The First Interferometric Measurements of NH$_2$D/NH$_3$ Ratio in Hot Corinos

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Abstract

The chemical evolution of nitrogen during star and planet formation is still not fully understood. Ammonia (NH$_3$) is a key specie in the understanding of the molecular evolution in star-forming clouds and nitrogen isotope fractionation. In this paper, we present high-resolution observations of multiple emission lines of NH$_3$ toward the protobinary system NGC1333 IRAS4A with the Karl G. Jansky Very Large Array. We spatially resolved the binary (hereafter, 4A1 and 4A2) and detected compact emission of NH$_3$ transitions with high excitation energies ($\gtrsim$100 K) from the vicinity of the protostars, indicating the NH$_3$ ice has sublimated at the inner hot region. The NH$_3$ column density is estimated to be $\sim$10$^{17}$–10$^{18}$ cm$^{-2}$. We also detected two NH$_2$D transitions, allowing us to constrain the deuterium fractionation of ammonia. The NH$_3$/NH$_2$D ratios are as high as $\sim$0.3–1 in both 4A1 and 4A2. From comparisons with the astrochemical models in the literature, the high NH$_3$/NH$_2$D ratios suggest that the formation of NH$_3$ ices mainly started in the prestellar phase after the formation of bulk water ice finished, and that the primary nitrogen reservoir in the star-forming cloud could be atomic nitrogen (or N atoms) rather than nitrogen-bearing species such as N$_2$ and NH$_3$. The implications on the physical properties of IRAS4A’s cores are discussed as well.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Star formation (1569)

1. Introduction

Nitrogen is the fifth most abundant element in the interstellar medium (ISM) with an abundance of $\sim$6 $\times$ 10$^{-5}$ with respect to hydrogen (Przybilla et al. 2008). Determining the main nitrogen reservoirs in molecular clouds is a fundamental problem in astrochemistry. The nitrogen budget in molecular clouds also affects the formation of nitrogen-bearing complex organics molecules and chemistry in planet-forming disks (e.g., Schwarz & Bergin 2014).

In molecular clouds, the main nitrogen reservoirs in the gas phase are expected to be molecular nitrogen (N$_2$), which are formed in the gas phase (e.g., Furuya et al. 2018; van Dishoeck et al. 1993; see also Öberg & Bergin 2021). While in the central region of the clouds N$_2$ is self-shielded against interstellar UV photons and thus abundant, a substantial amount of atomic nitrogen (or N atoms) could also be present in the outer regions where the density is relatively low. N and N$_2$ freeze-out onto the surface of dust grains in the molecular clouds, and subsequently form other nitrogen-bearing molecules such as ammonia (NH$_3$) via a sequence of hydrogenation (Fedoseev et al. 2015; Hidaka et al. 2011; Jonnasus et al. 2020). Nitrogen-bearing molecules are also formed via gas-phase reactions (e.g., Le Gal et al. 2014), and can successively deplete onto dust grain mantles (e.g., Caselli et al. 2022; Pineda et al. 2022).

However, the partition of elemental nitrogen into these species is still not well constrained (Öberg & Bergin 2021).

Observationally constraining the main nitrogen reservoirs is generally difficult. Neither N$_2$ nor atomic N in the gas phase can be observed due to the lack of low-energy transitions that can be excited at the low temperature in molecular clouds. Instead, Maret et al. (2006) used the N$_2$H$^+$ emission line in molecular cloud cores to constrain the N$_2$ abundance in the gas phase. N$_2$H$^+$ is primary formed by N$_2$ + H$_2^+$, and thus its abundance reflects the abundance of gaseous N$_2$. Based on the relatively weak N$_2$H$^+$ emission, they suggested that N$_2$ is not the main nitrogen reservoir, and instead atomic N in the gas phase would be. This is also consistent with the low N$_2$ abundance in comets. Rubin et al. (2015) made an in situ measurement of N$_2$ in the comet 67P/Churyumov–Gerasimenko, revealing that the N$_2$/CO ratio is depleted by a factor of $\sim$25 compared with the case where all protosolar carbon and nitrogen are in CO and N$_2$. Icy nitrogen-bearing species in molecular clouds have been observed in the infrared. While NH$_3$ ice absorption bands in the 3 $\mu$m band have long been debated, its 9.1 $\mu$m band has been clearly detected by (Lacy et al. 1998; see also Gibb et al. 2000). Observations with the Spitzer Space Telescope revealed that $\sim$10% of overall nitrogen is locked up in ices, mainly as NH$_3$ (e.g., Öberg et al. 2011; Bottinelli et al. 2010; see also Boogert et al. 2015). Still, these relatively low NH$_3$ abundances imply that N$_2$ and N can be the main nitrogen reservoir in molecular clouds. Alternatively, there are also possibilities that a substantial amount of NH$_3$ is converted into ammonium salts, and that they can constitute a significant portion of the nitrogen reservoir as
observed in the comet 67P (Altwege et al. 2020). In summary, observational constraints on the main nitrogen reservoir in molecular clouds and how they vary with the evolution from clouds to comets are still lacking.

The molecular D/H ratios of ice can probe the formation history of molecules. As deuterium fractionation is more efficient in dense, cold environments (e.g., molecular cloud cores; Millar et al. 1989), information about the formation stage of molecules is imprinted into molecular D/H ratios. Recently, Furuya & Persson (2018) proposed a new approach to constrain the main nitrogen reservoir in molecular clouds using the D/H ratios of NH3 ice, i.e., NH2D/NH3. They performed gas-ice astrochemical simulations to investigate the evolution of nitrogen-bearing species from the formation of molecular clouds, a dense prestellar core, and then to the protostellar stage. They showed that if most nitrogen is already locked up in NH3 ice in the molecular cloud stage, the NH2D/NH3 in bulk ice mantle, and thus the ratio in the sublimates in the central warm regions of protostellar envelopes (typically \( \lesssim 100 \) au and \( \gtrsim 100 \) K; so-called “hot corinos”), are as low as \( \sim 4 \times 10^{-3} \), similar to or slightly higher than the HDO/H2O ratio. If N atoms are the dominant nitrogen reservoir in molecular clouds and NH3 ice formation commences only in the prestellar stage, on the other hand, the NH2D/NH3 ratio in the protostellar stage could be a few percent or even higher (e.g., Aikawa et al. 2012; Furuya & Persson 2018). The NH2D/NH3 ratio in the hot corinos, where ices sublimate, tells us when the NH3 ice is mainly formed.

The deuteration of NH3 in the cold outer envelopes of Class 0 protostars has been measured by single-dish observations. NH2D/NH3 ratios in the gas phase have been derived to be as high as a few to a few tens of percent (e.g., Hatchell 2003; Shah & Wootten 2001). Even doubly- and triply-deuterated ammonia (ND2 and ND3) have been detected (e.g., Loinard et al. 2001; van der Tak et al. 2002). On the other hand, deuteration of NH3 in a hot corino has not been measured so far, as high-resolution and high-sensitivity observations by interferometers are needed.

One of the few sources where NH3 emission has been detected in the hot corino is NGC1333 IRAS4A (hereafter IRAS4A), a deeply embedded low-mass Class 0 protobinary system located at a distance of \( \sim 300 \) pc (Ortiz-León et al. 2018; Zucker et al. 2020). IRAS4A harbors two protostars, IRAS4A1 and IRAS4A2 (hereafter 4A1 and 4A2; Lay et al. 1995; Looney et al. 2000). The \( (J, K) = (2, 2) \) and \( (3, 3) \) inversion transitions of NH3 at 24 GHz have been observed by the Karl G. Jansky Very Large Array (VLA) toward 4A1 and 4A2 by Choi et al. (2007, 2010, 2011). Both 4A1 and 4A2 show compact emission of those transitions, indicative of the NH3 ice sublimation. Most recently, De Simone et al. (2022) also observed \( (J, K) = (3, 3) \) to \( (7, 7) \) inversion transitions of NH3 with the VLA, revealing abundant warm NH3 gas sublimated from ice in the hot corino.

In this paper, we report the first detection of singly-deuterated ammonia (NH2D) emission in the hot corinos of 4A1 and 4A2, using interferometric observations at centimeter wavelengths with the VLA. In Section 2, our observations and data reduction are described. We analyzed the NH3 and NH2D emission line profiles to constrain the NH2D/NH3 ratios in the central region of 4A1 and 4A2, as described in Section 3. In Section 4, constraints on the column densities of NH3 and NH2D, excitation temperatures, and NH2D/NH3 ratios are shown. We discuss the implications from the derived NH2D/NH3 ratios and constraints on the formation stage of NH3 molecules in Section 5. Finally, we summarize our results in Section 6.

### Table 1

| Specie | Transition | \( \nu_0 \) (GHz) | \( \log_{10} A_{fi} \) \((s^{-1})\) | \( g_v \) | \( E_v \) (K) |
|--------|------------|-------------------|---------------------|-----|----------|
| NH3    | \((2,2)\)  | 23.7226333        | -6.65631            | 10.0 | 64.44806 |
|        | \((3,3)\)  | 23.8701292        | -6.59744            | 28.0 | 123.52904 |
|        | \((4,4)\)  | 24.1394163        | -6.55545            | 18.0 | 200.52091 |
|        | \((5,5)\)  | 25.4329987        | -6.51738            | 22.0 | 295.37076 |
| NH2D   | \(3_{1,3}-3_{2,3}\) | 18.807888     | -7.42815            | 63.0 | 93.91931 |
|        | \(4_{1,4}-4_{0,4}\) | 25.023792         | -7.01363            | 27.0 | 152.25741 |

**Notes.** The spectroscopic data were obtained from the Jet Propulsion Laboratory (JPL) Catalogue (Pickett et al. 1998) and Cologne Database for Molecular Spectroscopy (CDMS; Müller et al. 2005) via the Splatalogue interface. The original data are presented in Yu et al. (2010) for NH3 and De Lucia & Helminger (1975), Cohen & Pickett (1982), and Fusina et al. (1988) for NH2D.

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**References:**

1. Hatchell, J. (2003).
2. Shah, V. N., & Wootten, E. (2001).
flagging and downweighting, we manually specified continuum regions in a cont.dat file for the spectral line windows. In order to identify the line-free channels in the spectral windows with many lines (e.g., NH₃ (1,1) hyperlines), we first Fourier transformed the visibilities of line spectral windows without any continuum subtraction. The line-free channels are manually selected by carefully inspecting the image cubes. Afterwards, continuum subtraction is done in the u-v plane using uvccontsub task for all line spectral windows specifying the line-free channels selected in the image plane.

The visibilities in all continuum spectral windows and line-free channels in line spectral windows are averaged to ~4 MHz channel widths, and deconvolved down to a 3 x rms noise level of the dirty image using the multiscale CLEAN algorithm implemented in the tclean task with scales of [0, 10, 30] pixels (with a pixel scale of 0″1) and a Briggs parameter of 0.5. To determine the CLEAN components, we used the automasking feature implemented in the tclean task with the parameters sidelobethreshold = 2.0, noisethreshold = 4.25, and lownoisethreshold = 1.5. We manually checked that all the emission components were masked by carefully inspecting the resulting image.

Figure 1 presents the 22.3 GHz (~1.3 cm) continuum image. The resulting beam size and rms noise level of the continuum image were 0″99 × 0″75 (P.A. = 82°) and 7.4 μJy beam⁻¹, respectively. The rms noise level was measured in the emission-free region. The continuum peak positions are estimated by the two-dimensional (2D) Gaussian fitting to be α(J2000) = 03h29m10s540, δ(J2000) = +03°13′30″893 for 4A1 and α(J2000) = 03h29m10s442, δ(J2000) = +03°13′32″011 for 4A2, which are consistent with those derived by De Simone et al. (2020). The peak intensities were 2.2 ± 0.3 mJy beam⁻¹ and 0.42 ± 0.06 mJy beam⁻¹ for 4A1 and 4A2, respectively. The flux calibration uncertainty was added in quadrature. These values are consistent with those derived by De Simone et al. (2020) within uncertainty.

The visibilities in line spectral windows are imaged using the multiscale CLEAN algorithm with scales of [0, 10, 30] pixels, a Briggs parameter of 2.0, 1.0 km s⁻¹ velocity channel widths, and the same automasking parameters as the continuum imaging. The properties of the images, such as beam sizes and rms noise levels (σRMS), are listed in Table 2.

Figure 2 shows a gallery of velocity-integrated emission maps for all NH₃ and NH₂D lines, generated using better-moments (Teague & Foreman-Mackey 2018). The image cubes are integrated over the velocity ranges listed in Table 2 encompassing all detected hyperfine components. The velocity ranges for integration are adjusted for each transition to include only the emission by visually inspecting the image cubes. The noise levels σ for these maps are calculated by better-moments as σ = σRMS × √N × dv, where N is the number of integrated channels and dv is the channel width (1.0 km s⁻¹). These values are reported in each panel of Figure 2. We clearly see the detection of all NH₃ lines toward both 4A1 and 4A2 at signal-to-noise ratios (S/N) of ~10–20, while NH₂D lines are detected toward 4A1 with S/Ns of ~5 and only tentatively detected toward 4A2 with S/Ns of ~3–5. These S/N values are reported in Table 2 as well.

3. Analysis

In order to estimate the column densities of NH₃ and NH₂D, first we extracted the spectra for all lines from a single pixel toward the continuum peak position estimated in Section 2 for each source. The extracted spectra are presented in Figures 3 and 4 for 4A1 and 4A2. For the following analysis, NH₃ (1,1) and (2,2) transitions are excluded: given their relatively low

Table 2

| Specie | Transition | rms (mJy beam⁻¹) | Synthesized Beam (P.A.) | Integration Rangeᵃ | S/Nᵇ |
|--------|------------|-----------------|------------------------|-------------------|------|
|        |            |                 |                        |                   | 4A1  | 4A2 |
| NH₃    | (1, 1)     | 0.69            | 1.35 × 0″99(75°)       | [−14, −11], [−3, 1], [4, 9], [12, 16], [23, 29] | 12   | 16  |
| NH₃    | (2, 2)     | 0.62            | 1.32 × 0″98(75°)       | [−13, −8], [4, 10], [21, 26] | 9.2  | 13  |
| NH₃    | (3, 3)     | 0.60            | 1.31 × 0″98(75°)       | [−16, −11], [3, 11], [25, 30] | 10   | 18  |
| NH₃    | (4, 4)     | 0.55            | 1.25 × 0″95(77°)       | [3, 10] | 11   | 13  |
| NH₃    | (5, 5)     | 0.60            | 1.27 × 1″02(73°)       | [3, 10] | 9.0  | 14  |
| NH₂D   | 3,3−3,3    | 0.59            | 1.52 × 1″23(81°)       | [4, 10] | 5.5  | 3.1 |
| NH₂D   | 4,4−4,4    | 0.58            | 1.76 × 0″92(74°)       | [4, 10] | 5.2  | 4.9 |

Notes.

ᵃ Integration ranges for velocity-integrated emission maps.
ᵇ Peak signal-to-noise ratios on the velocity-integrated emission maps.
excitation energies, the extended emission may contaminate the emission from the central hot region.

3.1. Estimates on the Emitting Region Size

To estimate the emitting region size, we inspected the visibility profiles in the \((u, v)\) plane (amplitude–baseline length plot) for each transition. However, all of the transitions show almost flat profiles, indicating that it is difficult to infer the emitting region size even from visibility data. Instead, we estimated the emitting region size of NH\(_3\) using our data and the data presented in Choi et al. (2010, 2011). Choi et al. (2010, 2011) observed NH\(_3\) (3,3) transitions toward the IRAS4A system with a circular beam of 0\(^\circ\)3 × 0\(^\circ\)3, which is a higher spatial resolution than our data. The difference in the beam sizes between the data in Choi et al. (2010, 2011) and our...
data allows us to evaluate the beam dilution and accurately estimate the emitting region size, assuming that both observations trace the region with the same physical condition and that the lines are optically thick. We will confirm that the main component of NH3 (3,3) is highly optically thick (τ ≳ 10) in the following section.

We fitted a Gaussian to the spectra presented in Figure 4 in Choi et al. (2011) and Figure 1 in Choi et al. (2010) for IRAS4A1 and IRAS4A2, resulting in peak brightness temperatures of 44.4 ± 2.3 K and 73.2 ± 2.5 K, respectively. We also fitted a Gaussian to the NH3 (3,3) main component of our data to obtain the peak brightness temperature. The observed peak brightness temperatures can be modeled as $T_{\text{int}} \times f$, where $T_{\text{int}}$ is the intrinsic temperature and $f$ is the beam filling factor, given as

$$f = \frac{\theta_s}{\sqrt{\theta_s^2 + \theta_{\text{maj}}^2}} \frac{\theta_s}{\sqrt{\theta_s^2 + \theta_{\text{min}}^2}},$$

where $\theta_s$ is the emitting region size and $\theta_{\text{maj}}$ and $\theta_{\text{min}}$ are the size of the beam major and minor axes, respectively. Here we assume that the emission distribution of the source is a symmetric 2D Gaussian with a FWHM of $\theta_s$. Assuming that $T_{\text{int}}$ is the same between the data, the relation between the observed peak brightness temperature and $\theta_s$ can be inferred. We constructed the likelihood function of the observed brightness temperature ratio and $\theta_s$. To sample the posterior distributions, we assumed local thermodynamical equilibrium (LTE) so that the observed spectra can be fitted by a common excitation temperature for NH3 and NH2D transitions under the assumption that they originate from the same gas. The LTE assumption should be valid for targeted sources because the H2 density in the vicinity of the protostar (≤ 100 au) should be ≥ 10⁶ cm⁻³ (e.g., De Simone et al. 2020; Persson et al. 2016), which is far higher than the critical densities of NH3 transitions (~10⁵ cm⁻³; e.g., Shirley 2015).

First, we fitted these models to the NH3 and NH2D line profiles simultaneously; the ortho-to-para ratios of NH3 and NH2D are fixed to 1 and 3, respectively, which are the statistical values expected in the warm (≥ 100 K) environments.

This resulted in 14 free parameters (Table 3): velocity dispersions ($\Delta V$) and systemic velocities ($v_{\text{sys}}$) for all five transitions, the logarithms of column densities of NH3 and NH2D ($\log N$(NH3) and $\log N$(NH2D)), and the common excitation temperature ($T_e$) and emitting region size ($\theta_s$) among all five transitions. We also ran a fit with the ortho-to-para ratio of NH3 as a free parameter to check if the assumption of statistical equilibrium affects the derived parameters.

We sampled the posterior distributions with MCMC method implemented in the emcee Python package. We used uniform priors for all parameters except for the emitting region size. We used tight Gaussian priors for emitting region sizes based on the estimates in previous subsections. We ran 200 walkers for 5000 steps, including an initial 2500 steps discarded as burn-in. During the fit, we initially generated model spectra with much higher velocity samplings and then resampled down to the ones in the actual data (1.0 km s⁻¹).

### 3.2. Hyperfine Fit of NH3 and NH2D Lines

We fitted the observed spectra with a synthetic model considering hyperfine splitting (Rosolowsky et al. 2008). The details of the model used in the present work are described in Appendix A. Among the observed NH3 and NH2D transitions, both ortho (NH3 (3,3) and NH2D (3,3)) and para (NH3 (4,4), (5,5), and NH2D (4,4)) transitions are included, which in principle allows us to estimate the ortho-to-para ratio of NH3 and NH2D. In our model, we assume local thermodynamical equilibrium (LTE) so that the observed spectra can be fitted by a common excitation temperature for NH3 and NH2D transitions under the assumption that they originate from the same gas. The LTE assumption should be valid for targeted sources because the H2 density in the vicinity of the protostar (≤ 100 au) should be ≥ 10⁶ cm⁻³ (e.g., De Simone et al. 2020; Persson et al. 2016), which is far higher than the critical densities of NH3 transitions (~10⁵ cm⁻³; e.g., Shirley 2015).

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### 4. Results

The observed spectra overlaid by the model spectra generated from posterior samples, as well as the residual
Table 3
Free Parameters of Hyperfine Fits for 4A1 and 4A2

| Parameter | Prior for 4A1 Fit | Prior for 4A2 Fit |
|-----------|------------------|------------------|
| \(\Delta V\) (km s\(^{-1}\)) | U [0.1, 10] | U [0.1, 10] |
| \(v_{\text{sys}}\) (km s\(^{-1}\)) | U [4, 10] | U [4, 10] |
| \(\log_{10}N(\text{NH}_3)\) (cm\(^{-2}\)) | U [14, 21] | U [14, 21] |
| \(\log_{10}N(\text{NH}_2\text{D})\) (cm\(^{-2}\)) | U [14, 21] | U [14, 21] |
| \(T_{\text{ex}}\) (K) | U [50, 350] | U [50, 350] |
| \(\theta_0\) (°) | G [0.25, 0.06] | G [0.30, 0.03] |
| \(\sigma/p\) | U [0.01, 100] | U [0.01, 100] |

Notes.

\(^a\) The prior distributions of the parameter. The type of prior (uniform or Gaussian) and its parameters are listed. “U” represents a uniform prior, followed by the lower and upper bound of the uniform prior. “G” represents a Gaussian prior, followed by the center and standard deviation of the Gaussian prior.

\(^b\) The priors are common for all transitions, while treated as individual parameters for each transition.

\(^c\) The ortho-to-para ratio of NH\(_3\). Used for fits with free ortho-to-para ratio only.

spectra after subtracting the model spectra, are presented in Figures 3 and 4. The results of the fits are summarized in Table 4.

For 4A1, high excitation temperatures are derived in both fits with the ortho-to-para ratio fixed and varied (98.2±5 K and 110.3±16 K, respectively). The total optical depth (including the hyperfine) of each NH\(_3\) transition is greater than unity, while the hyperfine satellites of the NH\(_3\) (3,3) transition provide the constraints on the column density of NH\(_3\). In the fits with free ortho-to-para ratio, the NH\(_3\) column density is more uncertain and the NH\(_3\) ortho-to-para ratio is not well constrained. Since a statistical NH\(_3\) ortho-to-para ratio of unity is expected in the hot region, we employ the fit with the fixed ortho-to-para ratio as the fiducial result. The NH\(_2\)D column densities result in similar values (\(\sim 7 \times 10^{17}\) cm\(^{-2}\)) in both fits. Particularly, the undetected hyperfine satellites of NH\(_2\)D (4,4–4,0,4) at \(\sim -16\) km s\(^{-1}\) and \(\sim 26\) km s\(^{-1}\) (see Figure 3) are helpful to constrain the column density. The line widths of the NH\(_3\) (4,4) and (5,5) transitions are broader than those of the NH\(_3\) (3,3) and NH\(_2\)D transitions (Table 4). This may indicate that these higher transitions of NH\(_3\) preferentially trace inner regions with a higher infall velocity than (3,3) transition of NH\(_3\) and NH\(_2\)D transitions. We will discuss this issue in more detail in Section 5. Finally, both fits yield high NH\(_2\)D/NH\(_3\) column density ratios of 0.96±0.79 and 0.28±0.23, consistent within the uncertainties.

For 4A2, the fit with a fixed ortho-to-para ratio yields a lower excitation temperature (87±13 K) than that with a free ortho-to-para ratio (160±20 K). In the former, the peak brightness temperature of the main component of the NH\(_3\) (3,3) transition is significantly underestimated (Figure 4), and thus the lower excitation temperature is not reasonable. In contrast, the spectra are better reproduced in the fit with a free ortho-to-para ratio, which suggests that the higher excitation temperature is more reasonable. However, the obtained ortho-to-para ratio of NH\(_3\) in the fit (4.5±1.5) is significantly higher than the statistical ratio of unity. This does not seem to be realistic since the ortho-to-para ratio of NH\(_3\) should be unity in the hot region, as indicated by the derived excitation temperature. Nevertheless, the column density estimates in the two fits agreed within the uncertainties. We thus adopt the NH\(_3\) column density derived from the fits with free ortho-to-para ratio as our fiducial value. The NH\(_2\)D column density is also well constrained, although the line widths are not well constrained due to the lower S/N. The widths of NH\(_3\) lines are typically \(\sim 2-5\) km s\(^{-1}\), and broader for higher excitation transitions (Table 4). This could again imply that the emitting region is smaller (i.e., inner region with higher velocity) for higher transitions. Finally, the fiducial fit yields a NH\(_2\)D/NH\(_3\) ratio of 0.48±0.17, consistent with that derived in the fit with fixed ortho-to-para ratio within the uncertainties.

5. Discussion

5.1. NH\(_3\) and NH\(_2\)D in the Hot Corino Region

We have detected high-excitation transitions of NH\(_3\) (4,4) and (5,5) toward both 4A1 and 4A2 in addition to the (2,2) and (3,3) lines which were previously detected by Choi et al. (2007, 2010). The excitation temperatures derived in the hyperfine fits (\(<\sim 100\) K for 4A1 and \(<\sim 150\) K for 4A2) are comparable to or higher than the typical NH\(_3\) sublimation temperature of 100–140 K, depending on the gas density and composition of ice mixtures (Furuya & Aikawa 2014; Hama & Watanabe 2013; Minissale et al. 2022). Since the gas and dust temperatures are expected to be well coupled in the high-density region, the high excitation temperatures indicate that the observed emission traces the NH\(_3\) ice sublimation zone in the vicinity of the protostars. This conclusion is also supported by the compact emitting regions (\(<\sim 0.25\) or \(<\sim 75\) au) and the high column density of NH\(_3\) (\(<\sim 10^{17}–10^{18}\) cm\(^{-2}\)). Taquet et al. (2013) derived the column density of sublimated H\(_2\)O to be (3–5) \(\times 10^{19}\) cm\(^{-2}\) toward IRAS4A, assuming an emitting region size of \(<\sim 0.4\). The NH\(_3\)/H\(_2\)O abundance ratio of \(10^{-2}–10^{-1}\) is consistent with the composition of interstellar ices observed toward low-mass protostars (Öberg et al. 2011). In addition to NH\(_3\), we have detected high-excitation transitions of NH\(_2\)D. The observed line profiles are reasonably reproduced by the same emitting region sizes and excitation temperature as those of NH\(_3\), suggesting that the observed emission traces NH\(_3\) sublimated from ices. The NH\(_2\)D column densities are also high, resulting in high NH\(_2\)D/NH\(_3\) ratios of \(<\sim 0.5–1\) toward both 4A1 and 4A2. The high NH\(_2\)D/NH\(_3\) ratios, higher than expected from Furuya & Persson (2018), motivate careful discussions and confirmation. First, the NH\(_3\) column densities may be underestimated, as the NH\(_3\) lines are optically thick. In particular, our spectral windows do not cover the hyperfine satellites of the NH\(_3\) (4,4) and (5,5) transitions that can be optically thin (\(\tau < 1\)). De Simone et al. (2022) observed higher excitation lines up to \((J, K) = (7, 7)\) covering all of the hyperfine satellites, which allowed them to accurately estimate the column density of NH\(_3\) with non-LTE large velocity gradient analysis. While our estimates of the NH\(_3\) column density in 4A2 (\(<\sim 1\times 10^{18}\) cm\(^{-2}\)) are consistent with the estimates by De Simone et al. (2022; (0.6–3) \(\times 10^{18}\) cm\(^{-2}\) with a best fit of 2 \(\times 10^{18}\) cm\(^{-2}\)), our estimate for 4A1 (\(<\sim 8 \times 10^{17}\) cm\(^{-2}\)) is lower by a factor of a few than their estimates ((1–5) \(\times 10^{18}\) cm\(^{-2}\) with a best fit of 2 \(\times 10^{18}\) cm\(^{-2}\)). In their work, the optically thin (7,7) transition allowed them to constrain the column density. Our analysis may indeed underestimate the NH\(_3\) column density, particularly in 4A1. It is also possible that the column density of para-NH\(_3\) that was constrained from NH\(_3\)
### Table 4
Results of Fits for 4A1 and 4A2

| o/p \(^a\) | \(\theta_e [^\circ]\) | \(T_{ex} (K)\) | \(\Delta V_{FWHM} \) (km s\(^{-1}\)) | \(N(\text{NH}_3) \) (cm\(^{-2}\)) | \(N(\text{NH}_2\text{D}) \) (cm\(^{-2}\)) | \(\text{NH}_2\text{D}/\text{NH}_3\) | Fiducial |
|-------------|-----------------|-------------|----------------------|-------------------|-------------------|-----------------|---------|
| **IRAS4A1** |                 |             |                      |                   |                   |                  |         |
| 1 (fixed)   | 0.25\(\pm0.06\) | 98\(\pm2\) | 1.9\(\pm0.1\)       | 3.9\(\pm0.7\)     | 3.5\(\pm0.7\)    | 1.8\(\pm0.8\)   | 1.6\(\pm1.1\) | 8.1\(\pm10\) \(\times10^{17}\) | 7.3\(\pm10\) \(\times10^{17}\) | 0.96\(\pm0.76\) |
| 11\(\pm8\)  | 0.25\(\pm0.06\) | 110\(\pm10\)| 1.3\(\pm0.3\)       | 4.7\(\pm1.0\)     | 4.3\(\pm1.0\)    | 1.9\(\pm0.5\)   | 1.6\(\pm1.1\) | 2.8\(\pm11\) \(10^{18}\) | 6.9\(\pm10\) \(\times10^{17}\) | 0.28\(\pm0.59\) |
| **IRAS4A2** |                 |             |                      |                   |                   |                  |         |
| 1 (fixed)   | 0.33\(\pm0.02\) | 87\(\pm10\) | 2.2\(\pm0.2\)       | 2.2\(\pm0.2\)     | 4.1\(\pm0.7\)    | 0.9\(\pm0.5\)   | 5.1\(\pm1.0\) | 7.9\(\pm10\) \(\times10^{17}\) | 3.1\(\pm10\) \(\times10^{17}\) | 0.38\(\pm0.17\) |
| 4.5\(\pm1.3\) | 0.26\(\pm0.02\)| 160\(\pm20\)| 2.0\(\pm0.2\)       | 3.0\(\pm0.6\)     | 4.7\(\pm0.6\)    | 2.0\(\pm1.0\)   | 5.1\(\pm2.0\) | 1.0\(\pm10\) \(\times10^{18}\) | 4.9\(\pm10\) \(\times10^{17}\) | 0.48\(\pm0.17\) |

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\(\text{Note.}\)

\(\text{a The ortho-to-para ratio of NH}_3.\)
(4, 4) and (5, 5) is underestimated due to the lack of hyperfines; this might cause the peculiar ortho-to-para ratio in one of the fits. The NH2D/NH3 best-fit ratios are still higher than the model prediction, 0.4 for 4A1 and 0.3 for 4A2, if we adopt the best-fit NH3 column densities derived by De Simone et al. (2022).

Another possible caveat is that the kinetic gas motion could deviate the line profile from a simple Gaussian, which also could alter the estimation of column density and NH2D/NH3 ratios. Gas inflow motion of the envelope can result in a blue-skewed or inverse P-Cygni profile, which has already been observed toward the IRAS4A system (e.g., CH3OH and H2O lines; Di Francesco et al. 2001; Kristensen et al. 2012; Mottram et al. 2013; Sahu et al. 2019). Indeed, the observed spectra of NH3 (3, 3) and (4, 4) toward 4A1 in Figure 3 show subtle deviations from a Gaussian with rapid intensity decreases at the redshifted wings, which may trace the infall motion of the envelope, although it could also be due to the noise. The disk rotation could affect the line profile as well. Keplerian rotation of the circumstellar disk with a significant inclination will result in a double-peaked profile. Although more sophisticated modeling that includes these physical structures is desirable to more accurately evaluate the deuteriation of NH3, our results of high deuteration would not change qualitatively as no clear evidence of infall or rotation is detected at the current spatial/spectral resolution and sensitivity.

Finally, we note that the line widths are different among the observed transitions (Table 4). In particular, the line widths of NH3 (4, 4) and (5, 5) are broad compared to the other transitions,10 which may indicate that these transitions trace the more inner regions where the gas inflow velocities are larger. If the freefall (∝ √r−0.5) is assumed as the gas kinetics, the difference in line widths between NH3 (4, 4) and (5, 5) (∼4 km s−1) and the other transitions (∼2 km s−1) indicates the 4 times smaller radius of the emitting region for the former. We thus conducted the fit described in Section 3 using only the NH3 (3, 3) and NH2D transitions, all of which show a similar line width. Assuming an ortho-to-para ratio of NH3 of unity, the column densities of NH3 and NH2D, and thus the NH2D/NH3 ratios, are consistent with those of fiducial fits in Table 4 within uncertainties. Therefore, the high NH2D/NH3 ratio should be trustworthy at the spatial scales traced by NH3 (3, 3) and NH2D transitions (i.e., ∼0.25″ or ∼75 au).

Yet it is possible that the distributions of NH3 (traced by (4,4) and (5,5)) and NH2D are different at smaller spatial scales. Namely, the narrower line widths of NH2D may imply that the line emission originates from more outer regions than the (4,4) and (5,5) NH3 lines, e.g., a ring-like distribution of NH2D. The NH2D/NH3 ratio derived in ∼0.25″ scale then would be a lower limit for the ring regions and upper limit for the inner region with higher velocity, while we need higher spatial and/or spectral resolution to confirm such radial distribution. The ring region of a very high NH2D/NH3 ratio could be due to sublimation of a multilayered ice mantle (see Section 5.2).
for details). We confirmed that the observed NH$_2$D emission is dominated by the emission from the hot corinos.

The very high NH$_2$D/NH$_3$ ratio and the possible ring-like distribution of NH$_2$D could be due to a multilayered structure of the ice mantle. Taquet et al. (2014), who calculated gas-grain chemistry of a star-forming core as in Furuya & Persson (2018), explicitly showed the fractional abundances of icy molecules in each monolayer of ice mantle. While the NH$_2$D/NH$_3$ ratio is $\lesssim 10^{-2}$ in the deep layers that are formed in early times, the ratio is $\sim 0.3$ in the surface layers of ice when the dense prestellar core is about to collapse. As the ice-coated grains enter the central warm region of the core, the highly deuterated ice on the grain surface will be the first to sublime.

Even though NH$_2$D may be distributed in a ring region, our observation suggests that N atoms are the major nitrogen reservoir in molecular clouds. The NH$_3$ column density estimated from the (3,3) transition, which has a similar line width as that of NH$_2$D, is similar to the column density derived from the combination with higher transitions (see Section 5.2). The ammonia formed in the cold prestellar stage with a high D/H ratio is thus at least comparable in amount to that in the innermost regions. Since icy ammonia is more efficiently formed via hydrogenation of N atoms on the grain surfaces than in the gas phase, atomic nitrogen should be abundant and remains as the main nitrogen reservoir in the prestellar core stage, where enhanced deuteration is possible. In the model of Taquet et al. (2014), which predicts relatively abundant NH$_3$ ice and very high NH$_2$D/NH$_3$ in the surface of ice mantle, the nitrogen is assumed to be all atomic in their initial condition.

Furuya & Persson (2018) showed that the [NH$_2$D/NH$_3$]/[NH$_2$D/NH$_3$] ratio could better trace the primary nitrogen reservoir than the NH$_2$D/NH$_3$ ratio alone. If the atomic nitrogen is largely converted into molecular forms such as N$_2$ and NH$_3$ in the early stage of molecular clouds, most of the ammonia ices should have formed by then, which results in a relatively low NH$_2$D/NH$_3$ ratio. NH$_2$D is yet formed mainly in the later prestellar stage, since it requires more deuterium atoms, and the NH$_2$D/NH$_3$ ratio will be higher than NH$_2$D/NH$_3$, i.e., [NH$_2$D/NH$_3$]/[NH$_2$D/NH$_3$] $> 1$. On the other hand, if atomic nitrogen remains the dominant nitrogen reservoir in the prestellar phase, which is likely the case for IRAS4A, all the deuterated isotopologues will be formed in the prestellar phase, and [NH$_2$D/NH$_3$]/[NH$_2$D/NH$_3$] will be the statistical ratio ($\sim 1/3$). Thus, observations of doubly-deuterated NH$_3$ emission are desirable to confirm our conclusion.

5.3. Comparison with Other Major Species in Hot Corinos and Comet 67P/Churyumov–Gerasimenko

The first measurement of the NH$_2$D/NH$_3$ ratios achieved in this work enables us to compare the molecular D/H ratios among molecules in hot corinos. Comparison with cometary D/H ratios is also important, since the molecules in hot corinos could be incorporated to protoplanetary disks and then to planetary material. The D/H ratios of major species such as water and methanol in the inner warm regions of protostellar cores have extensively been studied with regard to several sources including IRAS4A (e.g., Jensen et al. 2019; Persson et al. 2014; Taquet et al. 2019). Recent in situ measurements on the comet 67P/Churyumov–Gerasimenko (hereafter 67P) by the Rosetta project (Altwegg et al. 2019) has revealed the molecular D/H ratios in major volatiles. The observed molecular D/H ratios toward IRAS4A and comet 67P are summarized in Table 5. We note that the D/H ratios of water and methanol toward IRAS4A are available only toward 4A2 because the deuterated as well as normal isotopologues have not been detected in emission toward 4A1 in (sub)millimeter wavelengths, probably due to absorption by the highly optically thick dust. We note that the following comparison stands even if we adopt the NH$_3$ column density derived in De Simone et al. (2022), which results in NH$_2$D/NH$_3$ $\sim 0.3$.

Among water, methanol, and ammonia, water shows the lowest D/H ratios of $\sim 10^{-4}$ toward IRAS4A (Persson et al. 2014; see also Jensen et al. 2019). This has been interpreted as evidence that the water ices are mainly formed in the early molecular cloud phase (Furuya et al. 2016). We note that, in the comparison of the D/H ratios among molecules, we need to take into account the hydrogen number in the normal isotopologue; e.g., the chance for NH$_3$ to get one hydrogen replaced by deuterium is 3/2 times higher than for H$_2$O. The HDO/H$_2$O ratio is still significantly low compared with the deuterium fraction of CH$_3$OH and NH$_3$.

In contrast to water, methanol shows higher D/H ratios of $\sim 10^{-2}$ toward IRAS4A (Taquet et al. 2019), suggesting the formation of methanol ices in the cold prestellar core phase. Higher D/H ratios of methanol than water are also seen in other protostellar cores such as IRAS2A and IRAS 16293-2422 (Manigand et al. 2020; Persson et al. 2014; Jørgensen et al. 2018; Taquet et al. 2019). The D/H ratio of ammonia measured toward IRAS4A in this work ($\gtrsim 10^{-3}$) is higher than that of methanol. We note that the D/H ratio of NH$_3$ is still higher than that of methanol, even if we consider the statistical correction and uncertainties associated with the observations. The lower limit of the NH$_2$D/NH$_3$ ratio is $\sim 0.3$ in 4A2 if we consider the uncertainty discussed in Section 5.1. This is higher than the upper limit of the (CH$_3$DOH + CH$_3$OD)/CH$_3$OH ratio by a factor of $\sim 6$ (Table 5). With the statistical correction, the D/H ratio of NH$_3$ is higher than that of CH$_3$OH by a factor of $\sim 0$.

This indicates that the ammonia ices are mostly formed in the later stage of prestellar cores, possibly even later than the formation of methanol ices, where the deuteration is more efficient. Observations of ammonia deuteration toward other

| Source         | HDO/H$_2$O     | (CH$_3$DOH + CH$_3$OD)/CH$_3$OH | NH$_2$D/NH$_3$ | References |
|----------------|----------------|---------------------------------|----------------|------------|
| IRAS4A         | $5.4 \pm 1.5 \times 10^{-4}$ | $(1.5-4.7) \times 10^{-8}$ | $4.8_{-1.3}^{+5} \times 10^{-1}$ | 1, 2, 3, 4 |
| 67P/C-G        | $1.05 \pm 0.14 \times 10^{-3}$ | $5.6 \pm 1.2 \times 10^{-2}$ | $\sim 1 \times 10^{-3}$ | 5, 6, 7    |

**Note.** The values in IRAS4A2 are shown as representatives of the IRAS4A system.

**References.** (1) Persson et al. (2014); (2) Jensen et al. (2019); (3) Taquet et al. (2019); (4) this work; (5) Altwegg et al. (2017); (6) Drozdovskaya et al. (2021); (7) Altwegg et al. (2019).
hot corinos are desirable to confirm that the high D/H ratio and late formation of ammonia ices are general.

The D/H ratios of water and methanol in the comet 67P shows a similar trend to those in IRAS4A (i.e., water D/H is lower than methanol; Altwegg et al. 2017, 2019; Drozdovskaya et al. 2019), suggesting the inheritance of the volatiles in the star-forming core to the planetary materials. The correlation in COMs abundances between the hot corinos and the comets also supports such an inheritance (Bianchi et al. 2019; Drozdovskaya et al. 2019). On the other hand, the D/H ratio of ammonia in the comet 67P is lower than methanol, which is different from the relation in IRAS4A. It suggests some chemical reprocessing for ammonia ices, or nitrogen as a whole, during the accretion onto the protostellar disk or subsequent protoplanetary disk stage. In the coma of comet 67P, Altwegg et al. (2020) recently detected a substantial amount of ammonium salts, which implies the chemical processes of ammonia. Alternatively, 67P inherits the low D/H component of ammonia, which is probed as a high-velocity component in our observation, while the high D/H component is fully released to the gas phase as discussed in Section 5.1. Indeed, Furuya et al. (2017) showed that stellar UV radiation can selectively remove the high D/H component from the surface of the ice via photodesorption, and the D/H ratios of water can be lower in the protoplanetary disk than those in protostellar envelopes. The same mechanism may work for ammonia as well.

5.4. Physical Properties of 4A1 and 4A2 Cores Probed by NH3 and NH2D

Although detailed modeling of the line profiles is difficult due to the relatively low S/Ns and poor velocity resolutions, several implications about the physical and chemical structures of the 4A1 and 4A2 cores, including their similarities and differences, can be obtained based on the results of our hyperfine fits.

The derived excitation temperatures are significantly different between 4A1 and 4A2, i.e., the excitation temperature in 4A2 (≈150 K) is higher than that in 4A1 (≈100 K). This difference is also clearly indicated by the higher peak brightness temperature in 4A2 (Figure 4). Since the excitation is expected to be thermalized, i.e., satisfies the LTE condition, the excitation temperatures can be directly used as a proxy of kinetic temperature. A similar trend has already been suggested by De Simone et al. (2020): they detected the optically thick CH3OH emission to estimate kinetic temperatures of 100 K and 160 K for 4A1 and 4A2, respectively. The emitting region sizes of CH3OH in De Simone et al. (2020; 0′′20–0′′30) are similar to the NH3 emitting region sizes derived in the present work, suggesting that both CH3OH and NH3 trace a region with similar temperatures (see also De Simone et al. 2022). This is reasonable given that the sublimation temperature of CH3OH and NH3 are expected to be similar (100–140 K depending on the gas densities and major composition of the ice; e.g., Furuya & Aikawa 2014; Hama & Watanabe 2013; Minissale et al. 2022). The lower temperature of 4A1 may reflect either the higher column density of the dust or lower stellar and accretion luminosities.

The difference in the NH2D/NH3 ratios between 4A1 and 4A2 may in fact reflect the difference in the temperature. As discussed in the previous subsections, ices on the grain surface are expected to consist of two layers: the bulk mantle, with lower deuteration formed in the molecular cloud stage, and the surface component, with higher deuteration synthesized in the dense core stage (e.g., Furuya & Persson 2018; Furuya et al. 2016; Taquet et al. 2013). Thus, the higher NH2D/NH3 ratio with a lower temperature in 4A1 may indicate that only the NH3 ices in the surface layer have sublimated.

6. Summary

We have observed NH3 and NH2D high-excitation transitions at ≈1″ resolution toward the protobinary NGC1333 IRAS4A with the VLA to measure the NH2D/NH3 ratio in the warm gas around the protostars, where ammonia ices have sublimated. Our main findings are summarized as follows:

1. We have detected NH3 (1,1) to (5,5) inversion transitions with S/N of ≳10 toward both of the sources, 4A1 and 4A2. We have also detected NH2D 3J3−2J3 and 4J4−4J4 rotation transitions with S/N ≳5 toward 4A1, while they have been marginally detected with S/N ≳3–5 toward 4A2.

2. We have estimated the excitation temperature and column density of NH3 and NH2D, and NH2D/NH3 column density ratios from the spectral line fitting. We found high NH3 and NH2D column densities of ≲1017–1018 cm−2 with high excitation temperatures (≳100 K) for both 4A1 and 4A2, indicating that the NH3 and NH2D lines originate from the inner warm regions. The NH2D/NH3 ratios are remarkably high, ∼0.5–1. The ratio is ≳0.3, even if we take into account the slightly higher NH3 column density derived by De Simone et al. (2022).

3. The high NH2D/NH3 ratios indicate the efficient formation of ammonia ices in the prestellar core stage, which in turn suggests that the primary nitrogen reservoir in molecular clouds is atomic nitrogen rather than nitrogen-bearing molecules such as N2 and NH3.

4. In IRAS4A1, the line widths of NH2D are similar to that of the NH3 (3,3) transition, but are narrower than those of NH3 higher transitions. This may indicate a ring-like distribution of NH2D. The ring-like distribution of NH2D and very high NH2D/NH3 ratio could be due to sublimation of multilayered ice mantle. The highly deuterated NH3 ice is formed in the outermost layer of the ice mantle in the late stage of prestellar core and is the first to be sublimated when the grains fall onto the central warm regions.

5. The obtained D/H ratios of ammonia ices have been compared with those of other major volatiles in the IRAS4A core and the comet 67P. The higher D/H ratios of ammonia than those of water and methanol in IRAS4A indicate that ammonia ices are formed in the later stage of the prestellar core phase, where the deuteration is particularly efficient. The higher NH2D/NH3 ratio in IRAS4A than that in the comet 67P may suggest chemical reprocessing during the accretion onto the protostellar disk and subsequent protoplanetary disk phase. An alternative explanation is sublimation of a highly deuterated layer of ice mantle in IRAS4A.

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Table 6
Spectroscopic Data of NH₃ and NH₂D Used in Hyperfine Fits

| Transition | F  |  $v_0$ (GHz) | $g_a$ | log$A_{ij}$ (s⁻¹) | $r^a$ | $b_0^b$ (km s⁻¹) |
|------------|----|-------------|-------|-------------------|------|-----------------|
| NH₃ (3, 3) | 2-3 | 23.8678062  | 20.0  | -7.5449           | 0.0264 | 29.1753       |
|            | 3-3 | 23.8701279  | 28.0  | -6.6658           | 0.28   | 0.0163         |
|            | 4-4 | 23.8701296  | 36.0  | -6.6174           | 0.4024 | -0.005         |
|            | 2-2 | 23.8701303  | 20.0  | -6.642            | 0.2112 | -0.0138        |
|            | 3-3 | 23.8718076  | 28.0  | -7.6846           | 0.0268 | -21.0796       |
|            | 3-2 | 23.872452   | 28.0  | -7.6908           | 0.0264 | -29.1728       |
| NH₃ (4, 4) | 3-4 | 24.1369314  | 14.0  | -7.7529           | 0.0162 | 30.8605        |
|            | 4-4 | 24.1374943  | 22.0  | -7.9457           | 0.0163 | 23.8697        |
|            | 4-5 | 24.139415   | 18.0  | -6.5927           | 0.3007 | 0.0161         |
|            | 5-5 | 24.139417   | 22.0  | -6.5048           | 0.3919 | -0.0087        |
|            | 3-3 | 24.1394175  | 14.0  | -6.5771           | 0.2424 | -0.0149        |
|            | 4-5 | 24.1413376  | 18.0  | -7.8583           | 0.0163 | -23.861        |
|            | 4-3 | 24.1419011  | 18.0  | -7.8617           | 0.0162 | -30.8593       |
| NH₃ (5, 5) | 4-5 | 24.5303911  | 18.0  | -7.9088           | 0.0109 | 31.7426        |
|            | 6-5 | 24.5308986  | 26.0  | -8.0659           | 0.011  | 25.541         |
|            | 5-5 | 24.532987   | 22.0  | -6.5396           | 0.3113 | 0.0208         |
|            | 6-6 | 24.5329892  | 26.0  | -6.5211           | 0.384  | -0.0061        |
|            | 4-4 | 24.5329897  | 18.0  | -6.529            | 0.261  | -0.0122        |
|            | 5-6 | 24.5350777  | 22.0  | -7.9932           | 0.011  | -25.5275       |
|            | 5-4 | 24.5355856  | 22.0  | -7.9957           | 0.0109 | -31.734        |
| NH₂D 3₁₃–3₀₃ | 2-3 | 18.805907  | 15.0  | -8.3826           | 0.0265 | 31.5766        |
|            | 4-3 | 18.80649    | 27.0  | -8.6324           | 0.0268 | 22.2837        |
|            | 2-2 | 18.807831   | 15.0  | -7.4793           | 0.2116 | 0.9086         |
|            | 2-2 | 18.807831   | 27.0  | -7.4562           | 0.4018 | 0.9086         |
|            | 3-3 | 18.8080466  | 21.0  | -7.5037           | 0.2801 | -2.528         |
|            | 3-4 | 18.809385   | 21.0  | -8.523            | 0.0268 | -23.8618       |
|            | 3-2 | 18.8099083  | 21.0  | -8.5284           | 0.0265 | -32.203        |
| NH₂D 4₁₄–4₀₄ | 3-4 | 25.0216041  | 7.0   | -8.2179           | 0.0162 | 26.2117        |
|            | 5-4 | 25.0221167  | 11.0  | -8.4117           | 0.0163 | 20.0706        |
|            | 3-3 | 25.0237541  | 7.0   | -7.0417           | 0.2431 | 0.4541         |
|            | 5-5 | 25.0237746  | 11.0  | -7.0314           | 0.3911 | 0.2085         |
|            | 4-4 | 25.0238552  | 9.0   | -7.0582           | 0.3008 | -0.7572        |
|            | 4-5 | 25.0255132  | 9.0   | -8.3244           | 0.0163 | -20.6205       |
|            | 4-3 | 25.0260052  | 9.0   | -8.3268           | 0.0162 | -26.5148       |

Notes.

$^a$ Relative strengths of hyperfine transitions. Normalized as the sum of $r$ being 1.

$^b$ Velocity offsets with respect to the inversion or rotation transitions listed in Table 1.

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Software: astropy (Astropy Collaboration et al. 2013, 2018), bettermoments (Teague & Foreman-Mackey 2018), astroquery (Ginsburg et al. 2019), LIME (Brinch & Hogerheijde 2010), emcee (Foreman-Mackey et al. 2013)

**Appendix A**

Hyperfine Models for NH₃ and NH₂D

Here we describe details of the hyperfine models for the observed NH₃ and NH₂D transitions.

**A.1. NH₃ Model**

We follow the methodology described in Rosolowsky et al. (2008). Observed spectra in terms of brightness temperature $T_B(v)$ are modeled as

$$ T_B(v) = f(J_e(T_{ex}) - J_e(T_{bg}))(1 - e^{-\tau(v)}), $$  \hspace{1cm} (A1)

where $f$ is the beam filling factor as in Equation (1), $T_{ex}$ is the excitation temperature, $T_{bg}$ is the background temperature (i.e., a cosmic microwave background temperature of 2.73 K here), and $\tau(v)$ is the optical depth profile. For each transition of NH₃,
astroquery (Ginsburg et al. 2019). We assumed that the $\sigma_v$ and $v_0$ are common among the hyperfine components in the same inversion or rotational transition, given that they originate from the same temperature region.

The total optical depths of each transition are related back to the column density as in Friesen et al. (2009; see also Rosolowsky et al. 2008):

$$N(J, K) = \frac{Q(T_\text{rot})}{\nu_0} 1 + \exp[-h \nu_0/(k_B T_\text{ex})] T_0 (J, K),$$  \hspace{1cm} (A4)

where $N(J, K)$ is the column density of NH$_3$ at the $(J, K)$ metastable state. The column density $N(J, K)$ can be related with the total (ortho or para) NH$_3$ column density $N(\text{NH}_3)$ through the partition function $Q$ as

$$N(\text{NH}_3) = \frac{Q(T_\text{rot})}{\nu_0} N(J, K) \exp \frac{E_u}{T_\text{ex}}. \hspace{1cm} (A5)$$

where $\nu_0$ and $E_u$ are the statistical weight and energy of the upper state listed in Table 1. The partition function $Q$ is calculated following Wilson et al. (2009) as

$$Q(T) = \sum_{J=0}^{\infty} \sum_{K=0}^{J} 2J + 1 S(J, K) \exp \left[ -\frac{h(BJ(J+1) + (C-B)K^2)}{k_B T} \right],$$  \hspace{1cm} (A6)

where $B = 298117$ MHz and $C = 186726$ MHz are the rotational constants of NH$_3$, and $S(J, K)$ is the constant factor for the nuclear spin statistics. For ortho- and para-NH$_3$ transitions, $S(J, K) = 4, 2$, respectively.

In the LTE approximation, the excitation temperature ($T_\text{ex}$) that governs the inversion transition and the rotational temperature ($T_\text{rot}$) that governs the population between the metastable levels are assumed to be the same, and these temperatures can be directly used as a proxy of the kinetic temperature ($T_\text{kin}$). In our fit, all of these temperatures are assumed to be the same and are represented by $T_\text{ex}$.

### A.2. NH$_2$D Model

Our NH$_2$D model follows the same formulation as NH$_3$. The spectroscopic data used for NH$_2$D are listed in Table 6 (Cohen & Pickett 1982; De Lucia & Helminger 1975; Fusina et al. 1988). Since we observed only a single transition for each ortho- and para-NH$_2$D, we directly related the optical depth to the column density assuming that $T_{\text{ex}}$ is the same as that of NH$_3$:

$$N_\nu = \sqrt{2 \pi} \sigma_v \nu_0^3 \exp \left[ \frac{h \nu_0}{k_B T_\text{ex}} \right],$$  \hspace{1cm} (A7)

where $N_\nu$ is the NH$_2$D column density at the upper state of the transition. The total NH$_2$D column density is calculated as

$$N(\text{NH}_2\text{D}) = \frac{Q(T_\text{ex})}{\nu_0} N_\nu \exp \frac{E_u}{T_\text{ex}}. \hspace{1cm} (A8)$$

where $Q$ is the full (i.e., ortho+para) partition function of NH$_2$D retrieved from the CDMS (Müller et al. 2005).
Figure 7. Comparison of model spectra of NH$_2$D transitions predicted by the non-LTE simulation with central stellar masses of 1.0 $M_\odot$ (blue) and 0.08 $M_\odot$ (orange) and observed spectra toward 4A1 (top) and 4A2 (bottom). The zero intensity level is indicated by the gray dashed line.

Appendix B
Radiative Transfer Modeling

We simulated the spectra of NH$_2$D transitions using the non-LTE radiative transfer code LIME (Brinch & Hogerheijde 2010) to see if only the cold envelope component of NH$_2$D could reproduce the observed NH$_2$D emission. Here we will describe the simulation settings. As the density and temperature structures of the IRAS4A protostellar cores, we used the spherically symmetric envelope model presented in Persson et al. (2016). The gas density and dust temperature profiles are shown in Figures 5 and 6. The gas density follows a single power-law profile, $n = n_\text{in}(r/r\text{in})^{-\alpha}$, where the parameters $n_\text{in} = 3.1 \times 10^9$ cm$^{-3}$, $r_\text{in} = 33.5$ au, and $\rho_\text{env} = 1.8$ are constrained through simultaneous fits to submillimeter dust continuum radial profiles and spectral energy distributions (see also Jørgensen et al. 2002; Kristensen et al. 2012). For this profile of the gas density, the dust temperature profile is self-consistently calculated (Jørgensen et al. 2002; Kristensen et al. 2012; Persson et al. 2016) assuming the observed luminosity of 9.1 $L_\odot$. We adopted this dust temperature profile as the gas temperature profile, i.e., assuming that the gas and dust are well coupled and their temperatures are the same. The modeled dust temperature inside the observed emitting region size ($\sim$75 au) is $\lesssim 100$ K, consistent with the observed excitation temperatures of $\sim100$ and $\sim160$ K (see Section 4). The radial profiles are truncated at $r_\text{in}$ and $r_\text{out} = 33,500$ au.

For the kinetics of the gas, we simply employed a spherically symmetric free-falling envelope with a radial velocity of $v_\text{ff} = \sqrt{2GM_*/r}$. We assumed a protostellar mass of $M_\ast = 1$ $M_\odot$ for both 4A1 and 4A2, given that there are almost no measurements of the central stellar mass. For 4A2, Choi et al. (2010) estimated it to be 0.08 $M_\odot$ from the velocity gradient analysis of NH$_3$ emission. Thus, we took another run with $M_\ast = 0.08$ $M_\odot$ to evaluate the effect of the central stellar mass to the observed emission.

We calculated the NH$_2$D abundance in the cold envelope based on single-dish observations and the model H$_2$ column density. Hatchell (2003) observed the NH$_2$D rotation-inversion transition with the IRAM 30 m telescope (with a beam size of $\sim 25''$ or $\sim 7000$ au), and derived an NH$_2$D column density of $3.9 \times 10^{14}$ cm$^{-2}$. This value is divided by the model H$_2$ column density of $1.9 \times 10^{24}$ cm$^{-2}$ (see Table C.1 in Kristensen et al. 2012), resulting in an NH$_2$D abundance of $2.1 \times 10^{-10}$. A constant abundance with radius is employed. The ortho-to-para ratio of NH$_2$D is fixed to 3, as done for the observational data analysis (Section 3).

The collisional excitation rates of ortho-NH$_2$D and para-NH$_2$D are based on Daniel et al. (2014) and taken from the Leiden Atomic and Molecular Database (Schöier et al. 2005). Given that the collisional excitation rates for ortho-H$_2$ and para-H$_2$ are available, we employ the thermal ortho-to-para ratio of H$_2$ (Flower & Watt 1984, 1985):

$$\frac{n(\text{ortho} - \text{H}_2)}{n(\text{para} - \text{H}_2)} = 9 \exp\left(-\frac{170.5 \text{ K}}{T}\right),$$

where $T$ is the gas temperature. This ratio is low at low temperature, e.g., $\sim 0.03$ at 30 K.

We use the dust opacity with thin ice mantle presented in the fifth column of Table 1 in Ossenkopf & Henning (1994) and a standard gas-to-dust mass ratio of 100. The dust opacity is the same as the one used in the modeling by Persson et al. (2016).

We run the LIME code in its non-LTE mode to produce the model image cubes of the NH$_2$D $3_{1,3}$–$3_{0,3}$ and $4_{1,4}$–$4_{0,4}$ transitions. To simulate the observations, first we convolved the output image cubes by the 2D Gaussian with a FWHM of the beam major and minor axis. Then, we subtracted the continuum emission by the CASA task imcontsub and extracted the spectra toward the continuum peak by the same manner as the case of the observations.

The simulated spectra are compared to the observed spectra in Figure 7. The model with 0.08 $M_\odot$ stellar mass shows the
brighter peak intensity due to the narrower line width caused by lower free-falling velocities. For both models, the peak intensities of the model spectra are weaker compared to the observed spectra by a factor of $\approx 10$, except for NH$_2$D $3_{1,3}$–$3_{0,3}$ with a central stellar mass of 0.08 $M_\odot$. The cold component may partially contribute to NH$_2$D $3_{1,3}$–$3_{0,3}$ emission ($\approx 20\%$ in velocity-integrated intensity) if the central stellar mass is small. We note, however, that the hyperfine splitting is not considered in this modeling. If it is considered, the peak intensity can be weaker because the total emission will be distributed over the hyperfine satellites. This is particularly effective for NH$_2$D $3_{1,3}$–$3_{0,3}$, where it has a prominent splitting around the main component (see Table 6 for the hyperfine spectroscopic data). Thus, this comparison between model and observed spectra suggests that the observed emission cannot be reproduced by the cold component alone. Therefore, we suggest that the observed NH$_2$D emission indeed traces the NH$_2$D sublimated from ice in the hot corino rather than the cold envelope component, and the degree of NH$_3$ ice deuteration is indeed high in the protostellar cores of IRAS4A1 and 4A2. We emphasize that the purpose of the radiative transfer modeling presented here is to just evaluate the contributions of the cold component of NH$_2$D in the envelope to the observed emission. More detailed modeling is needed to reproduce the observed emission. Although the detailed physical structure on smaller scales can differ from the simple free-falling envelope model presented here (e.g., protostellar disk as considered by Choi et al. 2010), it is beyond the scope of the present work.

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