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Far-infrared laser emission from deuterated ammonia

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ABSTRACT By optically pumping the deuterated isotopomers of $^{14}NH_3$ and $^{15}NH_3$ using $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{18}O_2$, and $^{13}C^{18}O_2$ lasers, several new far-infrared (FIR) emission lines between 65 µm and 125 µm have been detected. The existing spectroscopy of ^{14}N-ammonia isotopomers has been used to identify many of these lines, as well as some previously observed but unidentified. The spectroscopic data have been analyzed to predict over 20 additional FIR laser lines that could be pumped by a more capable CO_2 laser. This effort was motivated by a need for strong laser lines in frequency coincidence with molecular transitions of astrophysical interest. Of particular note is the measurement of the 2680-GHz line of $^{14}NHD_2$, whose frequency is 4.9 GHz higher than that of the important $J = 1-0$ line of interstellar HD.

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1 Introduction

Ammonia is a very useful gas for optical pumping for several reasons. The large permanent dipole moment of ammonia implies high transition strengths with efficient pump absorption and concomitant high far-infrared (FIR) gain. The high absorption has the added benefit of reducing pump feedback, which in turn enhances the amplitude and frequency stability of the FIR line. The high rotational constant of ammonia leads to a small partition function, which also contributes to a high FIR gain. On the other hand, the small partition function leads to a sparse vibration–rotation spectrum for the ν_2 bands of NHD_2 and NH_2D and the ν_2 and ν_4 bands of ND_3, which overlap the frequency range of CO_2 or N_2O lasers. Consequently, relatively few ammonia lines can be optically pumped with fixed-frequency gas lasers. However, those that can be pumped have produced lasing transitions among the most efficient known [1].

Several techniques have been used to extend the number of possible pumping transitions and hence laser lines from ammonia: Stark tuning [2–5], isotopic pumping [6], two-step optical pumping [7], two-photon pumping [8], Raman off-resonance pumping [9], CO_2 sequence band pumping [10], and pumping of isotopomers of NH_3 with a continuously tunable 20-atm CO_2 laser [11]. We have used isotopic CO_2 lasers to optically pump deuterated ammonia isotopomers. This paper describes the new lines found and their identification, and presents predictions for several other coincidences that are likely to produce FIR lasing.

The impetus for this work was to find a laser line that could be used as a local oscillator (LO) in a heterodyne receiver to observe the 112.1-µm line of interstellar HD. The requirements for such a FIR laser line are that it be strong and stable, able to produce a few mW with moderate (≤ 10 W) CO_2 pump power (which implies a low threshold), and have a frequency within 15 GHz of the HD transition at 2674.987 GHz [12]. A possible LO candidate line was first reported by Davis et al. [6] when pumping $^{15}NH_3$ or a mixture of NH_3 and CD_3OD with the 10P14 transition of $^{13}C^{16}O_2$. However, calculation of coincidences to within 500 MHz between CO_2 pump lines and the ν_2 vibration lines of $^{14}NH_3$ and $^{15}NH_3$ by Frank et al. [13] did not predict this line. Weiss et al. [14] were also unsuccessful in assigning the 112-µm line, and since the observations of Davis et al. showed comparable strengths from $^{14}NH_3$ and $^{15}NH_3$, these authors tentatively concluded that the line is associated with some partially deuterated methanol isotopomer rather than with ammonia. However, as pointed out by Duxbury and Petersen [15], several $^{15}NH_3$ lines are known to lase just from the natural $^{15}NH_3$ abundance in $^{14}NH_3$. Therefore, we hypothesized that the 112-µm line might arise in a deuterated ammonia isotopomer, originally produced in the experimental configuration of Davis et al. [6] by an exchange reaction with residual CD_3OD. We used two complementary approaches to searching for this and other new lines in NH_3 isotopomers: calculational, based on published energy levels, and experimental. Both are described in the following sections.

2 Predictions

Coincidences of the ν_2 vibrational fundamental bands of $^{14}NH_3$ and $^{15}NH_3$ with various lines of CO_2 (including its isotopomers) and N_2O have been calculated previously [13]. We have extended this work to the coincidences between CO_2 isotopomers and the ν_2 bands of $^{14}NH_2D$ and $^{14}NHD_2$. Equivalent calculations could not be performed for $^{15}NH_2D$ and $^{15}NHD_2$ because of the lack of published spectroscopic data for these species.

Coincidences to within 50 MHz were identified using the tabulated frequencies of Kartha et al. [16] for the ν_2 band of

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$^{14}NHD_2$, Job et al. [17] for the ν_2 band of $^{14}NH_2D$, and Fusina et al. [18] for the ν_2 and ν_4 bands of $^{14}ND_3$. The frequency of the predicted FIR emission in the ν_2 band for each coincidence was then calculated from the difference in frequency between the pumping transition and another whose upper state is the lower state for the FIR emission, combined with the difference in the lower-energy levels for the two lines, obtained from tabulated ground-state inversion–rotation frequencies of Fusina et al. [19] for $^{14}NH_2D$ and $^{14}NHD_2$ and from Fusina et al. [20] for $^{14}ND_3$. Table 1 shows the coincidences and FIR frequencies calculated in this manner.

Table 1 makes clear the identification of the 112-µm line discussed previously, as arising from $^{14}NHD_2$. The line is pumped by the 10P16 line of $^{13}CO_2$, rather than the 10P14 line as reported by Davis et al. [6]. The association with CD_3OD in the laser reported earlier obviously comes from the required deuteration of the ammonia. It is not clear why this line was observed in equivalent strengths from $^{15}NH_3$ and $^{14}NH_3$, but probably this arises from the incomplete purity of the $^{15}NH_3$ used.

3 Experimental measurements

The CO_2 laser is a 1-m-long quartz tube with 13-mm ID, operating in the TEM_{00} mode. Frequency selection is obtained from an 80 lines/mm adjustable grating at one end. The output end has a 90% reflective curved mirror mounted on a piezoelectric transducer. The laser has a simple semi-confocal geometry. The low (10%) output coupling minimizes instabilities caused by reflection of unabsorbed pump radiation from the FIR laser. The CO_2 laser can be run either sealed (for the rarer isotopic forms of CO_2) or flowing, with maximum output powers of approximately 10 W and 15 W, respectively.

The FIR laser is a 1-m-long Pyrex waveguide tube with 22-mm ID. The CO_2 power is coupled in through a ZnSe antireflection-coated window, tilted 10–15° to avoid reflections back to the CO_2 laser, and a 0.5-mm-diameter hole in a flat mirror mounted on a metal bellows for FIR cavity length tuning. The output window is Z-cut quartz following a 1-mm-diameter hole in a stationary flat mirror. Output powers of several mW can be obtained from strong FIR laser lines with this system. The output radiation passes though a polarization diplexer, one arm of which is mounted on a micrometer. The wavelength of a FIR laser line can be crudely measured by adjusting the micrometer through 20 half-wave interference fringes and measuring the resultant travel. This method is used to verify FIR line identifications, and the measured wavelengths are accurate to three parts in 10^4.

More precise frequency measurement is made by mixing the FIR laser line with another FIR line of known frequency, generated by an identical laser system, along with

CO_2 pump	Absorption-pump (MHz)	Absorption (cm^{-1}, calc)	FIR transition	FIR λ (µm, calc)	FIR λ (µm, meas)
			$^{14}NH_2D$ $\nu_2 = 1$		
002-9R31 (626)	+30	1081.66327	$a(13, 2, 11) - s(12, 1, 11)$	47.1	
10R14 (626)	+51	971.93195	$s(10, 3, 7) - a(9, 2, 7)$	77.4	77.2
9P28 (628)	−30	1049.95059	$s(12, 1, 11) - a(11, 0, 11)$	62.3	
10R7 (628)	+51	971.93195	$s(10, 3, 7) - a(9, 2, 7)$	77.4	
10P18 (628)	−11	952.01588	$s(8, 3, 5) - a(7, 2, 5)$	106.5	
10P40 (628)	+7	931.74242	$s(3, 3, 1) - a(2, 2, 1)$	281.0	
011E 10P13 (636)	−43	872.63293	$s(8, 2, 6) - a(7, 1, 6)$	100.0	
10R22 (646)	−41	882.90961	$s(7, 7, 0) - a(6, 6, 0)$	86.0	
10P40 (828)	−42	933.98510	$s(5, 3, 3) - a(4, 2, 3)$	164.5	
9P4 (838)	−37	1024.09840	$s(9, 6, 3) - a(8, 5, 3)$	76.7	
			$^{14}NHD_2$ $\nu_2 = 1$		
10R50 (626)	+34	992.48593	$s(13, 11, 3) - a(12, 10, 3)$	58.1	
10P40 (626)	−15	924.97348	$a(9, 4, 6) - s(8, 3, 6)$	86.3	86.6
10P18 (628)	+21	952.01695	$s(12, 1, 11) - a(11, 0, 11)$	72.7	
10P16 (636)	+18	900.36924	$a(6, 5, 2) - s(5, 4, 2)$	111.9	111.9
10P26 (636)	+29	891.57492	$a(5, 5, 1) - s(4, 4, 1)$	124.8	124.7
002-10R13 (828)	−33	974.59320	$a(11, 10, 2) - s(10, 9, 1)$	62.7	
10P8 (828)	−34	961.21052	$a(11, 8, 3) - s(10, 7, 3)$	66.7	
10P8 (838)	−7	922.88403	$s(8, 7, 2) - a(7, 6, 2)$	96.9	97.0
9P2 (848)	+21	981.16170	$a(11, 11, 0) - s(10, 10, 0)$	60.9	
10P30 (848)	−15	866.40839	$a(4, 1, 3) - s(3, 0, 3)$	176.6	
			$^{14}ND_3$ $\nu_2 = 1$		
011E 10P17 (626)	−46	913.1165	$a(17, 12) - s(16, 12)$	57.2	
011E 10P37 (626)	+20	894.5238	$a(15, 6) - s(14, 6)$	65.1	
			$^{14}ND_3$ $\nu_4 = 1$		
9R40 (626)	−26	1090.0275	$s(11, 9) - a(10, 9)$	87.3	87.1
9P34 (626)	+54	1033.4898	$s(18, 15) - a(17, 15)$	53.7	
10P18 (628)	+6	1058.5724	$s(15, 10) - a(14, 10)$	64.5	
9P30 (628)	−43	1048.1606	$s(16, 15) - a(15, 15)$	60.5	
002-10P9 (636)	−22	903.5026	$a(16, 6) - s(15, 6)$	61.3	

TABLE 1 Predicted FIR laser lines from deuterated ammonia isotopomers

a microwave source of adjustable frequency. This latter source is scanned through several harmonic numbers to obtain a dc output signal. The mixer uses a sub-micron GaAs Schottky diode (University of Virginia, type 1T11 or 1T15). Precise frequency measurements were only made of two lines of possible astronomical interest (i.e. the wavelength measurements indicated that they might be close enough to astrophysical lines to be LO candidates). The FIR lines found experimentally are listed in Table 2. All of the observed lines had parallel polarization. Many of these lines are unidentified, but are attributed to deuterated variants of $^{15}NH_3$. The exact isotopic composition of the gas in the FIR laser at any time is unknown, since it was produced from a mix of $^{15}NH_3$ and $^{14}ND_3$. Relative strengths are indicated in Table 2 as S, M, or W, corresponding approximately to output power on the mixer of a few mW, about 1 mW, or fractions of a mW, respectively. No correction to the output power is made for atmospheric absorption at the line frequency, which can be significant (e.g. the calculated atmospheric absorption for the 119.1-μm line is 10 dB/m for typical laboratory conditions).

Several of the lines in Table 2 have been previously observed. Landsberg [22] reported the 77-μm line pumped by 10R14 (626), the 77-μm line pumped by 10R30 (626), and the 86.6-μm line pumped by 10P40 (626), but attributed them all to $^{14}NH_2D$. We have identified the line pumped by 10R14 as due to $^{14}NHD_2$, while the 10R30-pumped line remains unidentified. We did not see the 124-μm or 113-μm lines pumped by 10R14 (626) and 10P40 (626), respectively, which were reported by this author. The higher threshold of these two lines compared with that of the 77-μm and 87-μm lines produced by the same pump transitions suggests that they are produced in a cascade. With this assumption, we identified the 113-μm line as the $s(8, 3, 6) - a(7, 2, 6)$ transition in the $\nu_2 = 1$ state of NHD_2, which has a predicted wavelength of 112.2 μm. However, the 124-μm line pumped by 10R14 is not the cascade transition $a(9, 2, 7) - s(8, 1, 7)$, which is predicted to occur at 66.6 μm. We were unable to identify the observed line.

The $^{14}ND_3$ line at 87.1 μm has also previously been seen by Landsberg [22], who assigned this transition tentatively to $11_1 \rightarrow 10_1$ in the $\nu_4 = 1$ state. We have refined this identification, as shown in Table 1, and identify the pumping transition as $aPP(12, 10)$, as listed by Fusina et al. [18].

It is somewhat puzzling to note that none of our observed or predicted lines were seen by Schatz et al. [11], who used a high-pressure continuously tunable pulsed CO_2 laser to pump $^{14}NH_3$ and its deuterated variants, $^{15}NH_3$, and $^{15}ND_3$. However, their system was optimized for the production of Raman lasing, while our low-power cw laser was used to pump much lower pressure (approximately 100 mT) ammonia, and therefore we detect only direct inversion lasing from lines with a relatively low threshold.

We measured the frequencies of two of the lines using the method described above. The frequency of the 112-μm $a(6, 5, 2) \rightarrow s(5, 4, 2)$ transition of $^{14}NHD_2$ is $2\,679\,891.6 \pm 1.3$ MHz, which is 4.90 GHz higher than the frequency of the $J = 1 \rightarrow 0$ transition of HD. This line was eventually used as a LO in a search for HD in Jupiter, with a receiver aboard NASA's Kuiper Airborne Observatory in 1995. The frequency of the 125-μm $a(5, 5, 1) \rightarrow s(4, 4, 1)$ transition of $^{14}NHD_2$ was found to be $2\,404\,790.3 \pm 1.0$ MHz. The reference laser for both frequency measurements was tuned to the strong 2 522 781.6-MHz transition of CH_3OH [21].

4 Summary

We have used published transition frequencies of $^{14}ND_3$ and of various deuterated isotopomers of $^{14}NH_3$ to search for coincidences with isotopic CO_2 laser transitions to within 50 MHz. The results show that at least 25 new FIR laser lines could be produced with appropriate pumping. We observed several of these lines, some of which have been previously observed but with uncertain identification. Several other unidentified lines were also seen, and they are attributed to deuterated variants of $^{15}NH_3$. No identification of these lasing transitions is currently possible.

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CO_2 pump	FIR λ (μm)	Species	Relative power
10P40 (626)	86.6	$^{14}NHD_2$	S
10P4 (626)	88.3	?	W
10R12 (626)	77.5	?	M
10R14 (626)	77.2	$^{14}NH_2D$	S
10R16 (626)	77.6	?	W
10R30 (626)	77.0	?	W
9P44 (626)	67.4	?	W
9R40 (626)	87.1	$^{14}ND_3$	W
10P30 (636)	84.3	?	W
10P26 (636)	124.7[a]	$^{14}NHD_2$	S
10P22 (636)	110.0	?	S
10P16 (636)	111.9[b]	$^{14}NHD_2$	S
10P8 (838)	97.0	$^{14}NHD_2$	M
10R34 (838)	73.7	?	S

[a] Frequency measured to be 2404.790 GHz
[b] Frequency measured to be 2679.892 GHz

TABLE 2 Observed FIR laser lines from optically pumped $^{15}NH_3/^{14}ND_3$ mixtures

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