Triply deuterated ammonia in NGC 1333

F.F.S. van der Tak\textsuperscript{1}, P. Schilke\textsuperscript{1}, H.S.P. Müller\textsuperscript{2}, D.C. Lis\textsuperscript{3}, T.G. Phillips\textsuperscript{3}, M. Gerin\textsuperscript{4,5}, and E. Roueff\textsuperscript{5}

\textsuperscript{1} Max-Planck-Institut für Radioastronomie, Auf dem Hügel 69, 53121 Bonn, Germany
\textsuperscript{2} I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany
\textsuperscript{3} California Institute of Technology, Downs Laboratory of Physics 320-47, Pasadena, CA 91125, USA
\textsuperscript{4} Lab. de Radioastronomie Millimétrique, Dépt. de Physique de l’E.N.S., 24 Rue Lhomond, 75231 Paris, France
\textsuperscript{5} DEMIRM, Observatoire de Paris, 61 avenue de l’Observatoire, 75014 Paris, France

Abstract. The Caltech Submillimeter Observatory has detected triply deuterated ammonia, ND\textsubscript{3}, through its \(J_K = 1\text{\textsubscript{0}} \rightarrow 0\text{\textsubscript{0}}\) transition near 310 GHz. Emission is found in the NGC 1333 region, both towards IRAS 4A and a position to the South-East where DCO\textsuperscript{+} peaks. In both cases, the hyperfine ratio indicates that the emission is optically thin. Column densities of ND\textsubscript{3} are \(3 - 6 \times 10^{11}\) cm\textsuperscript{-2} for \(T_{\text{ex}} = 10\) K and twice as high for \(T_{\text{ex}} = 5\) K. Using a Monte Carlo radiative transfer code and a model of the structure of the IRAS source with temperature and density gradients, the estimated ND\textsubscript{3} abundance is \(3.2 \times 10^{-12}\) if ND\textsubscript{3}/H\textsubscript{2} is constant throughout the envelope. In the more likely case that ND\textsubscript{3}/H\textsubscript{2} is constant, ND\textsubscript{3}/H\textsubscript{2} peaks in the cold outer parts of the source at a value of \(1.0 \times 10^{-11}\). To reproduce the observed NH\textsubscript{3}/ND\textsubscript{3} abundance ratio of \(\sim 1000\), grain surface chemistry requires an atomic D/H ratio of \(\sim 0.15\) in the gas phase, >10 times higher than in recent chemical models. More likely, the deuteration of NH\textsubscript{3} occurs by ion-molecule reactions in the gas phase, in which case the data indicate that deuteron transfer reactions are much faster than proton transfers.

Key words. ISM: abundances – ISM: molecules

1. Introduction

Deuterium-bearing molecules have attracted attention in recent years. Physically, they appear to be good probes of the very cold phases of molecular clouds prior to star formation. Chemically, the isotopic composition of molecules is an important clue to their formation mechanism. There are two ways to make deuterated molecules. First, at temperatures \(< 70\) K, the gas-phase reaction equilibrium \(\text{H}_3^+ + \text{HD} \leftrightarrow \text{H}_2\text{D}^+ + \text{H}_2\) is shifted in the forward direction. Subsequent deuteron transfer from \(\text{H}_2\text{D}^+\) to, e.g., CO and N\textsubscript{2}, leads to the large observed abundance ratios of DCO\textsuperscript{+}/HCO\textsuperscript{+} and N\textsubscript{2}D\textsuperscript{+}/N\textsubscript{2}H\textsuperscript{+} of \(\sim 0.1\), four orders of magnitude higher than the Galactic D/H ratio (Turner 1998). The key species of this chemical scheme, \(\text{H}_2\text{D}^+\), was recently detected in the Class 0 source NGC 1333 IRAS 4A (Stark et al. 1999). The high densities and low temperatures in this object promote the formation of H\textsubscript{3}D\textsuperscript{+} out of H\textsubscript{3}\textsuperscript{+} and HD, and also prevent its destruction because the major destroyer of H\textsubscript{3}D\textsuperscript{+}, CO, is depleted by a factor of \(\sim 100\) due to freeze-out onto dust grains.

Alternatively, deuterium-bearing molecules can be formed on dust grains by surface chemistry. Accretion of H and CO onto grains, followed by reaction, is thought to produce solid H\textsubscript{2}CO and CH\textsubscript{3}OH. This mechanism favours deuteration because the atomic D/H ratio in the gas phase is much greater than the elemental ratio. The observed abundances of HDCO, CH\textsubscript{3}OD and D\textsubscript{2}CO in Orion and IRAS 16293 indicate their synthesis on dust grains (Turner 1990; Charnley et al. 1997; Ceccarelli et al. 1998). The same mechanism may work for NH\textsubscript{3}, provided most nitrogen is in atomic form, and support for this route comes from detections of solid NH\textsubscript{3} (Lacy et al. 1998; Gibb et al. 2000). However, these detections remain tentative (Dartois & d’Hendecourt 2001), and observations of N\textsubscript{2}H\textsuperscript{+} suggest that in dense clouds, most nitrogen is in molecular form (Womack et al. 1992).

While NH\textsubscript{2}D has been observed in many sources (Saïtta et al. 2000; Shah & Wootten 2001), ND\textsubscript{2}H has only been detected so far towards the cold, starless cores L134N and L1689N (Roueff et al. 2000; Loinard et al. 2001). The temperatures in these sources of \(\sim 10\) K are too low for significant evaporation of even the most volatile ices to occur. Gas-phase reactions can probably account for the observed abundance ratios (Rodgers & Charnley 2001), but observations of ND\textsubscript{3} would present a strong test, as the gas-phase route produces \(\sim 3\) times more ND\textsubscript{3} than the grain surface route. As a step towards measuring the relative importance of gas-phase and solid-state deuteration, we have observed the \(J_K = 1\text{\textsubscript{0}} \rightarrow 0\text{\textsubscript{0}}\) transition of...
The rotational energy levels of symmetric top molecules exhibit hyperfine structure due to coupling of the \(^{14}\text{N}\) nuclear spin with the rotational angular momentum. Splitting due to D, owing to its small quadrupole moment, is only \(\approx 200\) kHz and remains unresolved in our data. Thus, we have fitted the observed spectrum with three Gaussian profiles with optical depth ratios of 5:3:1 and assuming that the components have equal widths and excitation temperatures. Such a fit has four parameters: optical depth \(\tau\), central velocity \(V_0\), line width \(\Delta V\) and intensity \(T_{mb}\). We used the HFS method inside the CLASS package. Leaving all parameters free gives the values reported in columns 2–5 of Table [1]. For the IRAS 4A position, fixing \(V_0\) and/or \(\Delta V\) to values measured in other lines, 7.0 and 1.2 km s\(^{-1}\) ([Blake et al. 1995]) gives similar results. The fit results indicate that the line shape is consistent with the optically thin hyperfine intensity ratio of 5:3:1, but that the signal to noise is not high enough to constrain the optical depth. Without taking hyperfine broadening into account, \(\Delta V\) at the IRAS 4A position would be 2.6 km s\(^{-1}\), much broader than other lines from the cold component of this source ([Blake et al. 1995]). The line shape thus confirms the assignment of the line to ND\(_3\).
temperature of $T_{\text{bg}} = 2.7$ K, the velocity-integrated optical depth follows from

$$\int T_{\text{mb}} dV = \frac{h \nu}{k} \left( \frac{1}{e^{h \nu/kT_{\text{ex}}} - 1} - \frac{1}{e^{h \nu/kT_{\text{bg}}} - 1} \right) \int \tau dV$$

so that

$$\int \tau dV = \frac{\beta^3}{8 \pi \mu^3} AN_u (e^{h \nu/kT_{\text{ex}}} - 1)$$

with

$$N_u = \frac{g_u N}{Q(T_{\text{ex}})} e^{-E_{\text{up}}/kT_{\text{ex}}}$$

yields the column density estimates in column 7 of Table 1. Here, $Q(T_{\text{ex}})$ is the partition function $\sum_i g_i e^{-E_i/kT_{\text{ex}}}$, equal to 38.3 for $T_{\text{ex}}=10$ K. The Einstein A coefficient of 2.57 × 10^{-4} s^{-1} follows from the dipole moment of 1.49 D (di Lonardo & Trombetti 1981).

The assumed value of $T_{\text{ex}}$ represents a kinetic temperature at which chemical fractionation should be efficient. However, at densities well below the critical density of this line, 10^{-7} - 10^{-8} cm^{-3}, $T_{\text{ex}}$ will drop below $T_{\text{kin}}$, which changes the column density estimate. As an example, the last column of Table 1 gives the values for $T_{\text{ex}}=5$ K.

### 3. Abundance of ND$_3$

To estimate the abundance of ND$_3$ we have used the Monte Carlo radiative transfer program by Hogerheijde & van der Tak (2000, talisker.as.arizona.edu/~michiel/ratran.html). Lacking auxiliary data on the DCO$^+$ position, we concentrate on NGC 1333 IRAS 4A, for which we take the temperature and density structure from Stark et al. (1999). Between the outer and inner radii of 3100 and 10 AU, temperatures increase from 13 to 320 K, and densities from 2 × 10^6 to 4 × 10^{11} cm^{-3}; $N$(H$_2$) = 3.1 × 10^{23} cm^{-2} in a 13'' beam, but strongly depends on beam size due to the $R^{-2}$ density distribution. The radiative transfer model for ND$_3$ includes the 30 terms up to 100 cm^{-1} above ground, including the inversion splitting but not the hyperfine structure. Rate coefficients for de-excitation of NH$_3$ in collisions with H$_2$ from Danby et al. (1988) are used, scaled to the different reduced mass of the ND$_3$-H$_2$ system, and augmented with the terms that are Pauli-forbidden in NH$_3$, and with transitions that would be ortho-para conversions in NH$_3$. Initially, a constant abundance of ND$_3$ (relative to H$_2$) was assumed. The excitation of ND$_3$ as a function of radius is calculated with the Monte Carlo program. The result is integrated over the line of sight and convolved with a 25'' beam. The area under the synthetic line profile matches the observed value for ND$_3$/H$_2$ = 3.2 × 10^{-12}.

As an alternative model, the ND$_3$ abundance was assumed to follow that of H$_2$D$. The major chemical formation path to ND$_3$ starts with the reaction of NH$_3$ with H$_2$D$^+$ and its derivatives DCO$^+$ and N$_2$D$^+$, and proceeds through NH$_2$D and ND$_2$H. As a simple way to model this behaviour, we have assumed a constant H$_2$D$^+$/ND$_3$ ratio. However, this ratio would vary in the case of a varying NH$_3$ abundance, and if the alternative route starting with the reaction of N$^+$ with HD competes, which is slightly endothermic. In the absence of sufficient constraints, we keep H$_2$D$^+$/ND$_3$ constant. Our two assumed ND$_3$ abundance profiles could be tested indirectly by observations of key deuterated molecules such as DCO$^+$ and N$_2$D$^+$.

The H$_2$D$^+$ abundance profile in NGC 1333 IRAS 4A was calculated analytically by Stark et al. (1999), using assumed values for the cosmic-ray ionization rate ($\zeta = 5 × 10^{-17}$ s^{-1}) and the abundances of HD (2.8 × 10^{-5}) and D (2.8 × 10^{-6}), and using a CO abundance of 4 × 10^{-6} estimated from C^{12}O data. Due to the small energy difference between H$_3^+$ and H$_2$D$^+$, the H$_2$D$^+$ abundance is strongly peaked toward large radii where temperatures are low. We have re-calculated the H$_2$D$^+$ abundance profile using $\zeta = 2.6 × 10^{-17}$ s^{-1}, the mean of the values implied by observations of H$_3^+$ and H$_2$CO$^+$ towards seven massive young stars (van der Tak & van Dishoeck 2000). This calculation also includes dust radiation which the one by Stark et al. (1999) did not. The new calculations are still consistent with the measured H$_2$D$^+$ line flux, and indicate an H$_2$D$^+$ abundance increasing from 5 × 10^{-19} at a radius of 10 AU to 5 × 10^{-16} at $R = 3100$ AU. To model the ND$_3$ data, models were run for several values of the H$_2$D$^+$/ND$_3$ ratio, and agreement between observed and calculated line flux was found for H$_2$D$^+$/ND$_3$ = 46. The ND$_3$ abundance at large radii is then 1.0 × 10^{-11}, a factor of 3 higher than that found assuming a constant ND$_3$ abundance.

### 4. Chemistry of ND$_3$

Table 2 summarizes the measured column densities of NH$_3$ isotopomers toward NGC 1333 IRAS 4A. It is seen that $N$(NH$_3$)/$N$(NH$_2$D) = 10 and $N$(NH$_3$)/$N$(ND$_3$) = 1000; no observations of ND$_2$H exist yet. The available data suggest a trend where with each H→D substitution, the column density drops by an order of magnitude. Current models of gas-phase chemistry, on the other hand, predict...
that ND$_2$H/ND$_3$ > NH$_2$D/ND$_2$H > NH$_3$/NH$_2$D [Rodgers & Charnley 2001], unless deuteron transfer reactions are much more rapid than proton transfers. The same trend is expected in the case of grain surface chemistry. However, the measured column densities are uncertain by ≈30% due to calibration, so their ratios could be off by a factor of two and cannot be used to rule out either mechanism.

Since a straightforward comparison of column densities may be complicated by the differences in beam size of the data in Table 2, we have determined the NH$_3$ abundance toward NGC 1333 IRAS 4A using the approach of § 3. The same temperature and density structure as in § 2 are used, and the original collisional rate coefficients of Danby et al. [1988], based on the UMIST database [Le Teuf et al. 2001, www.rate99.co.uk], the rates of the major destruction reactions of NH$_3$ do not depend on temperature. Formation of NH$_3$ is mainly by dissociative recombination of NH$_2^+$, the rate of which has a $T^{-0.5}$ dependence, which in the model for NGC 1333 IRAS 4A corresponds to a factor of 5. This factor is dwarfed by the exponential increase in H$_2$D$^+$ so only constant-abundance models have been considered for NH$_3$. The observations of Shah & Wootten (2001) are reproduced for NH$_3$/H$_2$=1×10$^{-8}$.

Rodgers & Charnley (2001) present a chemical scheme to form deuterated ammonia in the gas phase, which assumes that the branching ratios of dissociative recombination are statistical and that the relevant reaction rates are isotope-independent. Using this scheme, for NH$_3$/NH$_2$D=10 (Table 2), an abundance ratio of NH$_3$/ND$_3$ of ≈10000 is expected. The observed value of $10^{-8}/10^{-11}$ = 1000 is inconsistent with this prediction. This disagreement may indicate that a detailed chemical network is needed instead of a statistical treatment. In addition, NH$_3$/NH$_2$D was measured in an arcmin-sized region and may be < 10 within the 25" CSO beam. Based on the observed NH$_3$/ND$_3$ ratio, NH$_3$/NH$_2$D could approach unity on small scales.

In the case of surface chemistry, the observed NH$_3$/ND$_3$ ratio implies an atomic D/H ratio of ≈0.15 in the gas phase (Rodgers & Charnley 2001). This is significantly higher than the values of $10^{-2} - 10^{-3}$ in the chemical models of Roberts & Millar (2000). Based on this discrepancy and on the closer agreement of the observed NH$_3$/ND$_3$ ratio with the gas-phase prediction for NH$_3$/NH$_2$D=10, we tentatively conclude that ion-molecule reactions are presently the preferred formation mechanism of NH$_3$ in NGC 1333. This mechanism can reproduce the observed deuteriation levels if deuteron transfer reactions are much faster than proton transfers. In the future, this conclusion should be tested through measurements of the NH$_3$, NH$_2$D, ND$_2$H and ND$_3$ abundances in a larger source sample. Any conclusion drawn from such data will be much stronger if the lines are measured with similar beam sizes. More detailed chemical networks are also needed. Such a project could constrain the relative importance of gas-phase and grain-surface deuteration as a function of environment.

**Acknowledgements.** The CSO is supported by NSF grant AST 99-80846. HSPM acknowledges support from the Deutsche Forschungsgemeinschaft (DFG) via grant SFB 494.

**References**

Blake, G. A., Sandell, G., van Dishoeck, E. F., et al. 1995, ApJ, 441, 689

Ceccarelli, C., Castets, A., Loinard, L., Caux, E., & Tielens, A. G. M. 1998, A&A, 338, L43

Charnley, S. B., Tielens, A. G. M., & Rodgers, S. D. 1997, ApJ, 482, L203

Danby, G., Flower, D. R., Valiron, P., Schilke, P., & Walmsley, C. M. 1988, MNRAS, 235, 229

Dartois, E. & d’Hendecourt, L. 2001, A&A, 365, 144

di Lonoardo, G. & Trombetti, A. 1981, Chem. Phys. Lett., 84, 327

Gibb, E. L., Whittet, D. C. B., Schutte, W. A., et al. 2000, ApJ, 536, 347

Helminger, P. & Gordy, W. 1969, Physical Review, 188, 100

Hogerheijde, M. R. & van der Tak, F. F. S. 2000, A&A, 362, 697

Lacy, J. H., Faraji, H., Sandford, S. A., & Allamandola, L. J. 1998, ApJ, 501, L105

Le Teuff, Y. H., Millar, T. J., & Markwick, A. J. 2000, A&AS, 146, 157

Lis, D. C., Roueff, E., Gerin, M., et al. 2002, ApJ, in press

Loiuard, L., Castets, A., Ceccarelli, C., Caux, E., & Tielens, A. G. M. 2001, ApJ, 552, L163

Müller, H. S. P., Thorwirth, S., Roth, D. A., & Winnewisser, G. 2001, A&A, 370, L49

Pickett, H. M., Poynter, R. L., Cohen, E. A., et al. 1998, J. Quant. Spectrosc. Radiat. Transfer, 60, 883

Roberts, H. & Millar, T. J. 2000, A&A, 361, 388

Rodgers, S. D. & Charnley, S. B. 2001, ApJ, 553, 613

Roueff, E., Tiné, S., Coudert, L. H., et al. 2000, A&A, 354, L63

Saito, S., Ozeki, H., Ohishi, M., & Yamamoto, S. 2000, ApJ, 535, 227

Shah, R. Y. & Wootten, A. 2001, ApJ, 554, 933

Stark, R., van der Tak, F. F. S., & van Dishoeck, E. F. 1999, ApJ, 521, L67

Turner, B. E. 1990, ApJ, 362, L29

—. 2001, ApJS, 136, 579

van der Tak, F. F. S. & van Dishoeck, E. F. 2000, A&A, 358, L79

**Table 2.** Column densities of ammonia isotopomers towards NGC 1333 IRAS 4A

| Species | N | Beam Beam | Reference |
|----|----|----|----|
| NH$_3$ | 3.1(4)×10$^{14}$ | 74 | Shah & Wootten (2001) |
| NH$_2$D | 2.2(7)×10$^{13}$ | 90 | Shah & Wootten (2001) |
| ND$_3$ | 2.9(9)×10$^{11}$ | 25 | this work |
Womack, M., Ziurys, L. M., & Wyckoff, S. 1992, ApJ, 393, 188