INTERSTELLAR TRIPLY DEUTERATED AMMONIA

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ABSTRACT

Research on interstellar ND₃ is reviewed and updated from the discovery papers. Results from observations of a dozen sources at centimeter and submillimeter wavelengths are presented. The two data sets are consistent, but do not constrain the excitation conditions in the ND₃-emitting gas. The column density ratios of NH₃/NH₂D, NH₂D/ND₂H and ND₃/NH₂D, observed in similar sized beams, are ≈10, and present a challenge for both the gas-phase and the grain-surface chemistry scenarios of deuteration fractionation. The role of shocks and of CO depletion in deuteration chemistry is discussed.

Key words: ISM: molecules – ISM: abundances

1. INTRODUCTION

Deuterium-bearing molecules are important as probes of the very cold phases of molecular clouds, prior to star formation. Moreover, the isotopic composition of molecules is a valuable clue to their formation mechanism. In the gas phase, deuteration fractionation occurs by reactions with H₂D⁺, CH₂D⁺ and C₂D⁺ (Millar, this volume). Alternatively, reactions on the surfaces of dust grains may enhance molecular D/H ratios. Both methods require low temperatures (<20 K) and high densities (> 10⁵ cm⁻³) such as found in dark clouds and pre-stellar cores. The grain surface route also needs a mechanism to return the molecules to the gas phase where they can be observed by the means of submillimeter spectroscopy. The gas-phase route can account for the deuteration of HCO⁺ and N₂H⁺, while grain surface chemistry may be important for H₂CO and CH₃OH.

Although astronomical detections of both singly and doubly deuterated NH₃ exist (Roueff et al. 2000), the deuteration mechanism for NH₃ is not clear. Despite early claims, searches for NH₃ ice based on the 2.21 and 9.0 μm features have not been successful (Taban et al. 2002), but the 3.47 μm feature indicates abundances of up to 7% of H₂O ice (Dartois et al. 2002). However, existence in the solid state does not imply formation on grain surfaces, since NH₃ may just passively accrete after forming in the gas phase. Soon after Rodgers & Charnley (2001) proposed ND₃ as test of theories of interstellar deuteration chemistry, searches were initiated.

The rotational energy levels of symmetric top molecules like ND₃ are labeled by the total angular momentum J and its projection on the molecular symmetry axis K. Inversion splits these levels into states which are symmetric (s) and antisymmetric (a) upon reflection in the plane of the D atoms. Coupling of the ¹⁴N nuclear spin I with the rotational angular momentum J causes additional hyperfine splitting (F = I + J). Current instrumentation cannot resolve the even finer splitting due to D, which, owing to its small quadrupole moment, is only ≈200 kHz. A complete line list is available from the CDMS catalog (Müller et al. 2001) at the URL http://www.cdms.de. Under the conditions favourable for deuteration enhancement, the strongest lines of ND₃ should be the ground state rotational line (1₀0 → 0₀0) at 309.9 GHz and the (1,1) inversion line (1₁₀ → 1₁₀) at 1589 MHz, which are both accessible from the ground.

Because the Pauli exclusion principle only holds for fermions, certain states are forbidden for NH₃ but allowed in ND₃. For example, the ND₃ ground state rotational line also has a 1₁₀ → 0₁₀ component at 306.7 GHz, which does not exist for NH₃. However, spin statistics make this line 10 times weaker than the 1₁₀ → 0₁₀ line, which is why it has escaped detection so far.

2. SUBMILLIMETER OBSERVATIONS

Emission in the Jₖ = 1₁₀ → 0₁₀ line has been detected in the dark cloud Barnard 1 (Lis et al. 2002), two positions in the star-forming region NGC 1333 (van der Tak et al. 2002), and several positions in the molecular cloud L 1689N (Roueff et al, in prep.). Table lists the results of a more extensive search, made with the Caltech Submil-
Table 1. Upper limits for ND$_3$ rotational line emission

| Source          | R.A. (1950) | Dec. (1950) | rms  |
|-----------------|-------------|-------------|------|
|                 | h m s       | ° ′ ″       | mK   |
| OMC-2           | 05 32 58.6  | -05 11 42   | 24   |
| HH1-C           | 05 33 51.5  | -06 47 57   | 25   |
| NGC 2264 C      | 06 38 26.3  | 09 32 18    | 39   |
| NGC 2264 G      | 06 38 25.7  | 09 58 54    | 31   |
| Serpens S68N    | 18 27 15.2  | 01 14 47    | 30   |
| Serpens FIRS1   | 18 27 17.3  | 01 13 16    | 28   |

Table 2. Upper limits for ND$_3$ inversion line emission and absorption

| Source          | R.A. (1950) | Dec. (1950) | rms  |
|-----------------|-------------|-------------|------|
|                 | h m s       | ° ′ ″       | mK   |
| Emission targets|             |             |      |
| NGC 1333        | 03 26 03.6  | +31 04 42   | 11-16|
| Barnard 1       | 03 30 15.0  | +30 57 31   | 9-12 |
| CB 17           | 04 00 35.0  | +56 48 00   | 16-22|
| L 1400 K        | 04 26 51.0  | +54 45 27   | 12-23|
| L 1544          | 05 01 15.0  | +25 07 00   | 35-38|
| NGC 2264        | 06 38 24.9  | +09 32 29   | 38-52|
| L 134N          | 15 51 32.0  | -02 42 13   | 15-20|
| L 1689N         | 16 29 27.6  | -24 22 08   | 30-46|
| S68 FIR         | 18 27 17.5  | +01 13 23   | 9-12 |

Absorption targets

| Source       | R.A. (1950) | Dec. (1950) | rms  |
|--------------|-------------|-------------|------|
| W 33         | 18 11 19.5  | -17 56 40   | 36-46|
| W 43         | 18 45 00.4  | -01 59 16   | 101-120|
| 37.763-0.216 | 18 58 33.1  | +04 07 41   | 43-62|
| W 49A        | 19 07 52.1  | +09 01 08   | 70-94|

3. Centimeter observations

Measurements of the pure inversion spectrum of ND$_3$ go back to the early days of microwave spectroscopy (Nuckolls et al. 1953); many lines have been measured since (Fusina & Murzin 1994). However, only recently, the hyperfine structure of the (1,1) line near 1589 MHz has been resolved (van Veldhoven et al. 2002).

In 2001-2002, we have used the 100-m Effelsberg telescope to search for the $(J, K) = (1, 1)$ 1589.006 MHz, (2,2) 1591.695 MHz, (3,3) 1599.645 MHz, and (4,4) 1612.997 MHz metastable inversion lines. The front end was the 1.3-1.7 GHz primary focus receiver; the back end was the 80′′ beam size autocorrelator. System temperatures were 20 cm flux densities, taken from the NVSS (45′ resolution) of >1 Jy, excluding Sgr B2 because of its low declination. The noise levels obtained for these sources (Table 2 bottom part) are higher than for emission sources, because the background H ii regions contribute significantly to the system temperature.

The inversion lines were also searched for in absorption towards bright Galactic H ii regions. Targets for this search were selected to have $N$(H$_2$CO) $>10^{14}$ cm$^{-2}$ as measured in 6 cm absorption (Wadiak et al. 1988) and to have 20 cm flux densities, taken from the NVSS (45′ resolution) of >1 Jy, excluding Sgr B2 because of its low declination. The noise levels obtained for these sources (Table 2 bottom part) are higher than for emission sources, because the background H ii regions contribute significantly to the system temperature.

The centimeter data limit $N$(ND$_3$) to $\lesssim 0.3$–1.5×10$^{12}$ cm$^{-2}$, consistent with the submillimeter data. However, the inversion lines can not only provide independent estimates of the ND$_3$ column density, they can also constrain its excitation. Column densities derived from the $J_K = 1_0^0 \rightarrow 0_0^0$ line are uncertain by factors up to 2 through the excitation temperature. The lower frequency of the $J_K = 1_4^4 \rightarrow 0_4^4$ line implies a much lower spontaneous decay rate and virtually ensures thermalization. However, being beyond the capabilities of 100-m class telescopes such as Effelsberg and the VLA (an effective 130-m telescope), its detection requires 300-m class telescopes or larger.
4. Abundance of ND$_3$

If the excitation of ND$_3$ cannot be measured, it can be calculated through a model of the physical and chemical structure of the source. Fig. 1 shows the model that van der Tak et al. (2002) used to determine the ND$_3$ abundance in NGC 1333 IRAS 4A. The density structure is obtained from interferometric dust continuum observations, while the dust temperature structure comes from a self-consistent calculation of the thermal balance as a function of radius. These quantities peak toward the center of the protostellar envelope. Cosmic-ray ionization makes H$_3^+$, at a rate that does not vary with radius. The reaction of H$_3^+$ with HD produces H$_2$D$^+$, and since it is faster at low temperatures, the H$_2$D$^+$ distribution peaks at large radii.

The distribution of ND$_3$ can either be assumed to follow that of H$_2$ or that of H$_2$D$^+$. These two situations may apply to the cases of grain-surface and gas-phase formation, respectively. The inferred abundance of ND$_3$ is $3 \times 10^{-12}$ if ND$_3$/H$_2$ is constant, and $1 \times 10^{-11}$ if ND$_3$/H$_2$D$^+$ is constant. Maps of the ND$_3$ emission will enable us to decide between these two possibilities. The Sub Millimeter Array (SMA) will soon provide the necessary resolution of $<10''$ at 310 GHz.

5. Chemical implications

Table 3 lists measured column densities of NH$_3$ isotopomers. Only in the case of NGC 1333 IRAS 4A, abundances of NH$_3$ and ND$_3$ have been derived by radiative transfer modeling, so we use column density ratios as proxies of abundance ratios. This approach is valid as long as the excitation conditions of all molecules are similar, which is likely true except perhaps for NH$_3$.

The column density ratios of NH$_3$/NH$_2$D, NH$_2$D/ND$_2$H and ND$_3$/ND$_2$H are each $\approx 10$ (Table 3). This strong fractionation presents a challenge to grain surface chemistry, and requires an atomic D/H ratio in the gas phase of $\approx 0.15$, which is $>10$ times higher than in the models by Roberts & Millar (2000). Unfortunately, observations do not constrain the atomic D/H ratio in molecular clouds well. While H I 21 cm data indicate H/H$_2 \approx 10^{-3}$ (Li & Goldsmith 2002), observing D I 92 cm is very difficult.

To determine the deuterium budget in dense interstellar clouds, measurements of the HD 119 $\mu$m line, with HIFI on Herschel and GREAT on Sofia, will be crucial (see Phillips, this volume).

However, standard models of gas phase chemistry also have some difficulty explaining the results of Table 3. To reproduce the observed column density ratios, the models require deuteron transfer reactions to be much faster than proton transfers. Indeed, laboratory data indicate that in the dissociative recombination of partially deuterated ions, H is easier ejected than D (Le Petit & Roueff 2002). On the other hand, recent experiments on the H$_3^+$ + HD reaction indicate a lower formation rate of H$_2$D$^+$ than the value used in most chemical models (Gerlich & Schlemmer 2002).

One potential problem with applying the surface chemistry route to pre-stellar cores is their temperatures which are too low for significant evaporation of even the most volatile ices to occur. One alternative may be nonthermal desorption by cosmic rays (Sajita et al. 2001), but quantitative predictions do not exist yet. However, Lis et al. (2002a) propose a connection between shocks and the chemistry of deuterium. Indeed, all ND$_3$ detections so far have been at or near bipolar outflow sources. Perhaps the shocks merely compress surrounding gas, which leads to the cold, dense conditions favourable for deuterium chemistry. However, the shocks may also desorb grain mantle material, while leaving the grain cores intact. Shock velocities of $\sim 10$ km s$^{-1}$ would be sufficient. Such shocks occur frequently in the interstellar medium. One possibility is that interstellar gas is periodically shocked by ongoing star formation activity.

Another avenue worth exploring is the connection of deuterium chemistry with CO depletion. Freeze-out of CO, the major destroyer of H$_2$D$^+$, onto dust grains helps channeling deuterium into heavy molecules (Roberts & Millar 2000) and correlations between enhanced deuteriation and CO depletion have indeed been observed (Hatchell...
Table 3. Observed column densities of NH$_3$ isotopomers

| Source | N(NH$_3$) | N(NH$_2$D) | N(ND$_2$H) | N(ND$_3$) | $T_{ex}^f$ |
|--------|-----------|-----------|-----------|-----------|----------|
|        | $10^{14}$ cm$^{-2}$ | $10^{13}$ cm$^{-2}$ | $10^{12}$ cm$^{-2}$ | $10^{11}$ cm$^{-2}$ | K |
| Barnard 1 | 21$^e$ | 58$^b$ | 48$^b$ | 13$^d$ | 5 |
| NGC 1333 IRAS 4A | 13.8$^a$ | 39.0$^a$ | <4.6$^b$ | 2.9$^c$ | 10 |
| NGC 1333 D-peak | 19.2$^a$ | 37.6$^a$ | <1.9$^b$ | 5.9$^c$ | 10 |

Beam size (″) 37 22 22 25

$^a$ From Hatchell (2002)
$^b$ Preliminary values based on IRAM 30m observations (Gerin et al., in prep.)
$^c$ From Effelsberg observations
$^d$ Data from Lis et al. (2002b), non-LTE calculation at $n$(H$_2$)=7×$10^4$ cm$^{-3}$ and $T$=12 K
$^e$ From van der Tak et al. (2002)
$^f$ Excitation temperature used to analyze the NH$_2$D and ND$_2$H data

2002; [Bacmann et al. 2002]. However, in the case of NH$_3$, such a trend does not provide direct evidence of formation in the gas phase. The formation of NH$_3$ and its isotopomers on grain surfaces requires a high abundance of N in the gas phase. While in molecular clouds, most nitrogen is in N$_2$ (Womack et al. 1992), depletion of CO suppresses the formation of N$_2$ and enhances N instead (Charnley & Rodgers 2002). One key question is therefore the major nitrogen carrier in pre-stellar cores. Although neither N nor N$_2$ cannot be observed directly, N$_2$H$^+$ can serve as a tracer of N$_2$. Correlation between the fractionations of N$_2$H$^+$ and NH$_3$ would thus constitute an important test of the formation mechanism of interstellar NH$_3$ and ND$_3$.

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