Ortho-to-Para Abundance Ratios of water from high-resolution spectra of water ion in the optical wavelength region

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Abstract

The ortho-to-para abundance ratio (OPR) of cometary molecules has been considered to be one of the primordial characteristics of cometary ices. We present OPRs of water in five comets based on our high-resolution optical emission spectra of water ion (H_2O^+) which is a dominant photo-ionization product of water in the cometary coma. Those spectra were taken by the HDS mounted on the Subaru telescope (Hawaii). We discuss about interpretations of OPR of cometary water based on our and previous observational results and recent laboratory studies.

Background

Comets as remnants of primordial icy small bodies formed in the solar nebula give us the information about the solar system formation. It is considered that the ortho-to-para abundance ratio (OPR) of cometary molecules is one of the primordial characteristics of comets. Usually observed OPRs are interpreted as nuclear spin temperatures (T_{spin}; defined as an excitation temperature that reproduces the observed OPR in thermal equilibrium). The OPRs of water (H_2O) as the most dominant species in cometary volatiles, were slightly smaller than the high-temperature limit (3.0 for water) and indicative of ~30 K as T_{spin} [MC11]. In the case of ammonia (NH_3) as the dominant N-bearing molecules in comet, OPR can be estimated from the high-resolution optical spectrum of NH_2 that is a dominant photo-dissociation product of ammonia by the solar UV radiation. Our early survey for OPRs of ammonia (through NH_2) also showed T_{spin} of ~30 K [Sh11].

Here we present our survey of OPR of H_2O^+ and discuss about the interpretation of OPRs based on recent laboratory studies about the OPR of water and nuclear spin conversion processes in the coma.

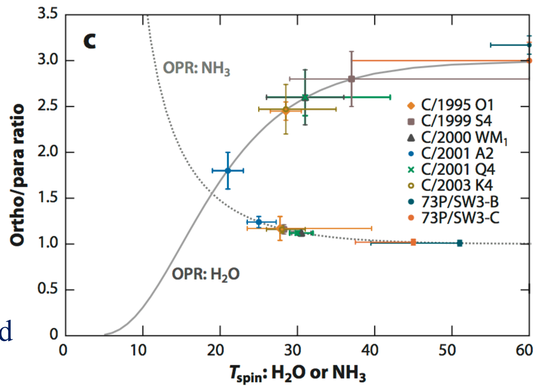


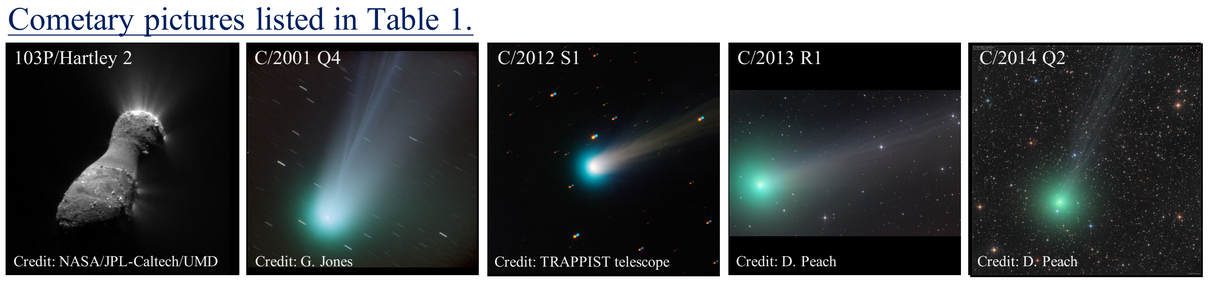
Fig. 1. Relationships between OPR and T_{spin} for H_2O and NH_3 [MC11].

Observations & Results

Table 1. Summary of our measurements of OPRs of H_2O^+ in comets

Comet	UT Date	R_h (AU)	Dynamical type [L04]	OPR of H_2O^+	T_{spin} (K)
103P/Hartley 2	2010 Oct. 18	1.067	Jupiter-family	2.14 +0.76/–0.46	34 +19/–4
C/2001 Q4 [S12]	2004 May 24	0.973	Dynamically new	2.6 ± 0.3	30 +10/–4
C/2012 S1	2014 Nov. 15	0.601	Dynamically new	2.19 ± 0.11	25 ± 2
C/2013 R1	2014 Nov. 15	1.066	Dynamically old	2.45 ± 0.20	29 +4/–3
C/2014 Q2	2015 Jan. 11	1.321	Dynamically old	2.77 ± 0.24	>30

Cometary pictures listed in Table 1.



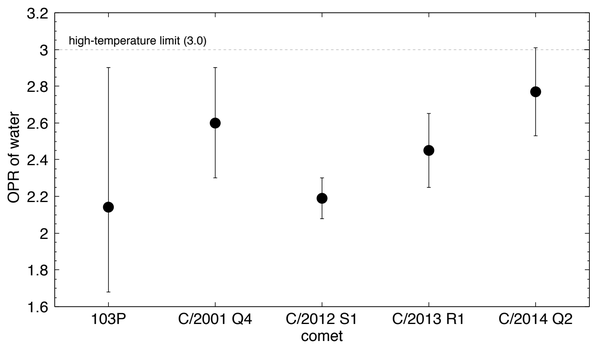


Fig. 2 (up). Summary of OPRs of H_2O^+ in five comets with various dynamical origins.

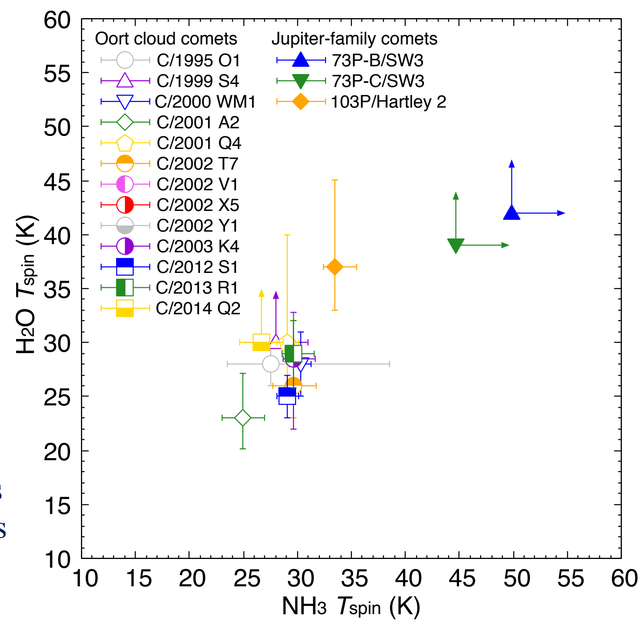


Fig. 3 (right). The relationship between T_{spin}s of H_2O and NH_3 for 16 comets [S16]. This figure may show a correlation between T_{spin}s of H_2O and NH_3.

Discussion & Conclusions

Recent laboratory experiments relevant to OPR of water

- Photo-desorbed water molecules formed on cold substrate at 10 K (Amorphous Solid Water: ASW) show a statistical value of OPR (3.0 as a high-temperature limit) [H16].
- Thermally desorbed (>150 K) water molecules originally formed at ~8K on the cold substrate show a statistical value of OPR (3.0) [H11]. T_{spin} of thermally desorbed water molecule does not reflect the formation temperature of water. The water (OPR=3) deposited on cold substrate at ~8 K (but relatively short duration in solid) also does not show the OPR corresponding to temperature of ices (~8 K).
- Nuclear spin conversion of water occurs rapidly in water cluster and ice (<100 μs) [Sl11]. Thus, the ortho-para conversion of water is possible in coma, if water clusters formed and interact with water molecules in coma.
- OPR of water relaxes with translational and rotational temperatures of water monomer in supersonic expansion gas at 20–30 K when N(water cluster)/N(water monomer) exceeded the threshold value of unity [T13]. N is number density.

Simplified calculation of a ortho-para conversion in coma

We calculate the number density of water monomer and water dimers with a steady state in each distance from the nucleus based on following processes:

FORMATION OF WATER DIMER

1. Three-body collision: $3H_2O \rightarrow (H_2O)_3^* \rightarrow (H_2O)_2 + H_2O$
2. Ion-molecule reaction: $H_3O^+ + H_2O \rightarrow (H_2O)_2^+ + H$, and $(H_2O)_2^+ + e^- \rightarrow (H_2O)_2$

DECAY OF WATER DIMER

1. Thermal sublimation: the unimolecular dissociation theory (UDT) (see Fig. 5)
2. Collision with H_2O: $(H_2O)_2 + H_2O \rightarrow 3H_2O$
3. Photo-ionization: $(H_2O)_2 + h\nu \rightarrow 2H_2O$

CONDITIONS

– $Q(H_2O)$ = 1e29 /s, R_h = 1.0 AU [BC87].

RESULTS

In the limited region of the coma (at ~30–120 km from the nucleus), the conditions for ortho-para conversion and relaxation by reactions with water clusters are satisfied.

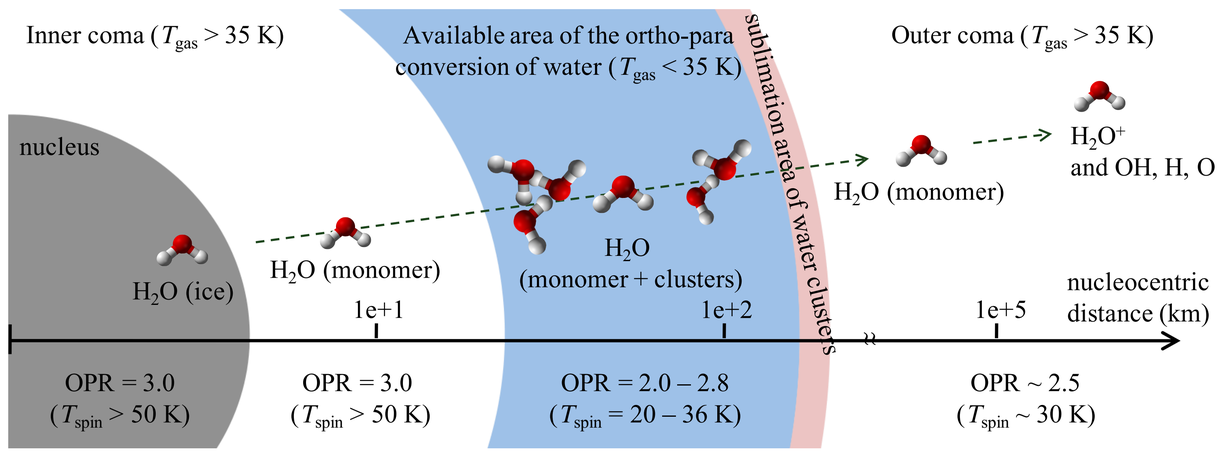


Fig. 4. Schematic of the ortho-para conversion of water in the inner coma. The nuclear spin conversion can occur in the limited region (blue and red hatches).

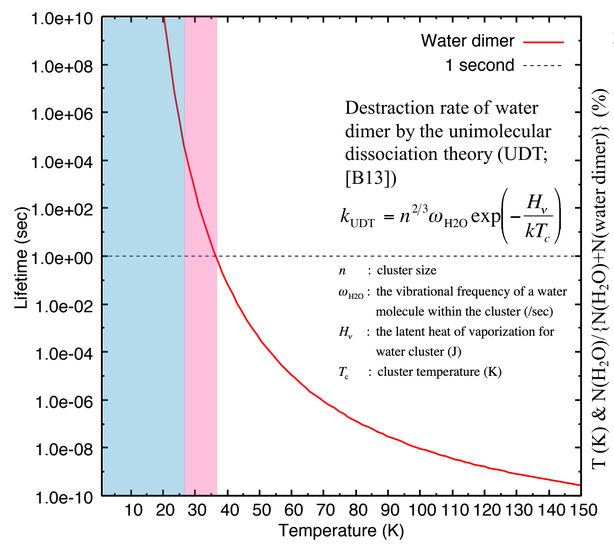


Fig. 5 (left). The lifetime of water dimer calculated by UDT ($1/k_{DUT}$). At ~<30 K, water dimer can survive only at low temperatures of < ~30 K.

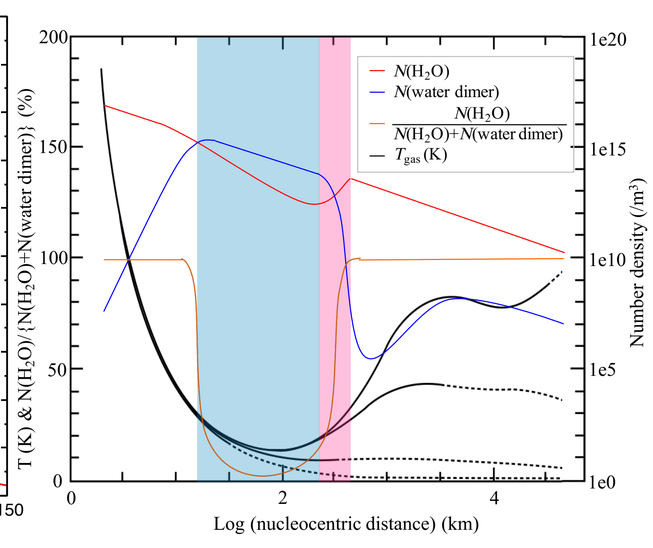


Fig. 6 (right). Number densities of H_2O (red) water dimer (blue), a fraction of water monomer (orange), and a gas kinetic temperature (K) by [BC87] (black) in coma.

Interpretation of OPRs of water and ammonia

– We should carefully interpret the observed OPRs of water in comets because the laboratory studies imply that (1) waters formed in/on surface of cold materials has the OPR of high-temperature limit (3.0) and the ortho-para conversion and relaxation in water clusters or ices rapidly occur in the inner coma.

– Since NH_3 can easily interact with water cluster (due to the intra-molecular force between H_2O and NH_3 as hydrogen-bonding), the OPR of NH_3 may be converted rapidly by such interactions with water clusters. Observed correlation between T_{spin}s of water and ammonia may indicate the interactions between them in terms of nuclear spin conversion. Nuclear-spin selective chemical reactions between NH_3 with water-group ions (e.g., H_3O^+, H_2O^+, etc.); e.g., $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$, and $NH_4^+ + e^- \rightarrow NH_3 + H$ [Recycling of NH_3 in coma], may also play an important role for the nuclear spin conversion of NH_3 in the inner coma.

– Further studies about the inner-coma chemistry in the consideration of nuclear spin states (including the interactions with water clusters) are strongly encouraged.

References. [B13] Borner et al., 2013, *J. Chem. Phys.*, **138**, 064302. [BC87] Bockelée-Morvan & Crovisier, 1987, *ESASO*, **278**, 2358. [H16] Hama et al., 2016, *Science*, **251**, 65. [H11] Hama et al., 2011, *ApJ*, **738**, L15. [L04] Levison, H. F., 1996, *APS Conf. Ser.*, 173. [MC11] Mumma & Charnley, 2011, *ARA&A*, **49**, 471. [S16] Shinnaka et al., 2016, in prep. [S12] Shinnaka et al., 2012, *ApJ*, **749**, 101 [Sh11] Shinnaka et al., 2011, *ApJ*, **729**, 81. [Sl11] Sliter et al., 2011, *J. Phys. Chem. A.*, **115**, 9682. [T13] Tanner et al., 2013, *J. Phys. Chem. A.*, **117**, 10105.

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