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SPIN TEMPERATURES OF AMMONIA AND WATER MOLECULES IN COMETS

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ABSTRACT

The nuclear spin temperature, which is derived from the ortho-to-para abundance ratio of molecules measured in cometary comae, is a clue to the formation conditions of cometary materials, especially the physical temperature at which the molecules were formed. In this paper we present new results for the nuclear spin temperatures of ammonia in comets Hale-Bopp (C/1995 O1) and 153P/Ikeya-Zhang based on observations of NH_2 at 26^{+10}_{-4} and 32^{+5}_{-4} K, respectively. These results are similar to previous measurements in two other comets, and the nuclear spin temperatures of ammonia in the four comets are concentrated at about 30 K. We emphasize that the nuclear spin temperatures of water measured thus far have also been about 30 K. In particular, the spin temperatures of ammonia and water are equal to each other within $\pm 1\ \sigma$ error bars in the case of comet Hale-Bopp. These nuclear spin temperatures of ammonia and water were measured under quite different conditions (heliocentric distances and gas production rates). There is no clear trend between the nuclear spin temperatures and the heliocentric distances, the gas production rates, or the orbital periods of the comets. The possibilities of the ortho-to-para conversion in the coma and in the nucleus are discussed. The present data set implies that the ortho-to-para ratios were not altered after the molecules were incorporated into the cometary nuclei. It appears that cometary ammonia and water molecules formed on cold grains at about 30 K.

Subject headings: comets: general — comets: individual (153P/Ikeya-Zhang, Hale-Bopp (C/1995 O1)) — molecular data

1. INTRODUCTION

Since comets are remnants of planetesimals formed in the early solar system, they should have contained primordial ices in their nuclei for a long time, about 4.6 Gyr. Therefore, cometary ices are a clue to the conditions in which the molecules were formed, in a molecular cloud or in the solar nebula (the protoplanetary disk of our solar system). One of the primordial characteristics of a comet is the ortho-to-para abundance ratio (OPR) of the cometary molecules. For a molecule with protons at symmetrical positions, the requirement of invariance of the wave function under exchange of identical nuclei leads to a segregation of the rotational levels according to the total nuclear spin (I). In the case of the ammonia (NH_3) molecule, which has three identical protons, the configuration for which the three proton spins are parallel is called "ortho" ($I = 3/2$), and otherwise it is called "para" ($I = 1/2$). The ortho and para species are not interconverted by either radiative or nondestructive collisional processes, and the OPR is thought to not change for a long time (Ho & Townes 1983). The nuclear spin temperature (or briefly, spin temperature) is defined as the temperature that can reproduce the OPR in thermal equilibrium (Mumma, Weaver, & Larson 1987).

OPRs of water were measured for the first time in comet 1P/Halley and then in comet Wilson (C/1986 P1) from the Kuiper Airborne Observatory (KAO; Mumma, Weissman, & Stern 1993). A spin temperature of ≈29 K for comet Halley and a lower limit of 50 K for comet Wilson were obtained. However, these determinations are questionable, since only part of the ν_3 vibrational band of water could be observed from the KAO because of telluric absorptions and because the difficulty in modeling opacity effects prevented the precise determination of the OPR (Bockelée-Morvan & Crovisier 1990; Irvine et al. 2000). The full ν_3 vibrational band was observed by the *Infrared Satellite Observatory* in comets Hale-Bopp (C/1995 O1) and 103P/Hartley 2 (Crovisier 2000). Observations showed spin temperatures of ≈28 and ≈34 K for comets Hale-Bopp and Hartley 2, respectively.

The meaning of the spin temperature is discussed by Mumma et al. (1993) and Irvine et al. (2000). In the case of comet Halley, Mumma et al. (1987) demonstrated that the OPR does not change significantly with sublimation from the nucleus surface and that subsequent processes in the coma do not modify the OPR significantly. Furthermore, it is unlikely that the OPR could reequilibrate at the interior temperature of a comet, as discussed by Irvine et al. (2000). Thus, OPRs may give information from in the past (probably before comets were formed). If the OPRs were initialized or modified in thermal equilibrium, the spin temperature can be used to infer the physical temperature at which the nuclear spins were last equilibrated (Mumma et al. 1987). However, there is no evidence to show that the nuclear spins were initialized or modified under thermal equilibrium conditions.

Although the importance of the OPRs of ammonia was pointed out by Crovisier (1998) and the inversion lines of NH_3 were measured in comet Hale-Bopp (Bird et al. 1997), the signal-to-noise (S/N) ratio might be insufficient for a significant determination. Recently, Kawakita (2002) established a way to derive the OPR of cometary ammonia from high-dispersion and high S/N ratio optical spectra of NH_2, which is the major photodissociation product of ammonia. Ammonia spin temperatures have been derived in comets C/1999 S4 (LINEAR) and C/2001 A2 (LINEAR) (Kawakita et al. 2001, 2002). The ammonia spin temperature is about 30 K in both comets. Since NH_2 is observed in the visible spectral range, it is easier to obtain more samples of ammonia than of water.

In this paper we present two more values of ammonia spin temperature, in comet Hale-Bopp (C/1995 O1) and 153P/Ikeya-Zhang. Here we discuss the meaning of the spin temperature by comparing the ammonia values with those of water. We revisit and discuss the possibility that the OPRs were last equilibrated after cometary formation by comparing the measured spin temperatures with observational conditions of the comets.

2. DATA MATERIALS AND ANALYSIS

The spin temperature of ammonia in comet Hale-Bopp is estimated from the high-dispersion spectra taken by the Coudé Echelle Spectrograph mounted on the 2.16 m telescope at Beijing Astronomical Observatory. The emission-line catalog is already published (Zhang, Zhao, & Hu 2001). We used their data taken on 1997 March 28, when the heliocentric and geocentric distances were 0.92 and 1.33 AU, respectively. The spectral resolving power was $R = 44,000$. In the case of comet Ikeya-Zhang, the ammonia spin temperature is derived from the high-dispersion spectra taken with the 3.5 m Telescopio Nazionale Galileo (TNG) on La Palma, Canary Islands, and the cross-dispersed echelle spectrograph SARG (Capria et al. 2002), providing a spectral resolving power of $R = 57,000$. The heliocentric and geocentric distances during the observation on 2002 April 19 were 0.89 and 0.43 AU, respectively.

The NH_2 (0, 9, 0) band is used to measure the OPR of NH_2 in the comet. This band is the strongest NH_2 band in the visible spectral range. Several ortho and para lines (more than 10 lines total; see Table 1) were measured in the NH_2 (0, 9, 0) band spectrum. The observed spectra were compared with spectra of NH_2 calculated using a model based on the solar fluorescence. We considered the following transitions of NH_2: (1) rovibronic transitions of $\tilde{A}(0,\ v_2',\ 0) - \tilde{X}(0,\ 0,\ 0)$, $v_2' = 1$–18; (2) rovibrational transitions of $\tilde{X}(0,\ v_2',\ 0) - \tilde{X}(0,\ 0,\ 0)$, $v_2' = 8$–13; (3) and pure rotational transitions in $\tilde{X}(0,\ 0,\ 0)$. More detailed information on the analysis is given in Kawakita et al. (2001, 2002). Regarding the vibronic and vibrational transition moments of NH_2, these were recently recalculated (Jensen, Kraemer, & Bunker 2003), and thus we replace them in our model. In our NH_2 fluorescence model, the OPR of NH_2 is a free parameter. We determined the optimal OPR of NH_2 based on a χ^2 fitting between observed and calculated spectra. Figure 1 shows the high-dispersion spectrum of NH_2 observed in comet Ikeya-Zhang and the calculated spectrum. The obtained OPRs of NH_2 are 3.42 ± 0.29 and 3.22 ± 0.12 for comets Hale-Bopp and Ikeya-Zhang, respectively.

Here we assume ammonia is the sole parent of NH_2. Because another possible parent of NH_2, NH_2CHO, was discovered in comet Hale-Bopp with an abundance of only 1%–2% of the ammonia abundance (Bockelée-Morvan et al. 2000; Bird et al. 1997), we can neglect its contribution to the OPR of NH_2. In order to derive the OPR of NH_3 from that of NH_2, we applied the nuclear spin selection rule to the photodissociation reaction of NH_3 into NH_2 and H. The existence of such a selection rule was theoretically anticipated by Quack (1977), and Uy, Cordonnier, & Oka (1997) gave the experimental evidence that the nuclear spin selection rules hold for gas-phase chemical reactions. Thus, OPRs of ammonia of 1.21 ± 0.15 and 1.11 ± 0.06, and the corresponding spin temperatures of 26^{+10}_{-4} and 32^{+5}_{-4} K, are obtained for comets Hale-Bopp and Ikeya-Zhang, respectively. In addition to these, based on the revised transition moments (Jensen et al. 2003), the ammonia

TABLE 1

MEASUREMENTS OF ORTHO- AND PARA-NH_2 LINES IN COMETS HALE-BOPP AND IKEYA-ZHANG

Assignment	Wavelength (Å)	Hale-Bopp	Ikeya-Zhang
(0, 9, 0) 3_{03}–2_{11} (o)...........................	5962.6	94.41 (5.86)	3191.5 (20.2)
(0, 9, 0) 2_{02}–1_{10} (p)...........................	5965.2	35.99 (5.30)	1245.6 (19.4)
(0, 9, 0) 1_{01}–1_{11} (o)...........................	5976.4	478.1 (4.05)	21672.0 (19.4)
(0, 9, 0) 2_{02}–2_{12} (p)	5976.9	. . .	6007.5 (16.8)
(0, 9, 0) 3_{03}–3_{13} (o)...........................	5977.2	. . .	9898.2 (23.8)
(0, 9, 0) 0_{00}–1_{10} (p)...........................	5984.6	153.2 (4.30)	6631.2 (19.4)
(0, 9, 0) 1_{01}–2_{11} (o)...........................	5995.0	479.8 (4.48)	21450.0 (18.6)
(0, 9, 0) 2_{02}–3_{12} (p)	6007.0	113.2 (5.65)	5013.8 (18.6)
(0, 9, 0) 3_{21}–2_{11} (o)...........................	6017.4	41.9 (5.65)	1858.8 (19.4)
(0, 9, 0) 3_{21}–2_{11} (o) + 2_{21}–1_{11} (o).....	6018.7	112.96 (5.33)	5121.9 (16.8)
(0, 9, 0) 2_{20}–1_{10} (p)...........................	6022.1	27.7 (4.61)	1688.8 (15.8)
(0, 9, 0) 3_{21}–3_{13} (o)...........................	6033.6	. . .	2510.4 (15.8)
(0, 9, 0) 2_{20}–2_{12} (p)	6034.0	. . .	1069.6 (14.8)
(0, 9, 0) 2_{21}–2_{11} (o)...........................	6037.5	47.74 (5.33)	2163.2 (20.2)
(0, 9, 0) 2_{21}–2_{11} (o)...........................	6039.2	54.33 (5.65)	2731.5 (16.8)

NOTE.—Measurements of flux are in arbitrary units for each comet, and 1 σ error levels are in parentheses.

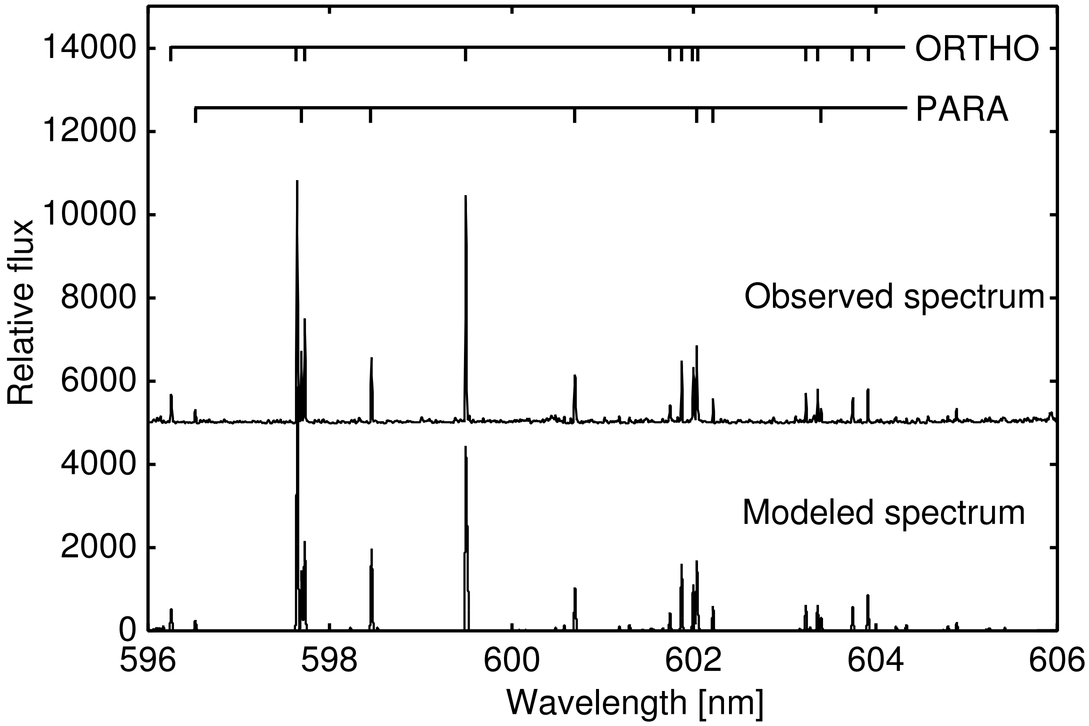

FIG. 1.—High-dispersion spectrum of comet Ikeya-Zhang taken on 2002 April 19 with the TNG telescope and SARG spectrograph. The modeled spectrum of NH_2 is for $OPR(NH_2) = 3.22$.

spin temperatures of comets C/1999 S4 (LINEAR) and C/2001 A2 (LINEAR) are recalculated to be 27^{+3}_{-2} and 25^{+1}_{-2} K, respectively. Table 2 shows the summary of the ammonia and water spin temperatures in the comets observed. The ammonia spin temperatures of these comets are similar, and they are in the range from 25 to 32 K.

3. DISCUSSION

3.1. *Comparison of Spin Temperatures between Ammonia and Water*

All comets in which the spin temperature of water or ammonia was derived are listed in Table 3 along with their orbital periods and origins. Comets are listed in increasing order of spin temperature. We cannot find any trend between the spin temperatures and orbital periods or origins. The spin temperatures of ammonia and water are nearly the same (25–34 K) in the six comets, except for comet Wilson.

In the case of comet Wilson (a dynamically new comet), Mumma et al. (1988) argued that the outer layer of dynamically new comets may consist of material that has been modified by cosmic-ray damage during the long stay in the Oort Cloud, while the interior of the cometary nucleus has remained relatively pristine. The cosmic-ray irradiation of the ice in the surface layer would break the hydrogen bonds of the molecules and make free H atoms and radicals. Such free H atoms might initiate spin conversion in water and other symmetric molecules through hydrogen atom exchange reactions (Mumma et al. 1993). The radiation processing would reset the OPR to the high-temperature limit (the statistically equilibrated value, i.e., 3 for water and 1 for ammonia). However, another dynamically new comet in Table 3 (comet C/1999 S4) shows a lower spin temperature than comet Wilson, so we consider that the cosmic-ray damage hypothesis should be reexamined. The OPR of water in comet Wilson may indicate cometary formation in a warmer region (>50 K), or the materials damaged by cosmic rays and existing in the outer layer of the nucleus might have been evaporated completely from the surface before our observations of that comet (the nucleus size of C1999 S4 before breakup was estimated to be smaller than for typical comets; Farnham et al. 2001).

The most interesting case in Table 3 is comet Hale-Bopp, in which the spin temperatures of both ammonia and water are derived. The ammonia spin temperature is equal to that of water within 1 σ error levels. This is quite an important fact for the OPR study. For example, in the case of molecular

TABLE 2

ORTHO-TO-PARA RATIOS OF NH_2 AND NH_3, WITH SPIN TEMPERATURES OF AMMONIA IN FOUR COMETS

Comet	OPR (NH_2)	OPR (NH_3)	Spin Temperature (K)
Hale-Bopp	3.42 ± 0.29	1.21 ± 0.15	26^{+10}_{-4}
Ikeya-Zhang	3.22 ± 0.12	1.11 ± 0.06	32^{+5}_{-4}
C/2001 A2	3.49 ± 0.10	1.25 ± 0.05	25^{+1}_{-2}
C/1999 S4	3.37 ± 0.11	1.19 ± 0.06	27^{+3}_{-2}

NOTE.—Error bars are ± 1 σ levels.

TABLE 3

SPIN TEMPERATURES OF WATER AND AMMONIA IN THE COMETS OBSERVED THUS FAR

Comet	Ammonia (K)	Water (K)	Orbital Period (yr)	Orbital Origin	References
C/2001 A2	25^{+1}_{-2}	...	40000	Oort Cloud	1
C/1999 S4	27^{+3}_{-2}	...	Dynamically new	Oort Cloud	1
Hale-Bopp	26^{+10}_{-4}	28 ± 2	4000	Oort Cloud	NH_3: 1; H_2O: 2
Halley	...	29 ± 2	76	Oort Cloud	3
Ikeya-Zhang	32^{+5}_{-4}	...	365	Oort Cloud	1
Hartley 2	...	34 ± 3	6.4	Kuiper Belt	2[a]
Wilson	...	>50	Dynamically new	Oort Cloud	3

NOTE.—Error bars are ±1 σ levels.

[a] This is a weighted average of the data obtained on different dates (the weight is the inverse square of the error).

REFERENCES.—(1) This work; (2) Crovisier 2000; (3) Mumma et al. 1993.

formation on dust grains, the formation heat could be dissipated into the grain, and the energy assigned to the rotational motion of the molecule could determine the OPR. However, the degree of heat transfer is considered to depend on various properties of the molecule and the grain surface, and the different molecular species generally show different spin temperatures. Therefore, the consistency between the spin temperatures of water and ammonia is supporting evidence that the OPRs of the molecules (at least, of water and ammonia) were initialized or modified under thermal equilibrium conditions.

The above discussion is based on the assumption that OPRs were not altered in the cometary coma and that OPRs reequilibrated with the interior temperature of the cometary nuclei or with the temperature at which the molecules formed or condensed (Mumma et al. 1987, 1993). Note that the observations of water and NH_2 were performed at different heliocentric distances for comet Hale-Bopp (at 2.9 and 0.9 AU, respectively) and that the observations of water and NH_2 sampled different ranges of the coma. If OPRs were altered via proton-transfer reactions and were also affected by ion-molecule spin-exchange reactions in the coma (Rodgers & Charnley 2002), the OPRs could have reequilibrated with the gas kinetic temperature in the inner coma. The physical conditions in the coma are quite different at different heliocentric distances and even vary with nucleocentric distances at a given heliocentric distance. Hence, the spin temperatures of water and ammonia may accidentally show similar values if ortho-to-para conversion occurs in the cometary coma. Although the possibility of ortho-to-para conversion in the coma was discussed for water and rejected in the early study by Mumma et al. (1987), we revisit this problem in § 3.2 based on recent results of OPRs.

3.2. *Ortho-to-Para Conversion in the Coma*

Figures 2 and 3 show the obtained spin temperatures with respect to the water production rates and the heliocentric distances during the observations (values are listed in Table 4), respectively. In these figures we cannot find any correlation between the spin temperatures and the conditions during the observations. Because the ortho-to-para conversion rates of water and ammonia in the coma seem to depend on the gas density and the gas kinetic temperature (these values depend on the heliocentric distance), Figures 2 and 3 may support that the OPRs cannot be changed significantly by chemical reactions in the coma. However, these figures may be misleading, because the observations of water and NH_2 sampled different regions in the coma, and the relationship between the OPRs and the gas kinetic temperature is unclear. We should check the possibility of ortho-to-para conversion in the coma from different points of view.

In the case of the water molecule, ortho-to-para conversion by chemical reactions in the inner coma seems to be impossible, because the number of collisions experienced by an individual water molecule is estimated to be much lower than the value required to convert its OPR, as discussed by Mumma et al. (1987). Furthermore, experiments with liquid water showed that the proton exchange between water molecules without ortho-to-para transitions can dominate in some cases (Tikhonov & Volkov 2002).

If the OPRs of water or ammonia were changed in the inner coma by chemical reactions, the OPRs would show variation with respect to nucleocentric distances. Therefore, we checked the ratio between strong ortho (1_{01}–1_{11}) and para (0_{00}–1_{10}) lines in the NH_2 (0, 9, 0) band. In the case of comet Ikeya-Zhang, the ratio was nearly constant within the range up to ≈800 km from the nucleus. The variation of the ratio was 2.7% for the 1 σ error level in this region. In the case of comet C/2001 A2 (Kawakita et al. 2002), there was also no evidence that the OPR of NH_2 depended on the nucleocentric distance. The flux ratio between the ortho and para lines was constant up to ≈1200 km from the nucleus, and the standard deviation was 5%. Unfortunately, we could not show invariance of the OPR of NH_2 with nucleocentric distance because of the lack of an

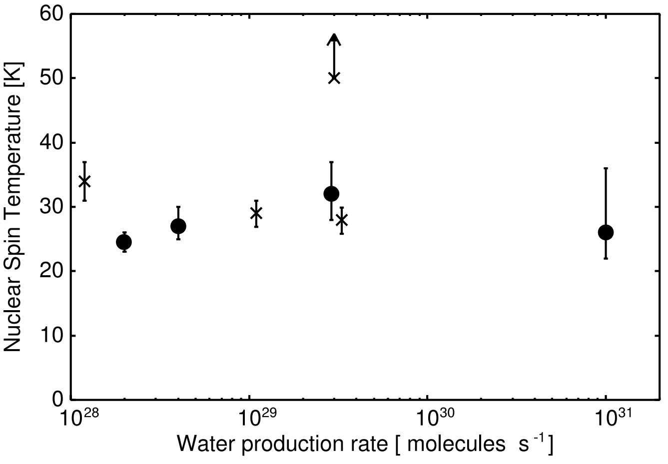

FIG. 2.—Spin temperatures with respect to the water production rates during the observations of OPRs. The filled circles indicate ammonia values and the crosses indicate water values. The spin temperatures seem to be independent of the water production rates.

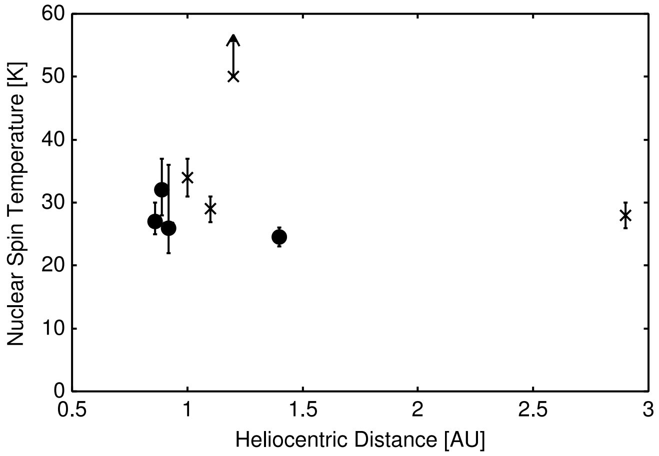

Fig. 3.—Spin temperatures with respect to the heliocentric distances of the observations. The filled circles indicate ammonia values and the crosses indicate water values. The fact that no clear trend is visible here means that the spin temperature could not reflect the temperature of nucleus surface.

S/N ratio, except for comets Ikeya-Zhang and C/2001 A2. The gas kinetic temperature calculated by the hydrodynamic approach shows a significant change in the inner coma and also shows a minimum around hundreds of kilometers away from the nucleus (Combi 2002; Combi et al. 1997). Therefore, the invariance of the NH_2 OPR may indicate that the chemical reactions in the inner coma could not affect the OPR of NH_2 significantly.

The above discussions are consistent with the calculations by Rodgers & Charnley (2002). The recent calculation of chemical reactions in the coma showed that deuterium-to-hydrogen (D/H) ratios are not affected significantly in the coma (Rodgers & Charnley 2002). Since the D/H ratios can be modified by proton-transfer or ion-molecule spin-exchange reactions as OPRs are altered in the coma, it is unlikely that the OPRs of water and ammonia are changed significantly by the chemical reactions in the coma (Rodgers & Charnley 2002).

Thus, it is reasonably assumed that the OPRs of water and ammonia are unaltered in the coma, and the consistency between the spin temperatures of ammonia and water in comet Hale-Bopp means that the OPRs were initialized or modified in thermal equilibrium. In this case, the spin temperature reflects the physical temperature at which the nuclear spins were last equilibrated. In the following subsections, we discuss when and where the nuclear spins of the molecules were last equilibrated in order to understand what is represented by the spin temperature.

3.3. *Resetting of the OPR on the Cometary Nucleus Surface*

The OPR might be reset by a rapid reequilibration with the temperature of the nucleus surface, as reported in the case of methane (Weaver et al. 1997). Such rapid reequilibration was investigated by theoretical and laboratory studies (Nijman & Berlinsky 1980 and references therein). The spin temperature is considered to be the physical temperature of the nucleus surface in this case. The problem is whether or not such a process occurs for ammonia and water molecules. If such rapid reequilibration could occur for ammonia and water molecules, the spin temperatures should depend strongly on the heliocentric distance, since the surface temperature of the comet depends on the incident solar flux. However, we can find no trend in Figure 3. The heliocentric distances during the observations range from 0.89 to 2.9 AU, and the incident solar flux at 0.89 AU is larger than that at 2.9 AU by a factor of 11. It is unlikely that the surface temperatures were about 30 K and nearly constant in the range of heliocentric distance from 0.89 to 2.9 AU. We suggest rejecting the rapid reequilibration of the OPRs of ammonia and water molecules in comets.

3.4. *Reequilibration of the OPR in the Interior of the Nucleus*

The spin temperature might reflect the interior temperature of the nucleus. Irvine et al. (2000) discussed this mechanism for the case of water. They pointed out that the water spin temperatures in comets Halley, Hale-Bopp, and Hartley 2 are nearly the same (about 30 K), even though the orbital periods range from only 6 to several thousands of years. It is unlikely that the temperatures in the interior of the nuclei were the same for these comets (Irvine et al. 2000). Now we refer to both the ammonia and water spin temperatures. The orbital periods of the comets range from 6 to more than 10^4 yr in Table 3, and the spin temperatures are nearly the same for all of them, except for comet Wilson (the OPR in comet Wilson might be the result of cosmic-ray damage). It is difficult to believe that the physical temperatures inside the nuclei are 30 K for all these comets. Thus, the latest result of the spin temperatures supports the conclusion of Irvine et al. (2000).

TABLE 4

Heliocentric Distances and Water Production Rates during OPR Observations

Comet	Heliocentric Distance (AU)	Water Production Rate (molecules s^{-1})	References
C/1999 S4	0.86	4×10^{28}	1
Ikeya-Zhang	0.89	2.9×10^{29}	2
Hale-Bopp	0.92	1×10^{31}	3
Hartley 2	1.0	1.2×10^{28}	4
Halley	1.1	1.1×10^{29}	5
Wilson	1.2	3×10^{29}	6
C/2001 A2	1.4	2×10^{28}	2
Hale-Bopp	2.9	3.3×10^{29}	4

Note.—Water production rates are estimated by assuming an $r^{-3.5}$ law at a heliocentric distance of r (AU).

References.—(1) Bockelée-Morvan et al. 2001; (2) Lecacheux et al. 2003; (3) Biver et al. 2002; (4) Crovisier 2000; (5) Mumma et al. 1987; (6) Larson et al. 1989.

3.5. *Modification of the OPR on the Grain Surface*

A nuclear spin flip without exchange of protons requires a strong nonuniform magnetic field (Mumma et al. 1993). It has been considered that ortho-to-para conversion on the surface of a magnetic compound might occur. Furthermore, as reviewed by Le Bourlot (2000), the conversion of ortho- to para-H_2 on the cold (10 K) surface of a nonmagnetic compound (graphite) can be observed in the laboratory, and ortho-to-para conversion may be possible on interstellar grains. The induced magnetic dipole between physically adsorbed H_2 and an unpaired electron of the substrate may interact with the nuclear spin and result in a modification of the nuclear spin (Le Bourlot 2000), or the collisions of H_2 with ortho-H_2 (with a weak magnetic moment) on the surface may cause the spin conversion of H_2.

In the case of cometary ice, the refractory grain is covered by an amorphous water ice mantle. Then, since water is a polar molecule, amorphous water ice molecules are weakly hydrogen-bonded. The binding energy of H_2O with H_2O ice is $\approx$5000 K (Sandford & Allamandola 1993), and the mobility of a water molecule is quite small at $\approx$30 K. This will likely prevent the collisions of H_2O with ortho-H_2O in low-temperature cometary ice (Mumma et al. 1993). Ammonia is also polar, and it is hydrogen-bonded with the water molecule on the surface (the binding energy between NH_3 and H_2O is comparable to the binding energy between H_2O molecules). Hence, collisional nuclear spin exchange will be prevented under low-temperature conditions.

On the other hand, a magnetic dipole may be induced between adsorbed H_2O (or NH_3) and an unpaired electron of some radical on the icy mantle, and the interaction between the magnetic moment and the nuclear spin may cause the ortho-to-para conversion. This is, however, just an idea. Unfortunately, there is no experimental evidence that ortho-to-para conversions occur on icy grains by such processes.

3.6. *Initialization of the OPR at the Molecular Formation*

Finally, we should consider the possibility that the spin temperature reflects the physical temperature at the molecular formation, as previously discussed by Mumma et al. (1993), Irvine et al. (2000), and Kawakita (2002). If the molecules are formed by gas-phase chemical reactions, the formation heat of the molecules should be quite large (higher than 10^4 K for water or ammonia), and the spin temperatures should become nearly infinite. In this case, the OPR is set to the nuclear spin statistical weight ratios (3 for water and 1 for ammonia). Therefore, the spin temperature of about 30 K may be evidence that ammonia and water molecules formed on cold dust grains.

On a dust grain, the formation heat of the molecules could be dissipated into the grain or its icy mantle, and local thermal equilibrium (LTE) may be achieved in a short time. In this case, the OPR would have been initialized to the value corresponding to the dust temperature. In order to achieve LTE between the newly formed molecules and the grain surface, an efficient energy transfer mechanism between them is necessary. Otherwise, the newly formed molecules can easily escape from the grain surface before LTE is achieved, since the binding energy of the molecules on the surface is about 1 order of magnitude smaller than the formation energy (Tielens & Allamandola 1987). Regarding this point, a recent laboratory study on the formation of water molecules on a Pt(111) surface revealed that about 66% of water molecules can be thermalized on the surface; moreover, up to 90% of water can be thermalized when the hydrogen bonds exist on the surface (Biener et al. 2002). Such a thermalization process seems to be effective for the formation of water (and ammonia) molecules on a water-rich icy mantle because of the existence of hydrogen bonds. Thus, it is most likely that the spin temperature reflects the physical temperature of the dust grain where the molecule was formed. This hypothesis can explain the spin temperature of $\approx$30 K for both ammonia and water molecules. We should note that the grain temperature at the molecular formation might be different from the value before the molecular formation, since the formation heat could make the grain warmer, at least partially.

The hypothesis that OPRs of ammonia and water molecules were initialized at molecular formation and that the obtained spin temperatures reflect the grain temperature can be examined from the viewpoint of chemical abundance of cometary ices. The D/H ratio is another clue to the formation conditions of the molecules. The D/H ratios in water (HDO/H_2O) have been obtained in three comets thus far (Irvine et al. 2000). In particular, in comet Hale-Bopp D/H ratios of hydrogen cyanide (DCN/HCN) were obtained in addition to the D/H ratios of water (Meier et al. 1998). According to the calculation of the D/H ratios of water and hydrogen cyanide in a dense molecular cloud based on interstellar ion-molecule chemistry (Fig. 2 in Meier et al. 1998), it appears that the D/H ratios obtained in comet Hale-Bopp indicate molecular formation at a temperature of 25–35 K. Aikawa & Herbst (1999) showed that the observed D/H ratios could be achieved in the solar nebula at a temperature of 25–30 K. Bergin, Neufeld, & Melnick (1999) reported that the D/H ratios in water and the CO_2/H_2O ratios observed in comets can be explained by molecular formation at a temperature of 25–40 K during the evolution from the initial gas cloud to the molecular hot core (they considered the chemical change to be induced by the passage of an interstellar shock in well-shielded regions). Regarding the abundance of CO in cometary ices, Notesco, Bar-Nun, & Owen (2003) reported that the amount of argon (equivalent to CO) trapped in condensed water ice indicates that the cometary ices formed at about 25 K based on their laboratory experiments. All these facts support the hypothesis that the spin temperature reflects the temperature at the molecular formation.

4. CONCLUDING REMARKS

In this work we present the ammonia spin temperatures that are derived from NH_2 observations with the fluorescence model based on the revised transition moments of NH_2. By comparing them with water spin temperatures, we discuss the meaning of the OPRs of ammonia and water. The spin temperatures of ammonia are close those of water in six comets. In particular, we showed that the spin temperatures of ammonia and water are similar in the case of comet Hale-Bopp. Since the OPRs were not changed by chemical reactions in the coma, this fact implies that the OPRs were initialized or modified in thermal equilibrium. By comparing the spin temperatures with orbital periods, heliocentric distances, and gas production rates during the observations, we conclude that the spin temperature reflects the physical temperature of dust grains where the molecules formed.

The present data show that cometary water and ammonia ices formed at about 25–34 K in the six comets, except for comet Wilson. Comet Wilson seems to be peculiar among all comets ever observed if the obtained spin temperature is reliable. Because the spin temperature in comet C/1999 S4 (a dynamically new comet) is 27 K and much smaller than the lower limit in comet Wilson, the cosmic-ray damage hypothesis proposed to explain the high spin temperature in the dynamically new comet Wilson (Mumma et al. 1988) may be reexamined in future studies. Future observations of dynamically new comets will be important for confirming the cosmic-ray damage hypothesis in comet Wilson.

If the spin temperature provides information on the comet formation region in the solar nebula, the birthplace of comet Wilson might have been a region warmer than that for the other six comets. According to the solar nebula model by D'Alessio et al. (1998), the physical temperature of the equatorial plane around the Uranus-Neptune orbits is consistent with ≈ 30 K. The spin temperature of Jupiter-family comets (which probably originated in the Kuiper Belt region) would be lower than that of Oort Cloud comets (which originated in the giant-planet region), based on the solar nebula model (about 20 K or less for the Kuiper Belt region). However, a full two-dimensional treatment of radiative transfer gives a different temperature distribution in the solar nebula (Millar, Nomura, & Markwick 2003). In such a model, the temperature at the midplane decreases out to ≈ 25 AU from the young Sun, and beyond 25 AU it rises again. The temperature is 20–30 K in the region between 15 and 40 AU from the Sun. The spin temperature of comet Hartley 2 (a Jupiter-family comet) was derived to be 34 K, and this measurement may support the later model, although the origin of comet Hartley 2 is controversial.

The argument that comet Hartley 2 originated in the Kuiper Belt rests on its Tisserand parameter. However, A'Hearn et al. (1995) pointed out that this comet might have originated in the giant-planet region, according to its chemical composition and a new taxonomy based on their photometric observations of 85 comets. A'Hearn et al. (1995) reported that Jupiter-family comets tend to be *carbon-chain depleted*, and they proposed that carbon-chain depleted comets might originate from the Kuiper Belt region. Note that Schulz et al. (1998) considered such a new taxonomy problematic, since comet 46P/Wirtanen (a Jupiter-family comet) would be classified as carbon-chain depleted beyond about 1.6 AU, whereas it shows typical abundances at smaller heliocentric distances. In addition, comet Hartley 2 is the only Jupiter-family comet known to contain crystalline silicates (Crovisier et al. 1999), and this is consistent with an origin within 30 AU of the young Sun.

At any rate, the sample of Jupiter-family comets is still too small to discuss the difference in the spin temperatures statistically according to the dynamical origin of the comet. Future observations should be planned not only for Oort Cloud comets but also for Jupiter-family comets, in order to make clear what the spin temperatures reflect. If there is no difference in the spin temperatures between Jupiter-family comets and Oort Cloud comets, even though the solar nebula model predicts a difference in temperature at the midplane of the solar nebula, spin temperatures of about 30 K will be considered to reflect the physical temperature in the presolar molecular cloud. In the present data set, there is no clear difference in the spin temperature between Jupiter-family comets and Oort Cloud comets, which seems to indicate that the temperature of the presolar molecular cloud was ≈ 30 K.

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