The Spin Temperature of NH_3 in Comet C/1999S4 (LINEAR)

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A high-dispersion spectrum of Comet C/1999S4 (LINEAR) was obtained in the optical region with the high-dispersion spectrograph on the Subaru telescope when the comet was 0.863 astronomical units from the Sun before its disintegration. We obtained high signal-to-noise ratio emission lines of the cometary NH_2 bands from which an ortho-to-para ratio (OPR) of 3.33 ± 0.07 was derived on the basis of a fluorescence excitation model. Assuming that cometary NH_2 mainly originates from ammonia through photodissociation, the derived OPR of NH_2 molecules should reflect that of ammonia, which provides information on the environment of molecular formation or condensation and of the thermal history of cometary ices. Assuming that the OPR of ammonia in comets was unchanged in the nucleus, the derived spin temperature of ammonia (28 ± 2 kelvin) suggests that a formation region of the cometary ammonia ice was between the orbit of Saturn and that of Uranus in the solar nebula.

Comets are thought to be relics preserving information from the early solar nebula. Recent progress in modeling the chemical evolution of the solar nebula allows us to compare the model results with the observed chemical composition of comets (*1*, *2*). A second line of inquiry involves the isotopic composition of comets, especially the deuterium-to-hydrogen (D/H) ratios of water (H_2O) and hydrogen cyanide (HCN), which have been investigated (*3*–*5*).

Another important key to understanding conditions of the early solar system is the ortho-to-para ratio (OPR). The spin temperature determined from the OPR is believed to be primordial because the spin conversions between the ortho and para species through nondestructive collisions and radiative transitions are strictly forbidden (*6*). The OPR of water in comet 1P/Halley and three other comets indicates a spin temperature of about 30 K that may reflect the formation temperature of cometary water (*7*). It is important to investigate water in comets because water is most abundant in cometary ices (typically more than 80%). There are few reports on the OPRs of other cometary molecules that have hydrogen atoms at symmetrical positions (*8*). Here, we report a determination of the OPR of NH_2, which is thought to be produced from the photodissociation of ammonia by solar ultraviolet radiation (*9*, *10*).

Ammonia (NH_3) is important in comets as a reservoir of nitrogen atoms and is a key product in the network of chemical reactions related to the nitrogen atoms in the solar nebula (*1*). However, the OPR of cometary ammonia has never been determined, although ammonia has been detected for a few comets (*11*). Because ammonia only exists near the cometary nucleus where collisions between molecules are dominant, we must consider the collisional excitation and deexcitation of the ammonia molecule to calculate its emission spectrum in the coma. Although collisions between ammonia and water are important in the inner coma, the precise collisional cross section is not known. Furthermore, optically thick conditions near the nucleus require detailed radiative transfer calculations in the coma to determine the OPR of ammonia. These conditions make it difficult to calculate accurately the emission from cometary ammonia molecules (*7*). Second, it is difficult to obtain the ammonia spectra with a high signal-to-noise (S/N) ratio with the existing facilities. Even for the brightest comet in the past decade, C/1995O1 (Hale-Bopp), the obtained spectra of ammonia did not have a sufficient S/N ratio to determine an accurate OPR (*11*).

The OPR of ammonia can be calculated from the observed OPR of NH_2 assuming photodissociation of ammonia to NH_2. The advantages for using NH_2 are (i) there are strong NH_2 emission bands usually seen in visible spectra of a comet at around 1 astronomical units (AU) from the Sun, (ii) NH_2 molecules mainly exist further from the nucleus than ammonia where the coma is optically thin, and (iii) collisions between NH_2 and water can be neglected in this outer part of the coma. The first advantage leads to high S/N spectra of NH_2, and the last two simplify modeling the emission from NH_2 in the coma and translating the observed emission line strengths into the OPR.

To obtain high S/N emission lines of NH_2, we observed comet LINEAR (C/1999S4) with the high-dispersion spectrograph (HDS) (*12*) on the Subaru telescope (Table 1). This comet came from the Oort cloud (a reservoir of comets at $\sim 10^4$ AU from the Sun) and approached the Sun late in July 2000 and then disintegrated into many fragments (*13*). Our observation was performed early in July 2000, before disintegration.

From the calibrated spectrum (*14*), we extracted four emission bands of NH_2, the (0,10,0), (0,9,0), (0,8,0), and (0,7,0) bands (*15*). Among them, we concentrated on the NH_2 (0,7,0) and the (0,9,0) emission band because they had the highest S/N ratio and there were fewer telluric absorption lines in their wavelength regions. Our model calculation was similar to that of (*15*) except that we added some transition lines and levels that were not included in previous models (*16*). We calculated the population distribution among energy levels assuming the fluorescence process by solar radiation. The Swings effect, which was caused by a Doppler shift of the solar spectrum due to cometary motion relative to the Sun, was considered in our calculation. The population equations (*17*) were solved numerically.

The observed spectrum can be reproduced by the model calculation (Figs. 1 and 2), except for several unidentified lines that were also reported in other studies (*18*). We measured the flux of the following lines: 1_{01}-1_{11} (ortho), 1_{01}-2_{11} (ortho), and 2_{02}-2_{12} (para) in the (0,7,0) band and 1_{01}-1_{11} (ortho), 1_{01}-2_{11} (ortho), 0_{00}-1_{10} (para), and 2_{02}-3_{12} (para) in the (0,9,0) band. The S/N ratio of the measured flux was higher than 80 for these lines. As the result of least squares fitting for these bands, the derived OPR value of NH_2 was 3.33 ± 0.07. Assuming

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the photodissociation by solar ultraviolet radiation from ammonia to NH_2, we expect that only ortho-NH_2 was generated from an ortho-ammonia, and both ortho- and para-NH_2 were generated from a para-ammonia with a 1:1 ratio (*19*). Thus, the OPR of ammonia was equal to 1.17 ± 0.04 for comet LINEAR. The OPR of ammonia approaches 1.0 if ammonia ice formed and equilibrated under the high-temperature conditions (≥40 K), whereas it becomes larger under the low-temperature conditions (e.g., more than 10 at 5 K) (*20*). The OPR of 1.17 ± 0.04 derived here indicates the spin temperature of 28 ± 2 K. Compared with the spin temperature of water in the Oort cloud comets (e.g., comet Hale-Bopp), about 25 to 35 K, the temperature range for ammonia in comet LINEAR is consistent with the temperature range for water.

The most likely formation process of ammonia is the gas-grain chemistry in the presolar molecular cloud or in the solar nebula, in which ammonia formed on the icy mantle of grains (*21*). In this case, the spin temperature of ammonia may reflect the temperature of grains where the ammonia molecules formed. The temperature at the molecular cloud from which the low-mass stars originated is about 10 to 20 K. Therefore, the temperature of 28 ± 2 K seems to be higher for the ammonia formation in presolar molecular cloud. This temperature range corresponds to the region between the orbit of Saturn and that of Uranus (10 to 20 AU from the Sun) (*22*). Our results excluded the high-temperature limit (OPR = 1 for ammonia). This can eliminate the possible formation of cometary ammonia in the gas phase. Because the chemical reaction in the gas phase is exothermic, the OPR of ammonia formed in the gas phase should be unity according to the nuclear spin statistical weights of the ortho and para species.

Our results are consistent with temperatures determined for comet Hale-Bopp from D/H ratios of water and hydrogen cyanide (*5*). Recently, argon was detected in comet Hale-Bopp (*23*). The presence of argon requires that the interior of the comet has never been exposed to 35 to 40 K temperatures. If the argon also existed in comet LINEAR, the formation region of the comet was restricted. The highly volatile species such as CO, CH_4, and C_2H_6 were depleted in comet LINEAR compared with the other Oort cloud comets that formed near the orbit of Neptune in the solar nebula (*24*). This fact suggests that comet LINEAR formed in the warmer region (5 to 10 AU from the Sun). Our result is not consistent with the formation at such a warmer place. It may be possible to explain this discrepancy by the scenario that the icy grains on which ammonia (and other cometary molecules) formed near the orbit of Uranus (temperature ~28 K) migrated into the inner region of solar nebula during an accretion phase of solar nebula and the highly volatile species sublimated from the ice (but the OPR of ammonia did not change), and then the cometary nucleus formed from the icy grains at the warmer place.

Finally, we must note the other possible interpretation for the OPR of ammonia. The spin temperature was believed to reflect the temperature at the formation or condensation of molecules, and the reequilibration in a cometary nucleus during the long storage time in Oort cloud (~10^9 years) seems to be impossible, at least for water ice (*6*). However, it may be possible that the ammonia ice in the nucleus could change its OPR during its long stay in the Oort cloud, where the ambient temperature is less than 10 K. If the reequilibration of OPR of ammonia occurred in the nucleus, the OPR would be larger, more than 4 corresponding to ≤10 K. The experiments for the spin relaxation in an environment similar to the interior of cometary nucleus should be investigated in the future.

Further observations of the OPRs of cometary ammonia are also required for not only other Oort cloud comets but also the short-period (Kuiper belt) comets. These observations may be able to reveal the origin of these comets. Furthermore, if the OPR of ammonia could reequilibrate in the nuclei, there would be a variety of the OPRs according to the difference in aphelion distances of comets because the temperature of interior of cometary nucleus should be lower with larger aphelion distance (*6*). The method of the OPR determination for cometary ammonia established in this study should be applied to other comets, in order to know the OPR variety, if any.

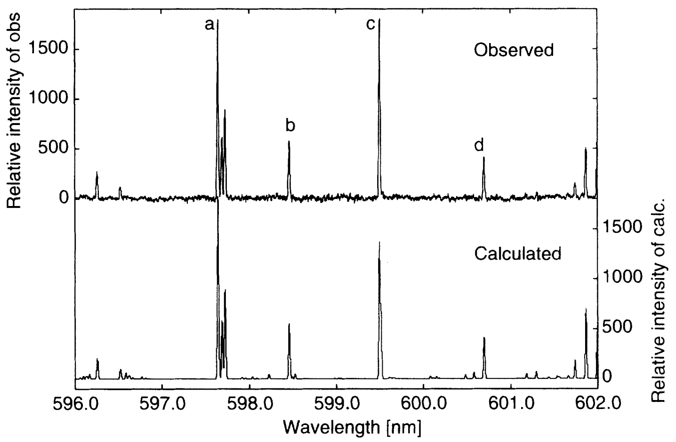

Fig. 1. **(Top)** Observed spectrum of the NH_2 (0,9,0) band in C/1999S4(LINEAR) on July 5.42 2000 (UT). The continuum component (the reflected sunlight by cometary dust grains) has been removed. The Doppler shift caused by cometary motion relative to Earth has been corrected. **(Bottom)** The synthetic fluorescence spectrum of cometary NH_2 for its OPR of 3.33, which is the best fit for the emission lines labeled by a to d. Emission lines labeled by a, b, c, and d are 1_{01}-1_{11} (ortho), 0_{00}-1_{10} (para), 1_{01}-2_{11} (ortho), and 2_{02}-3_{12} (para), respectively. These lines belong to the $\tilde{A}(0,9,0)$—$\tilde{X}(0,0,0)$ transition.

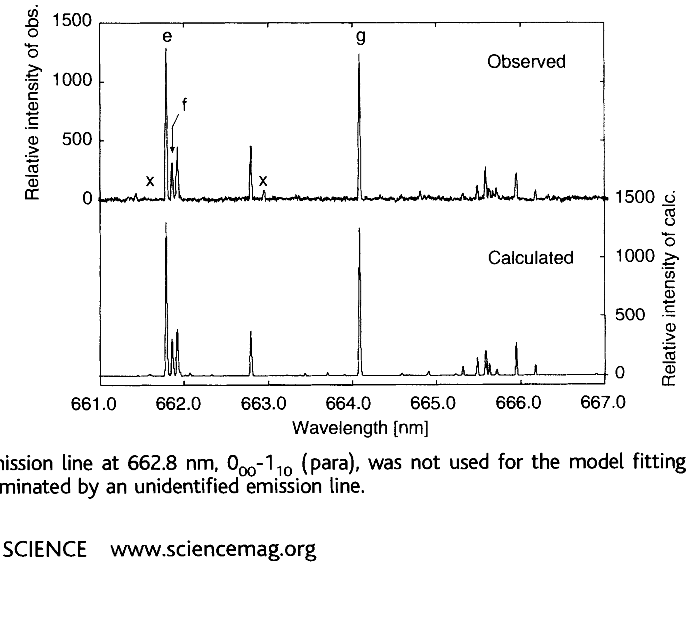

Fig. 2. **(Top)** Observed spectrum of the NH_2 (0,7,0) band in C/1999S4(LINEAR). The lines marked by x are unidentified lines in the cometary spectra. **(Bottom)** The synthetic fluorescence spectrum of cometary NH_2 for its OPR of 3.33 (the best fit for the lines labeled by e to g). Emission lines labeled by e, f, and g are 1_{01}-1_{11} (ortho), 2_{02}-2_{12} (para), and 1_{01}-2_{11} (ortho), respectively. These lines belong to the $\tilde{A}(0,7,0)$—$\tilde{X}(0,0,0)$ transition. The strong emission line at 662.8 nm, 0_{00}-1_{10} (para), was not used for the model fitting because this line is contaminated by an unidentified emission line.

Table 1. Relevant observation parameters.

Date (UT)	July 5.42 2000
Heliocentric distance of C/LINEAR	0.863 AU
Geocentric distance of C/LINEAR	0.823 AU
Total exposure time	1200 s
Slit size	8.3 arcsec × 1.2 arcsec*
Spectral resolution ($\lambda/\Delta\lambda$)	30,000
Wavelength coverage	510–780 nm

*The slit was put on the optical center of the comet.

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10. Most of NH_2 molecules in comets are thought to be photodissociation products of ammonia. Another possible parent of NH_2 is NH_2CHO, which was detected in C/1995O1(Hale-Bopp) for the first time, but its abundance was less than 1/50 that of ammonia (*2*). Thus, we assume that all NH_2 is produced from ammonia through photodissociation.
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16. The included transitions in our model are as follows (*27*): (i) the ro-vibronic transitions, $\tilde{A}(0,v_2',0)$—$\tilde{X}(0,v''_2,0)$, $18 \geq v_2' \geq 1$, $v_2'' = 0$ and 1; (ii) the ro-vibrational transitions, $\tilde{X}(0,v_2',0)$—$\tilde{X}(0,v''_2,0)$, $13 \geq v_2' \geq 8$, $v_2'' = 0$ and 1; (iii) the ro-vibrational transitions, $\tilde{X}(1,0,0)$—$\tilde{X}(0,0,0)$, $\tilde{X}(0,1,0)$—$\hat{X}(0,0,0)$, $\tilde{X}(0,0,1)$—$\tilde{X}(0,0,0)$; and (iv) the pure rotational transitions in $\tilde{X}(0,0,0)$. The vibrational transition moment for (iii) and the permanent dipole moment were determined by ab initio calculation. The rotational part of transition moment was calculated by ASYROT program (*28*).
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29. We thank S. Saito for a fruitful discussion on the OPR in the NH_2 generated from the ammonia through the photodissociation and D. C. Boice for improving our manuscript. NSO/Kitt Peak Fourier transform spectrometer data used here were produced by NSF/NOAO. This report is based on data collected at Subaru Telescope, which is operated by the National Astronomical Observatory of Japan.

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Preservation of Species Abundance in Marine Death Assemblages

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Fossil assemblages of skeletal material are thought to differ from their source live communities, particularly in relative abundance of species, owing to potential bias from postmortem transport and time-averaging of multiple generations. However, statistical meta-analysis of 85 marine molluscan data sets indicates that, although sensitive to sieve mesh-size and environment, time-averaged death assemblages retain a strong signal of species' original rank orders. Naturally accumulated death assemblages thus provide a reliable means of acquiring the abundance data that are key to a new generation of paleobiologic and macroecologic questions and to extending ecological time-series via sedimentary cores.

The fidelity of fossil assemblages to their source communities has haunted paleontologists for decades (*1–4*), and this issue has become especially acute with the growing realization that relative abundance data are required to address such dynamical problems as taxonomic survivorship, clade interactions, and ecological structure over evolutionary time (*5–7*). The potential reliability of naturally accumulated death assemblages is also important to ecology, where longer temporal perspectives on community composition are needed to discriminate natural and anthropogenic factors in ecosystem change (*8, 9*).

Paleoecological reliability has been estimated primarily via field tests comparing the live community with associated assemblages of dead remains in modern environments [reviewed by (*10*)]. Strong quantitative guidelines have been developed via such live-dead studies for some groups, most notably pollen and macroflora, permitting modern and prehistoric records of continental ecosystem change to be integrated (*11*). In contrast, the many tests conducted in marine molluscan communities, which dominate post-Paleozoic to Recent sedimentary seafloors, have yielded substantial variation in live-dead fidelity, especially for species abundance (*12*), and it is unclear how this variation is partitioned among methodological artifacts and true preservational bias.

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To acquire a robust estimate of taphonomic (postmortem) bias, I reanalyzed numerical abundance at the species level from 85 molluscan data sets (bivalves and gastropods) to standardize the metric of live-dead agreement (Spearman rank-order correlation coefficient). The 85 data sets span fine- to coarse-grained seafloors (no reefs or hardgrounds) from marsh to middle shelf settings and are drawn from 19 independent studies by other authors in low and middle latitudes (0° to 54°N, median 34°) (*13*). Although individual sample size, number of stations per habitat, and species richness vary among data sets, all reflect quantitative benthic sampling of the uppermost 10 or 20 cm of the sedimentary column. In the majority of studies, live data reflect a single census, thus providing a very conservative estimate of true live diversity. In 12 of the 85 habitats,