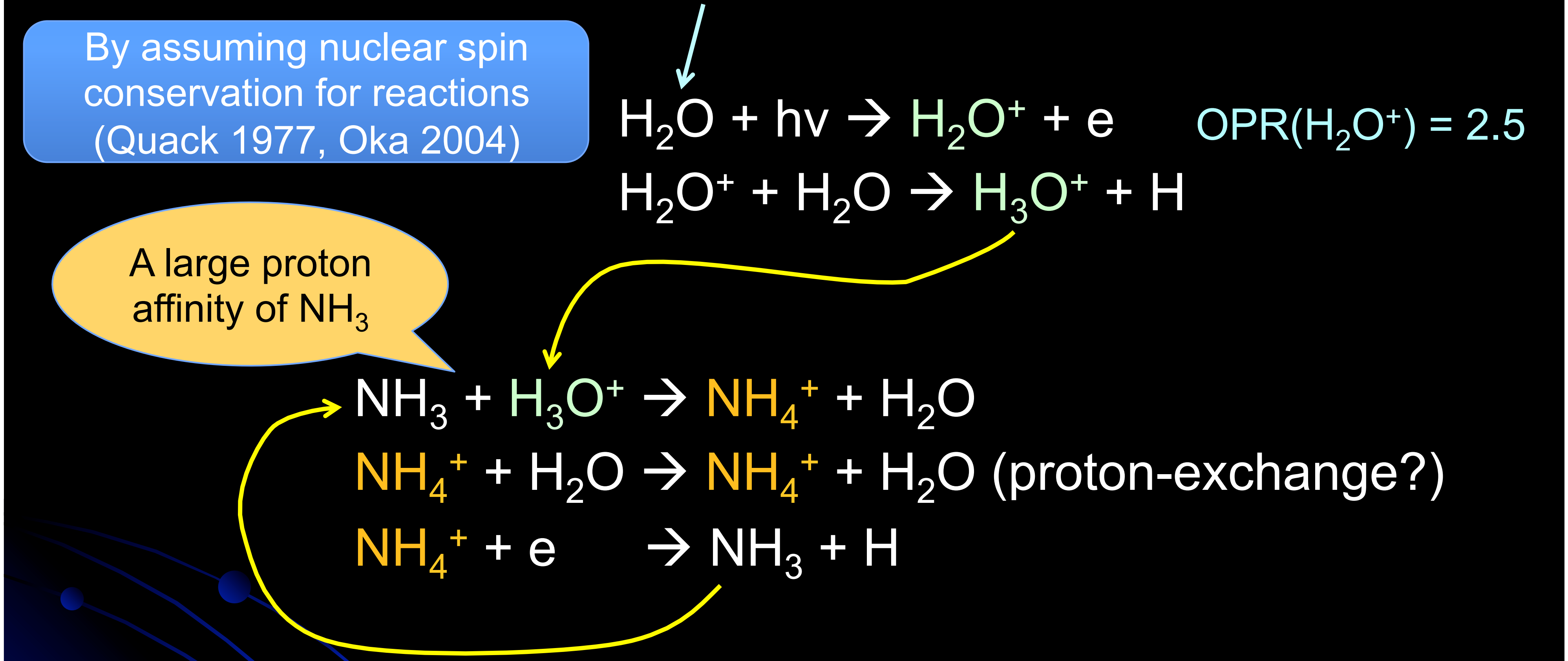




Larger proton-affinity of NH_3 than H_2O.

Species	Proton affinity (eV)
HO	6.16
H_2O	7.17
H_2S	7.32
H_2CO, HCN	7.40
HCOOH	7.70
CH_3OH	7.83
HCNO	7.87
HNC	8.02
NH_3	8.86

In the case of $n(H_2O) >> n(NH_3)$ in cometary coma (NH_3/H_2O ~1%)
and $OPR(H_2O) = 2.5$ (o-p conversion is assumed for water)



By assuming nuclear spin conservation for reactions (Quack 1977, Oka 2004)

$H_2O + h\nu \rightarrow H_2O^+ + e$ $\quad OPR(H_2O^+) = 2.5$

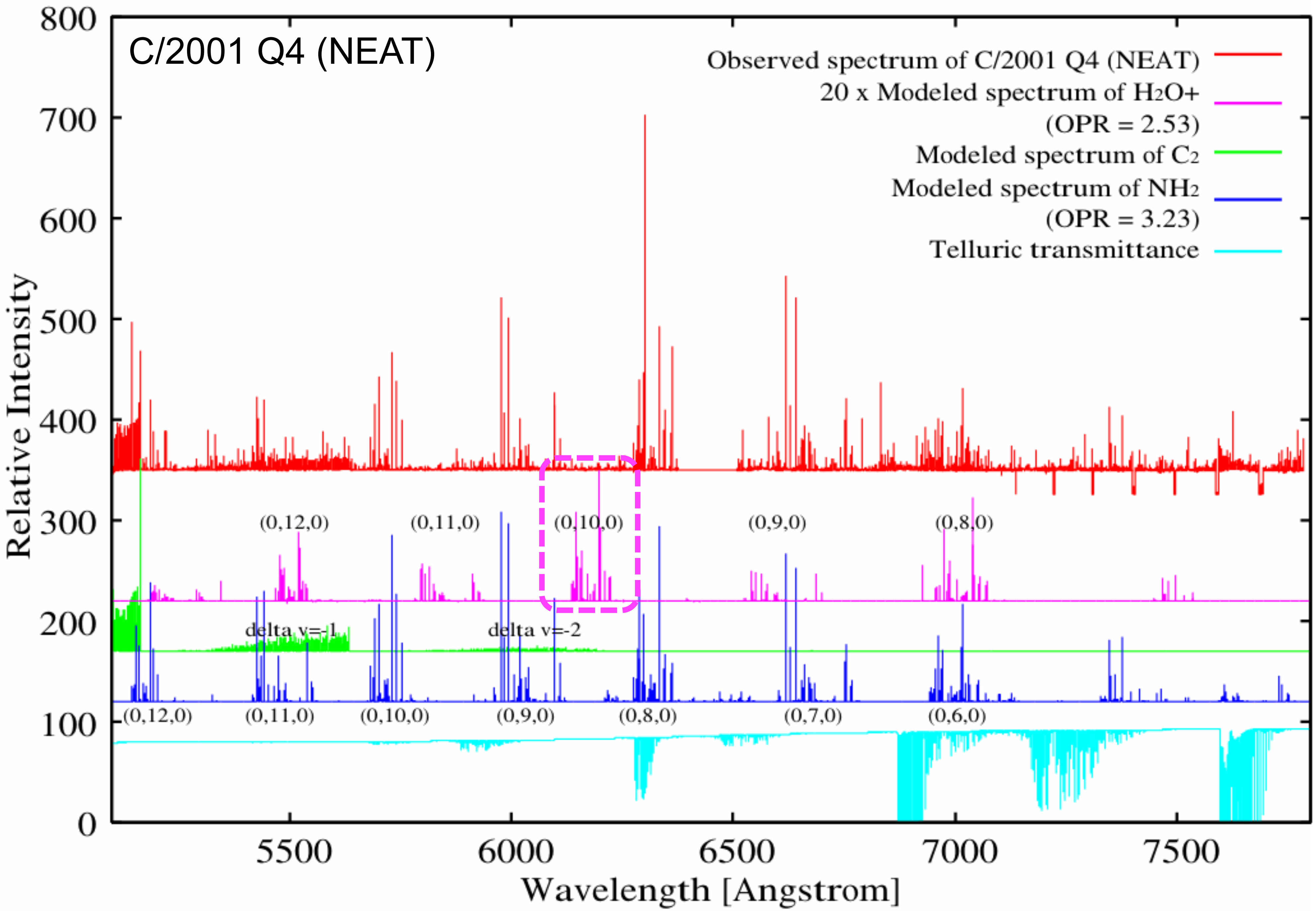
$H_2O^+ + H_2O \rightarrow H_3O^+ + H$

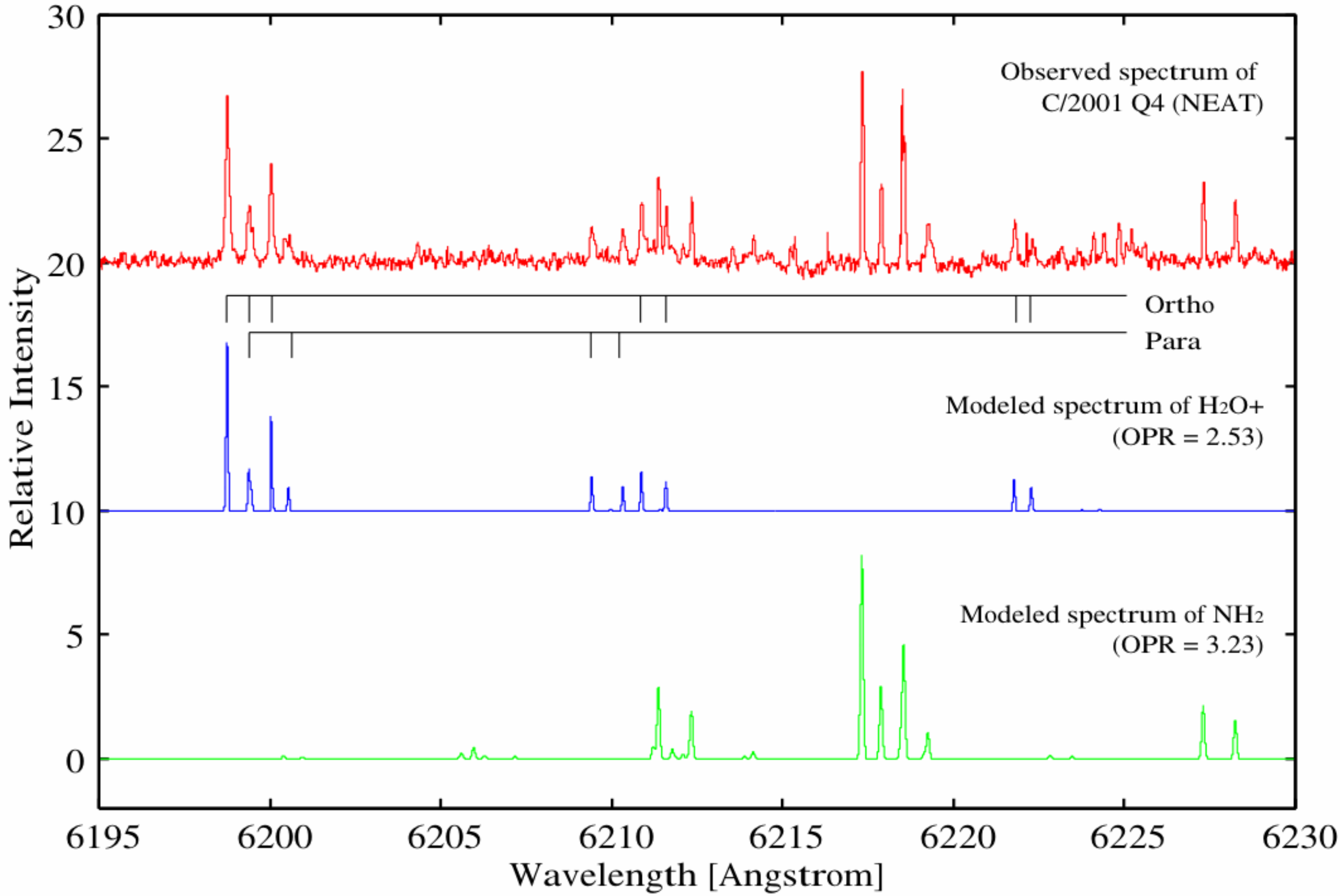
A large proton affinity of NH_3

$NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$

$NH_4^+ + H_2O \rightarrow NH_4^+ + H_2O$ (proton-exchange?)

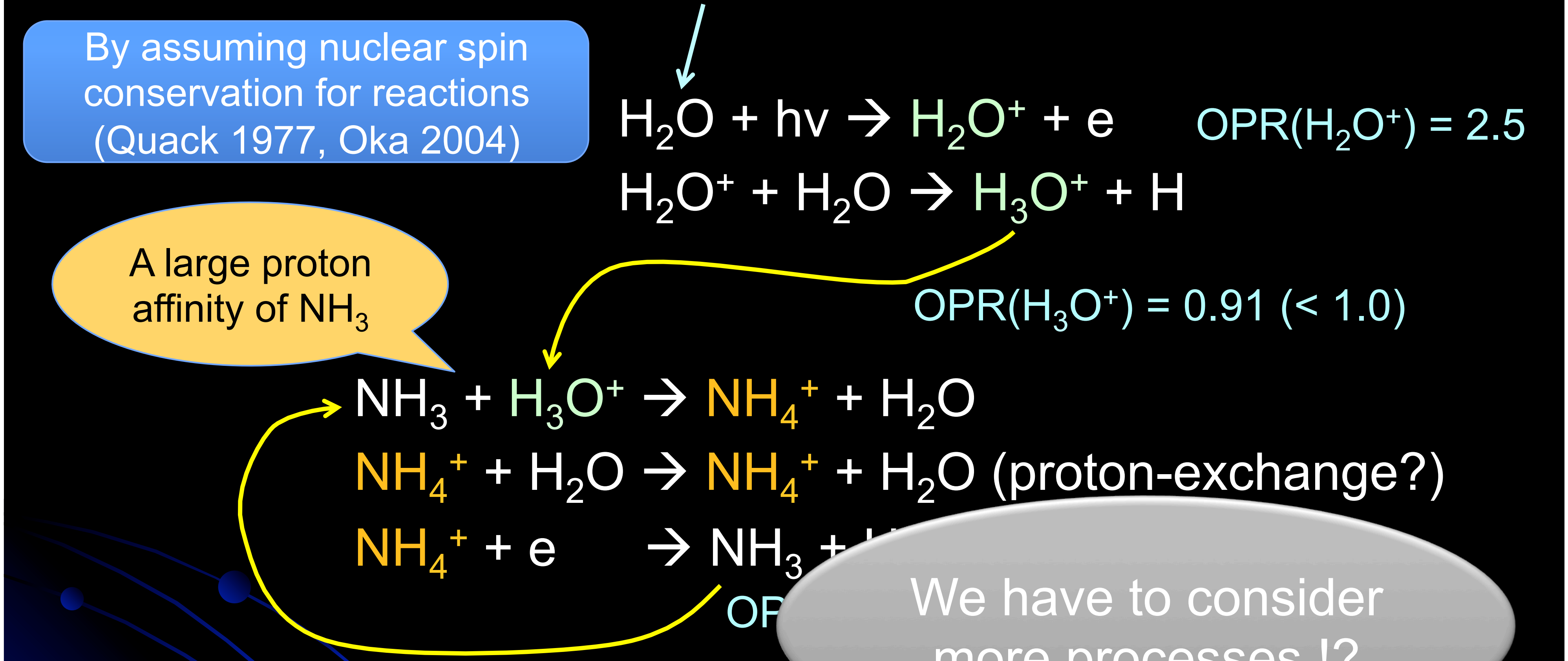
$NH_4^+ + e \rightarrow NH_3 + H$


C/2001 Q4 (NEAT)
Observed spectrum of C/2001 Q4 (NEAT)
20 x Modeled spectrum of H2O+ (OPR = 2.53)
Modeled spectrum of C2
Modeled spectrum of NH2 (OPR = 3.23)
Telluric transmittance
(0,12,0)
(0,11,0)
(0,10,0)
(0,9,0)
(0,8,0)
delta v=-1
delta v=-2
(0,12,0)
(0,11,0)
(0,10,0)
(0,9,0)
(0,8,0)
(0,7,0)
(0,6,0)
Relative Intensity
0
100
200
300
400
500
600
700
800
5500
6000
6500
7000
7500
Wavelength [Angstrom]



The OPR of water derived from H_2O^+ is consistent with the direct measurement in the near-infrared in some cases.

In the case of $n(H_2O) >> n(NH_3)$ in cometary coma (NH_3/H_2O ~1%)
and $OPR(H_2O) = 2.5$ (o-p conversion is assumed for water)



By assuming nuclear spin conservation for reactions (Quack 1977, Oka 2004)

$H_2O + h\nu \rightarrow H_2O^+ + e$ $OPR(H_2O^+) = 2.5$

$H_2O^+ + H_2O \rightarrow H_3O^+ + H$

$OPR(H_3O^+) = 0.91$ (< 1.0)

A large proton affinity of NH_3

$NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$

$NH_4^+ + H_2O \rightarrow NH_4^+ + H_2O$ (proton-exchange?)

$NH_4^+ + e \rightarrow NH_3 +$

OP

We have to consider more processes !?

OPR(NH_3) will decrease through this cycle value (~0.97), almost unity but a little bit smaller, if we assume the nuclear spin conservation for the reactions (Quack 1977, Oka 2004, Rist et al. 2013).

→ This cycle doesn't achieve $OPR(NH_3)$~1.1 (typical in comets) if we start from $OPR(NH_3)$=1.0 as expected.

Other possible processes …

✓ Collisions of cometary molecules with the paramagnetic species.
  - the paramagnetic molecules like O_2
  - the paramagnetic grains such as fayalite (Fe_2SiO_4)

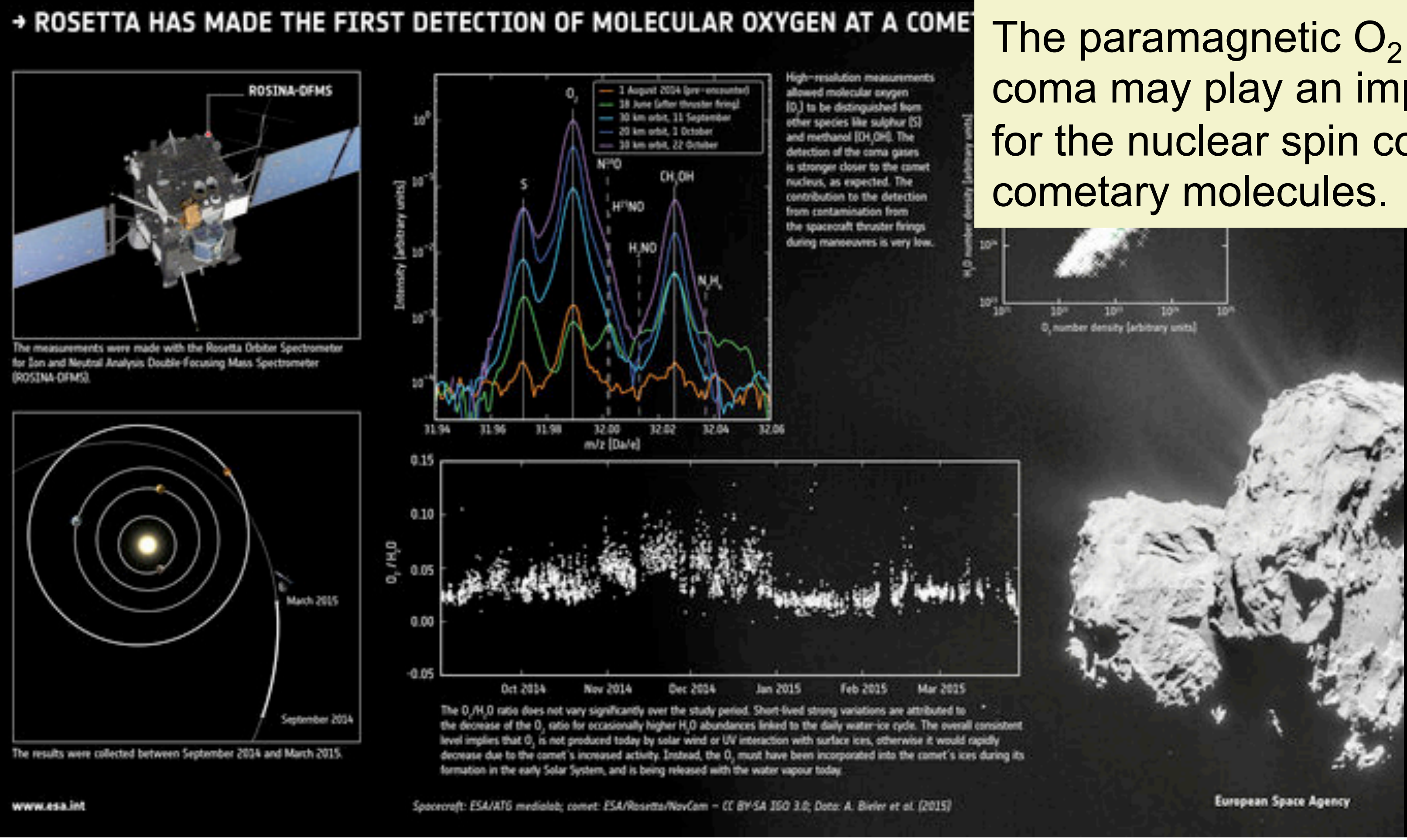
Paramagnetic Molecules in Coma

Collisions with paramagnetic molecules like O_2 could promote *ortho* – *para* conversion（Hama & Watanabe 2013）.

→ First detection of O_2 in comet 67P/C-G by Rosetta/ROSINA
（Bieler et al. 2015）→ $O_2/H_2O = 3.80±0.85\%$

→ Confirmed in comet Halley（Rubin et al. 2015） → $O_2/H_2O = 3.7±1.7\%$

The paramagnetic O_2 molecules in coma may play an important role for the nuclear spin conversion of cometary molecules.



→ ROSETTA HAS MADE THE FIRST DETECTION OF MOLECULAR OXYGEN AT A COMET

The measurements were made with the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis Double-Focusing Mass Spectrometer (ROSINA-DFMS).

High-resolution measurements allowed molecular oxygen (O_2) to be distinguished from other species like sulphur (S) and methanol (CH_3OH). The detection of the coma gases is stronger closer to the comet nucleus, as expected. The contribution to the detection from contamination from the spacecraft thruster firings during manoeuvres is very low.

The results were collected between September 2014 and March 2015.

The O_2/H_2O ratio does not vary significantly over the study period. Short-lived strong variations are attributed to the decrease of the O_2 ratio for occasionally higher H_2O abundances linked to the daily water-ice cycle. The overall consistent level implies that O_2 is not produced today by solar wind or UV interaction with surface ices, otherwise it would rapidly decrease due to the comet's increased activity. Instead, the O_2 must have been incorporated into the comet's ices during its formation in the early Solar System, and is being released with the water vapour today.

www.esa.int

Spacecraft: ESA/ATG medialab; comet: ESA/Rosetta/NavCam – CC BY-SA IGO 3.0; Data: A. Bieler et al. (2015)

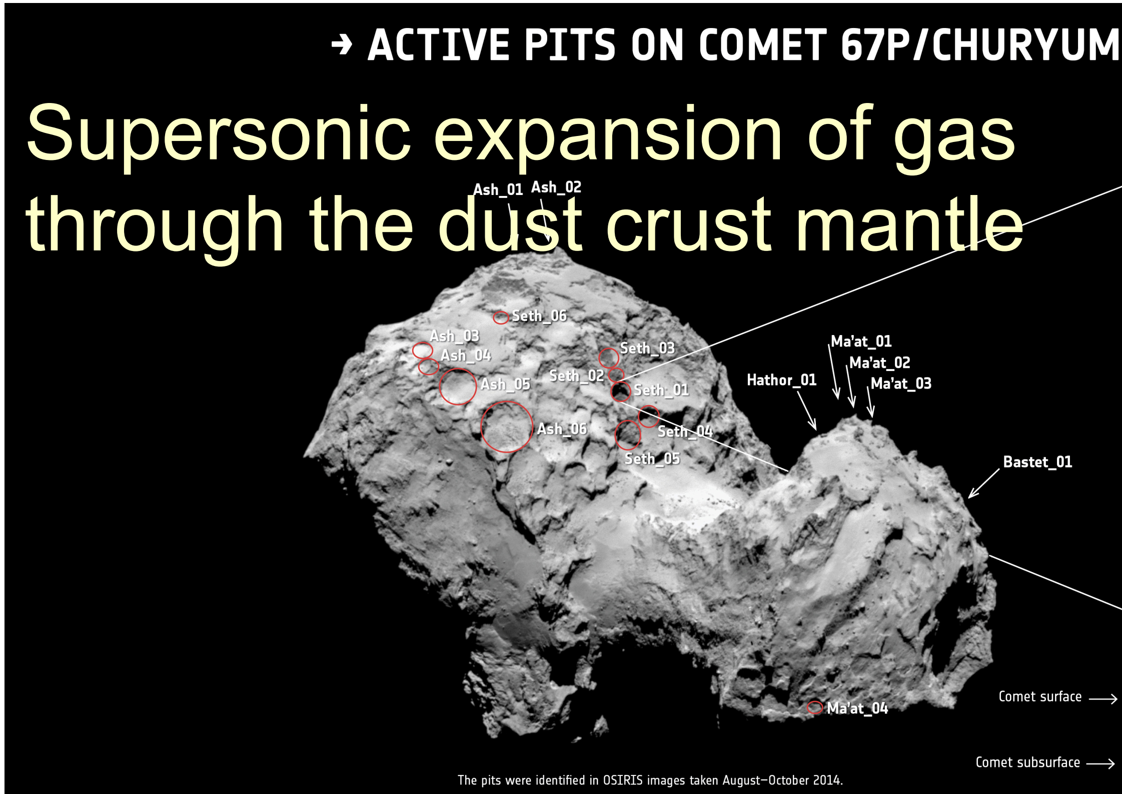
European Space Agency

Other possible processes …

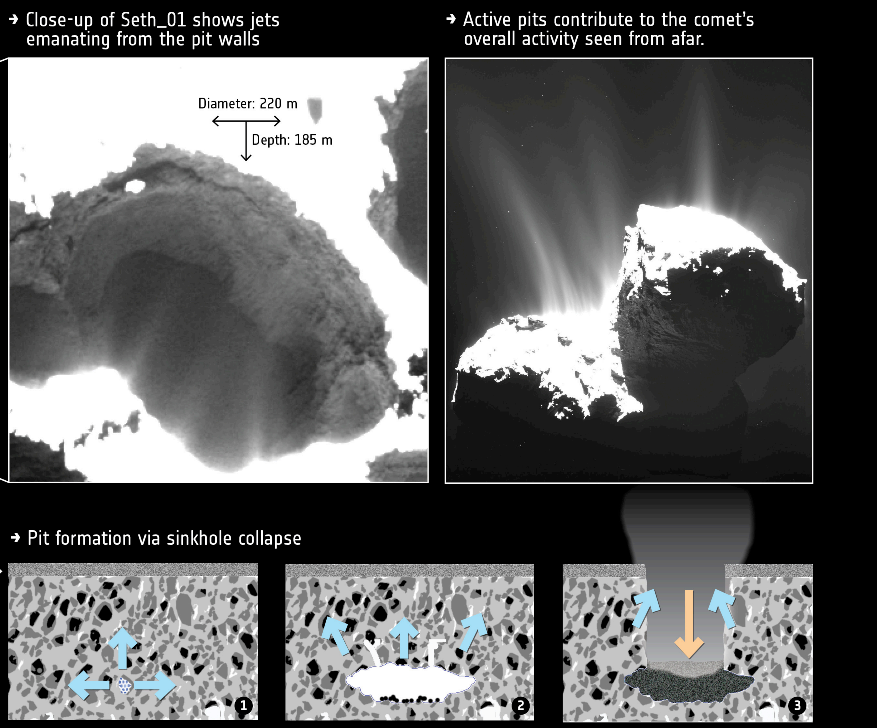
✓ Collisions of cometary molecules with the paramagnetic species.
  - the paramagnetic molecules like O_2
  - the paramagnetic grains such as fayalite (Fe_2SiO_4)

✓ Collisions of cometary molecules with water clusters $(H_2O)_n$, or icy grains.

Supersonic expansion of gas through the dust crust mantle



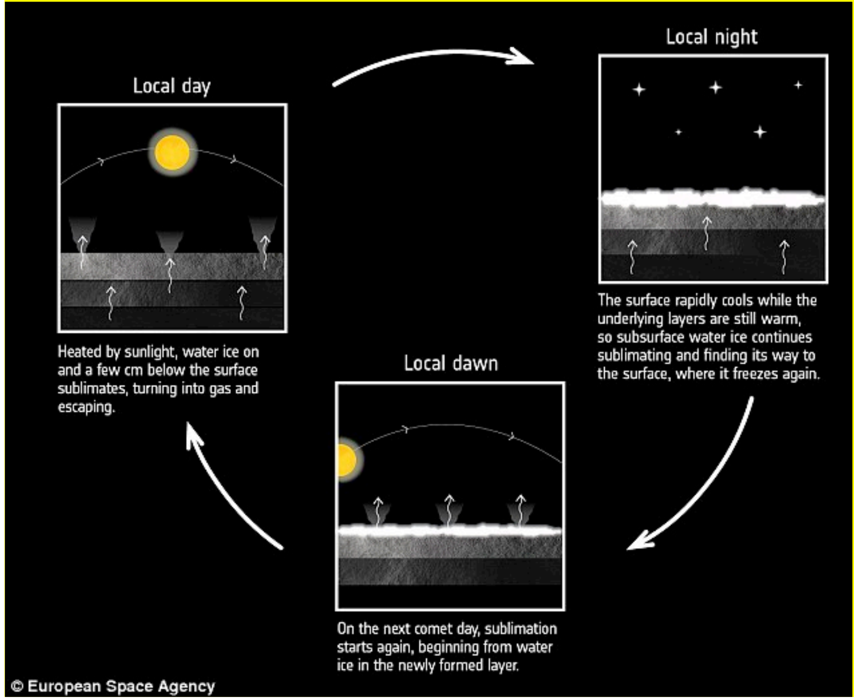
The pits were identified in OSIRIS images taken August–October 2014.



1. Heat causes subsurface ices to sublimate (blue arrows), forming a cavity (2). When the ceiling becomes too weak to support its own weight, it collapses, creating a deep, circular pit (3, orange arrow). Newly exposed material in the pit walls sublimates, accounting for the observed activity (3, blue arrows).

ESA/Rosetta/MPS for OSIRIS Team MPS/UPD/LAM/IAA/SSO/INTA/UPM/DASP/IDA; J-B Vincent et al (2015)

European Space Agency



Heated by sunlight, water ice on and a few cm below the surface sublimates, turning into gas and escaping.

The surface rapidly cools while the underlying layers are still warm, so subsurface water ice continues sublimating and finding its way to the surface, where it freezes again.

On the next comet day, sublimation starts again, beginning from water ice in the newly formed layer.

© European Space Agency

✓ Collimated jets (similar to the supersonic expansion of gas in laboratory) may promote nuclear spin conversion.

→ Manca Tanner et al. (2013).

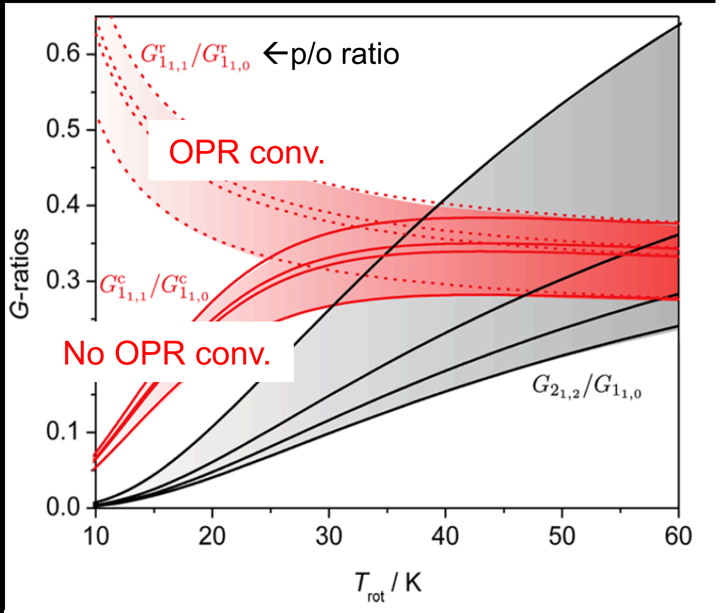
H_2O in supersonic expansion with Ar gas at 20–30 K

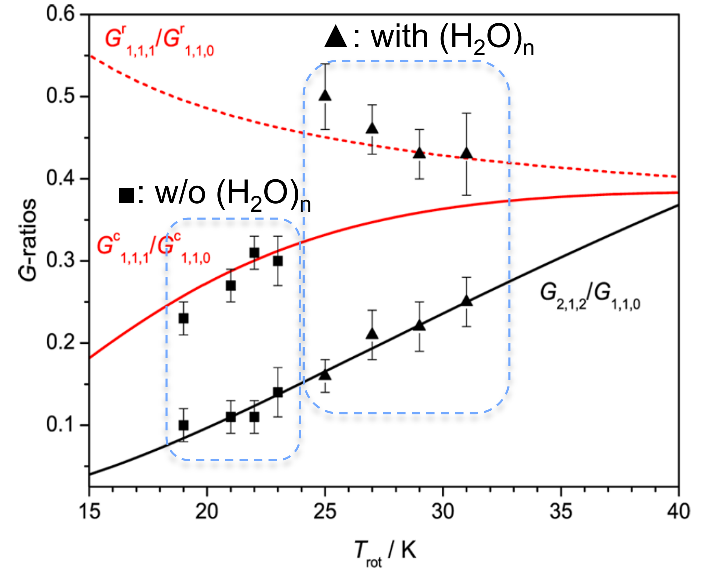
Manca Tanner et al. (2011, 2013) →

Supersonic expansion of a gas mixture (H_2O + Ar) at T=20–30K shows the *ortho*–*para* conversion when the water abundance is high enough.
→ $(H_2O)_n$ formed in the jet may convert OPR of water.

$$\boxed{H_2O + (H_2O)_n \rightarrow (H_2O)^*_{n+1} \rightarrow H_2O + (H_2O)_n.}$$

→ Probably in comets, too.





No nuclear spin conversion is observed for …

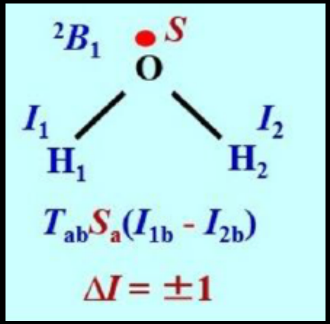
× CH_4 (25% in Ar gas)	Hepp et al. (1991, 1994)
× CH_3OH (7% in Ar gas)	Hepp et al. (1994)
× NH_3 (5% in Ar gas)	Hepp et al. (1992)

However, the nuclear spin conversion is found in …

○ NH_3 (10% in Ar gas)	Hepp et al. (1992)

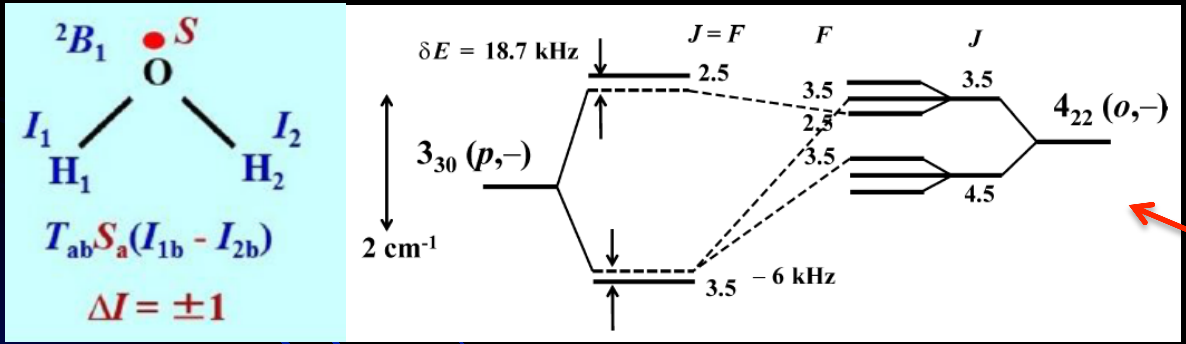
Other possible processes …

- ✓ Collisions of cometary molecules with the paramagnetic species.
  - the paramagnetic molecules like O_2
  - the paramagnetic grains such as fayalite (Fe_2SiO_4)
- ✓ Collisions of cometary molecules with water clusters $(H_2O)_n$, or icy grains.
- ✓ Ortho – para transition in ‘open-shell’ molecules.
  → due to the interaction between the magnetic moments of the unpaired electron and protons.

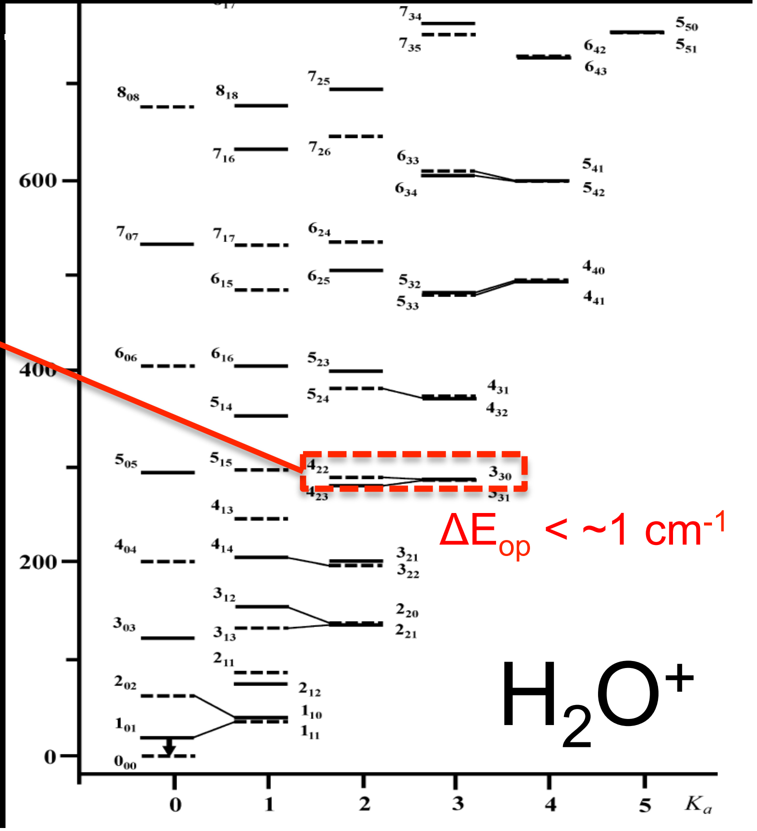


Ortho–para transitions for ‘open-shell molecules

For a molecule with an unpaired electron such as free radicals and radical ions (‘open-shell molecules’) like H_2O^+, H_3O^+, NH_4^+, the probability of *ortho* – *para* transition may be much higher than the ordinary molecules like H_2O due to the interaction between the magnetic moments of the unpaired electron and protons (Tanaka et al. 2013, H_2O^+).



→ Small energy difference between *ortho* and *para* levels causes the mixing of wave-functions and promotes the *ortho* – *para* transition.



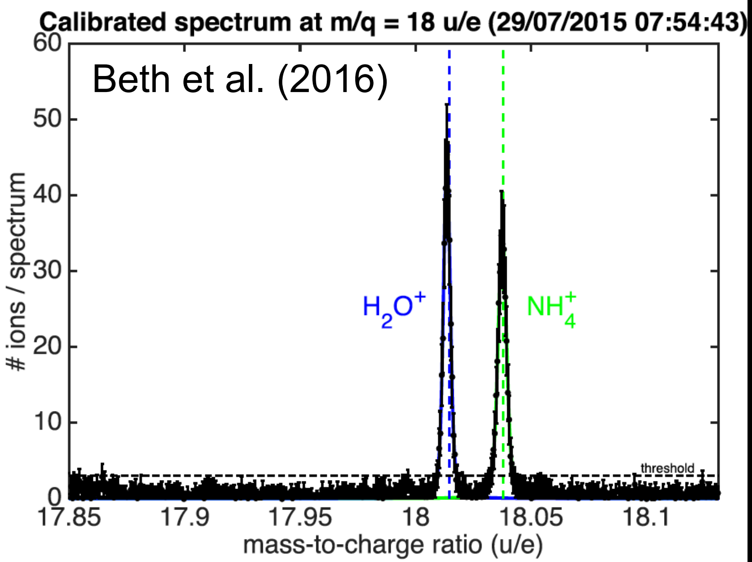
Ortho–para transitions for 'open-shell molecules

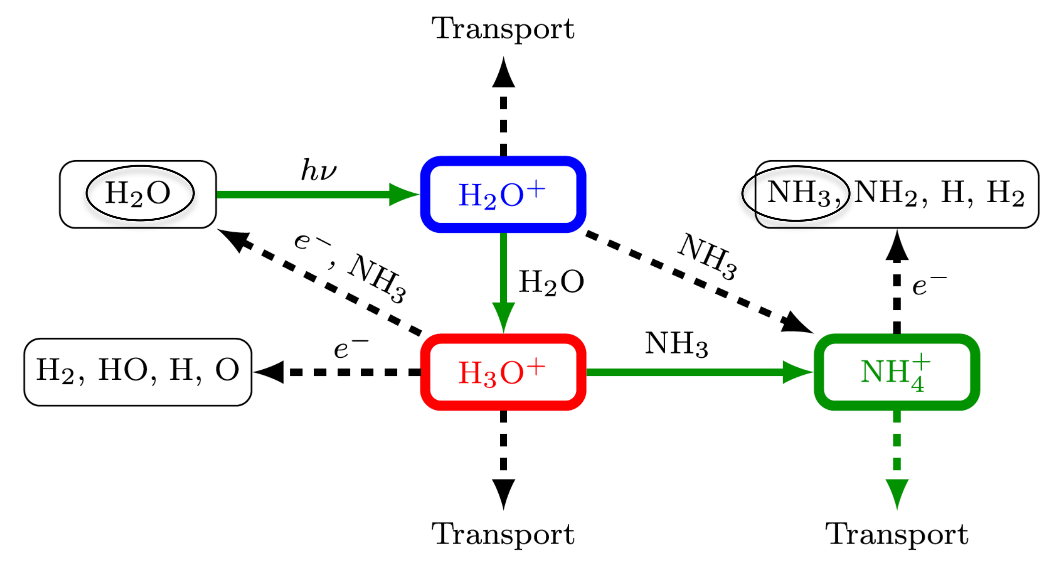
For a molecule with an unpaired electron such as free radicals and radical ions ('open-shell molecules') like H_2O^+, H_3O^+, NH_4^+, the probability of *ortho – para* transition may be much higher than the ordinary molecules like H_2O due to the interaction between the magnetic moments of the unpaired electron and protons (Tanaka et al. 2013, H_2O^+).

→ The smallness of energy difference between *ortho* and *para* energy levels is essentially important for the *ortho – para* transition.

For example, the nuclear spin conversion rate for H_2O^+ is higher by 8 orders of magnitude than H_2O (Tanaka et al. 2013) → However, not effective for cometary coma, still too slow.

First *in situ* detection of NH_4^+ in 67P/C-G by Rosetta/ROSINA





Larger proton-affinity of NH_3 than H_2O.

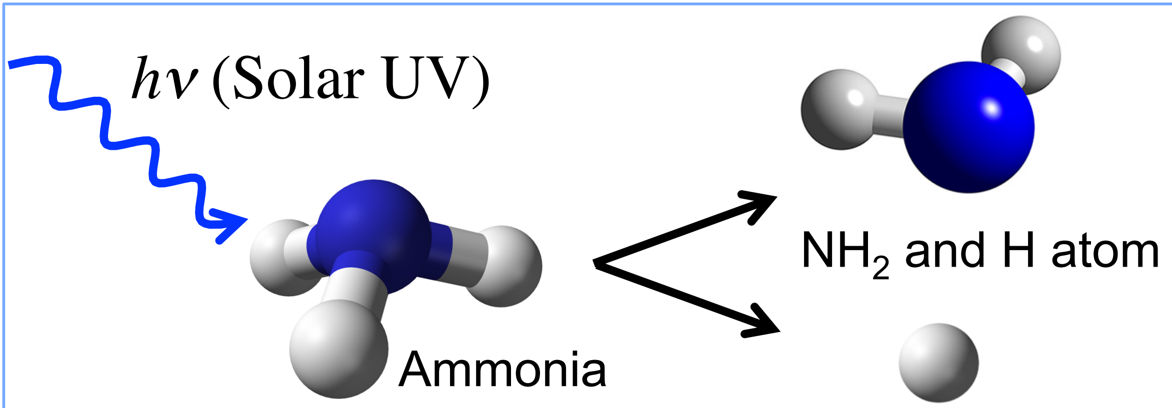
※ We should check the possibilities of *ortho* – *para* transitions for 'open-shell' molecules in cometary coma; especially for H_3O^+ and NH_4^+

Species	Proton affinity (eV)
HO	6.16
H_2O	7.17
H_2S	7.32
H_2CO, HCN	7.40
HCOOH	7.70
CH_3OH	7.83
HCNO	7.87
HNC	8.02
NH_3	8.86

Summary

- ✓ Cometary NH_3 shows OPR~1.1 (slightly higher than unity as a statistical value) while NH_3 in comets might form in the molecular cloud or the solar nebula at ~10K based on the measurements of $^{14}N/^{15}N$ in cometary NH_3.
- ✓ Since NH_3 OPR is expected to be unity just after desorption from cometary ice (NOT old memory), some processes in coma could change OPRs of cometary molecules.
- ✓ Observed trend for OPRs of H_2O and NH_3 suggests the nuclear spin conversion caused by the gas-phase chemical reactions in coma, related to both H_2O and NH_3.
- ✓ Many of possibilities for nuclear spin conversion of the molecules in cometary coma (and near nucleus surface) should be investigated.
  → Possible nuclear spin conversions in coma by collisions with …
  the paramagnetic molecules like O_2, the paramagnetic grains,
  the water cluster $(H_2O)_n$, the icy grains, & the 'open-shell' molecules
- ✓ Otherwise, we may have to re-examine our assumptions for the photo-dissociation of NH_3 in coma.

Re-examine our assumptions!?

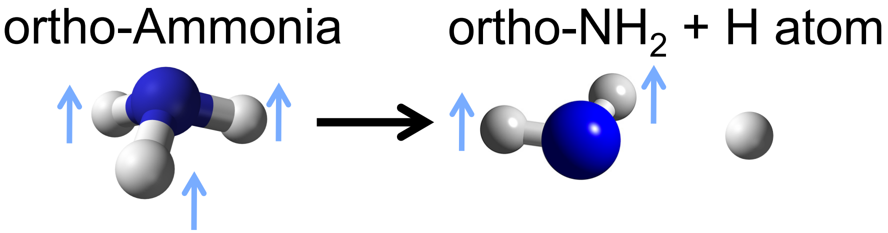


hν (Solar UV)

Ammonia

NH_2 and H atom

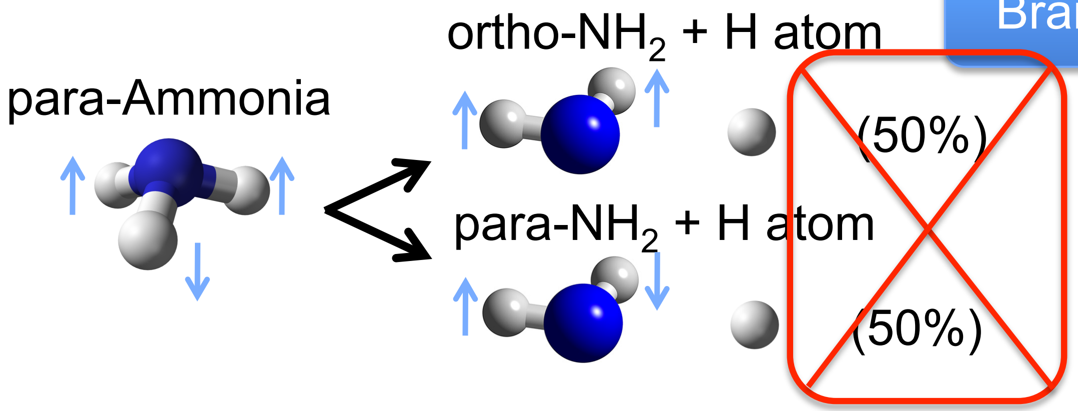
Branching ratio of NH_3 to NH_2 ~ 95%



ortho-Ammonia

ortho-NH_2 + H atom

Photo-dissociation rates are different for ortho-NH_3 and para-NH_3?



para-Ammonia

ortho-NH_2 + H atom ~~(50%)~~

para-NH_2 + H atom ~~(50%)~~

Branching ratio for para-NH_3 is not 1:1?

(based on Quack 1977; Oka 2004)