Laboratory Observation of Maser Action in NH_3 through Collisional Cooling

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We report the observation of maser emission from the $J = 4$, $K = 3$ inversion transition of ammonia, $^{14}NH_3$, at temperatures from 10 to 27 K. The necessary population inversion is apparently created by selective collisional energy transfer as the ammonia is cooled in collisions with cold helium atoms in a cryogenic cell. Several other inversion transitions were also observed; however, only the (4,3) line was seen in emission. When the experiment was repeated using hydrogen molecules in place of helium, maser emission was not observed for any transition.

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The purpose of this Letter is to report the laboratory observation of an ammonia maser which is pumped by selective relaxation of inversion levels as NH_3 molecules cool in a background of cold He atoms. While previously reported laboratory ammonia masers used electrostatic fields to establish a population inversion [1], in the present experiment this is accomplished solely through collisional energy transfer as ammonia molecules are cooled through collisions with ~ 10 K helium atoms. This behavior could be described as a new class of gas-dynamic laser (or maser in this case), in which the cooling which produces a population inversion is accomplished by collisions rather than through the rapid expansion of a heated gas. In fact, if a suitable cavity were constructed, it seems probable that self-sustaining maser oscillation could be achieved. In a sense, this is an intriguing realization of the "thermal maser" first suggested in 1959 [2] and later fulfilled as the CO_2 gas-dynamic laser [3]. The collisional pumping mechanism also appears to be closely related to proposed explanations for the excitation of certain interstellar ammonia masers [4–6].

Of the nine (J, K) inversion lines observed in this experiment, only the (4,3) line is seen in emission, indicating that the population inversion is highly dependent upon state-to-state NH_3-He rotational energy transfer rates. When cold H_2 replaces He as the collision partner, emission is no longer seen for the (4,3) or any other observed inversion line. While several ammonia inversion lines have been observed in maser emission from astronomical sources [7], the (4,3) transition is not among them. However, the mechanism which appears to be responsible for the population inversion between the (4,3) levels is virtually identical to that proposed by Walmsley and Ungerechts to explain the weak (3,3) maser line near the interstellar source, DR21 [4]. Thus, our result may be useful for gaining a more complete understanding of this and possibly other interstellar NH_3 masers. It should be understood, however, that while the kinetic temperatures of the molecules in our cell are similar to those in interstellar clouds, the number densities are many times greater. In addition, by far the dominant collision partner for interstellar ammonia is H_2, not He. However, owing to the relative difficulty of obtaining *ab intio* potential surfaces for H_2-NH_3, collisional rates calculated from He-NH_3 potentials are often used in the absence of H_2 rates. In fact, the analysis of the (3,3) interstellar maser mentioned above relied on He-NH_3 rather than H_2-NH_3 rates [4]. Our observation of masing on the (4,3) line with He, but not with H_2, appears to indicate that the assumption that H_2 in $J = 0$ behaves like He in collisions can lead to misleading or incorrect results, especially in considerations of collisional excitation of interstellar masers. In any event, the present results provide experimental confirmation that under certain conditions collisional energy transfer can produce maser emission in ammonia inversion levels.

The experiments reported here utilize a recently developed technique for observing gas-phase molecular spectra in equilibrium at liquid helium temperatures. This technique, known as collisional cooling, has been used to obtain low-temperature helium pressure broadening data for a number of molecules [8,9]. Figure 1 shows a cross section through the experimental apparatus. The 7 cm diameter copper cell is cooled by a commercial open-cycle liquid helium refrigerator, and a static pressure of 1–50 mTorr of helium or molecular hydrogen is maintained in the cell. Ammonia molecules enter through copper needle tubing, insulated from the cell. A straightforward calculation shows that after fewer than 100 collisions with cold helium atoms a molecule will be cooled translationally to the same temperature as the helium background. The degree to which the molecules are cooled rotationally and vibrationally depends upon several factors, such as the rotational and vibrational energy level spacing and the temperature at which the molecules enter the cell [10,11]. In the region near the center of the cell, the helium-to-sample gas ratio is estimated to be on the order of 10^3–10^4:1.

The YIG oscillator-based microwave spectrometer used for this experiment has been described in detail elsewhere [9]. The spectrometer is swept through the spectral region of interest at a 100 Hz rate. As an aid in signal recovery, the detected signal without gas flowing into the

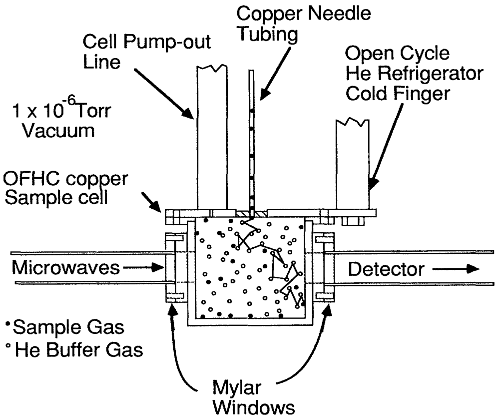

FIG. 1. Cross section through the low temperature cell. Not shown is a cooled radiation shield which surrounds the cell.

cell is subtracted from the signal with gas. Typically, 200 sweeps (100 with gas, 100 without) are averaged, subtracted, and recorded for each data file.

Ammonia is a pyramidal symmetric top molecule. It exists in two distinct ortho and para forms, distinguished by different relative orientations of nuclear spin. These two symmetry species do not readily interconvert, either radiatively or collisionally, and for most purposes can be assumed to be noninteracting. Molecules with rotational orientation quantum number $K = 3n\,(n = 0, 1, 2, \ldots)$ are of the ortho form, while those with $K \neq 3n$ are of the para-ammonia form. Each (J, K) rotational level is split into two inversion states [12,13]. As shown in the NH_3 energy level diagram of Fig. 2, each rotation-inversion level has a definite parity, + or −. For a given rotational level, the two inversion levels have opposite parity. The Pauli exclusion principle allows only one inversion level for the $K = 0$ states. Transitions between the two inversion states are dipole allowed, and in the ground vibrational state, the frequencies of these inversion transitions fall between 18 and 40 GHz.

We have observed spectra of the (1,1), (2,1), (3,1), (2,2), (3,2), (3,3), (4,3), (5,3), and (4,4) inversion transitions at cell temperatures of 10–100 K. The (4,3) line at 22 688.24 MHz was seen in stimulated emission at temperatures below ~27 K, while all other lines were seen in absorption. In emission the fractional gain for the (4,3) line was ~0.2%, giving a gain coefficient of 8×10^{-4} cm^{-1}, assuming a 2.5 cm interaction path length. Above ~27 K the (4,3) line was observed in absorption. Figure 3 shows the (4,3) line in emission at 10 K and in absorption at 35 K. A flow-rate dependent effect was also observed: At a temperature of 26–27 K the (4,3) line could be changed from emission to absorption by simply increasing the ammonia flow rate slightly. This was probably in reality a temperature effect, the increased flow of warm gas into the cell producing a local heating of the background helium causing the line to go from emission to absorption. The strength of the emission line was also pressure dependent. As the helium pressure was increased, the strength of the emission decreased, the line disappearing completely for helium pressures $\gtrsim$5 mTorr. We speculate that the pressure effect was due to improved rotational thermalization as the NH_3-He collision frequency increased as the pressure was raised. We repeated the experiment with molecular hydrogen (H_2) rather than helium as the buffer gas and found all observed lines, including the (4,3) line, appearing in absorption from 15 to ~100 K.

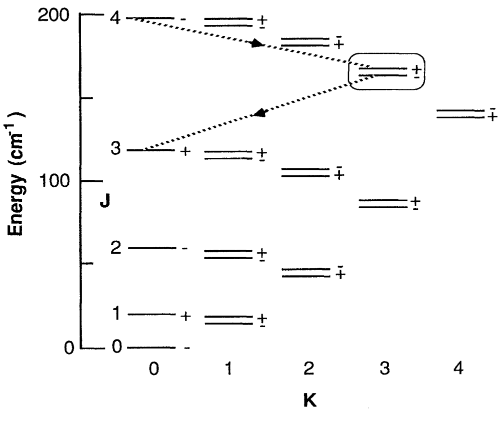

FIG. 2. Rotation-inversion levels of NH_3 for some of the lower lying states. The (4,3) level is circled. The dashed lines depict the main collisional pathways believed to contribute to a population inversion. Spacing between inversion doublets has been exaggerated.

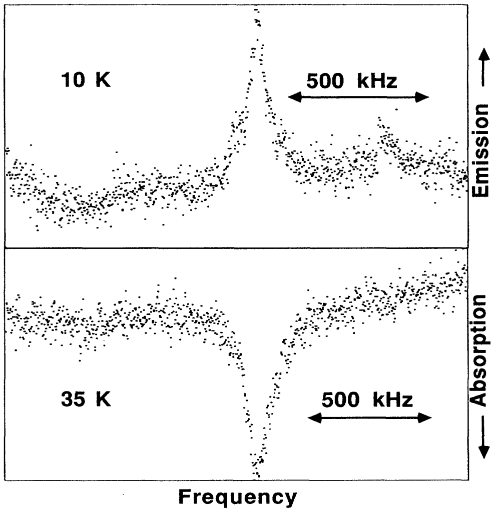

FIG. 3. The (4,3) inversion transition of NH_3 at cell temperatures of 10 and 35 K. Frequency scales differ slightly in the two plots. The small feature on the right in the 10 K plot is emission from one of the (4,3) hyperfine satellites.

The creation of a population inversion in the (4,3) inversion doublet can be explained from an understanding of the experimental conditions and dynamics of NH_3-He collisional energy transfer. From a comparison of the fractional absoprtions in the (1,1) and (2,2) inversion lines, a 40 ± 10 K rotational temperature was determined at a cell temperature of 15.0 K, indicating that the NH_3 is not in rotational equilibrium when it interacts with the probing microwave radiation. Since rotational equilibrium has not been reached, there will be net transfer of population among the various rotation-inversion levels. The (4,3) level can only transfer internal energy to other members of the $K = 3n$ ortho class, the closest energetically lower levels being the (3,0) state, which differs in energy by 46.1 cm^{-1}, and the (3,3) level is 79.6 cm^{-1} lower. The (3,0) level, with $K = 0$, has only one, + parity, inversion level, while (3,3) has both inversion levels (see Fig. 2). The upper and lower (4,3) inversion levels are + and − parity, respectively. If there is a propensity rule which favors parity change over parity conservation in NH_3-He collisional energy transfer, then we expect that the rate out of the lower $(4,3)^-$ level into the $(3,0)^+$ level will be faster than the corresponding rate out of the upper $(4,3)^+$ level. An additional contribution can come from the $(4,0)^-$ level, 33.4 cm^{-1} above the (4,3) level. Since (4,0) is − parity, a propensity for parity changing would transfer population into the upper $(4,3)^+$ level faster than into the lower $(4,3)^-$ level. Conversely, a parity changing propensity would tend to be negated in energy transfer into the (3,3) level, since both parities are present there.

In fact, a preference for parity changing in collisions with both He and H_2 has been noted in several investigations, both experimental [14,15] and theoretical [16–20]. The calculated NH_3-He collisional excitation rates of Green [17] show a parity changing $(4,3)^-$ to $(3,0)^+$ collision rate which, at a kinetic temperature of 15 K, is over 5 times greater than the $(4,3)^+$ to $(3,0)^+$ parity conserving rate. Although a direct experimental measurement of (4,3) to (3,0) rates has not been made, Schleipen and ter Meulen [15] recently observed a strong propensity for parity changing in the (4,3) to (0,0) state-to-state cross sections. Walmsley and Ungerechts, using the NH_3-He rates of Green [17], predicted masing on the (3,3) interstellar line owing to a propensity for parity change in collisions between the (3,3) inversion levels and the $(0,0)^-$ level [4]. A short time later the (3,3) line was seen in maser emission near the continuum source, DR21 [6]. This same mechanism has also been suggested to explain the $^{15}NH_3$ (3,3) interstellar maser [5]. The present results appear to confirm that a propensity for parity changing in collisions can indeed produce maser emission in ammonia inversion levels.

Green has calculated helium collisional rate constants for orthoammonia among levels with J up to 7 for $K = 0$, 3, and 6 at eight kinetic temperature, T_{kin}, between 15 and 300 K [17]. We have used these state-to-state rate constants to calculate the ratio of net collisional energy transfer rates for the two (4,3) inversion levels at kinetic temperatures of 15, 25, and 50 K. In calculating the net rates, the population in each (J,K) level was taken as proportional to $(2J + 1)\exp[E(J,K)/kT_{\mathrm{rot}}]$, where T_{rot} is the rotational temperature and $E(J,K)$ is the energy of the inversion level out of which the population is being transferred. For each kinetic temperature total rates out of the two (4,3) levels were calculated over a range of rotational temperatures. This procedure was repeated using the NH_3–para-H_2 rate constants of Danby *et al.* at $T_{\mathrm{kin}} = 15$ K [19]. Figure 4 shows the ratio, $q_{\mathrm{net}(4,3)^-}/q_{\mathrm{net}(4,3)^+}$, of the total rates out of the (4,3) inversion levels versus rotational temperature for NH_3-He at $T_{\mathrm{kin}} = 15$, 25, and 50 K and for NH_3–para-H_2 at a kinetic temperature of 15 K.

When $q_{\mathrm{net}(4,3-)}/q_{\mathrm{net}(4,3+)} > 1$, the rate out of the lower (4,3) inversion level is greater than that out of the upper level, resulting in a population inversion and the possibility of observing the (4,3) line in maser emission. As seen in Fig. 4, for $T_{\mathrm{kin}} = 15$ and 25 K, emission should be observed for all rotational temperatures plotted. This is in agreement with our experimental observations. However, while we observed absorption at 50 K, the ratio of the net rates predicts that emission should be observed at this temperature. We believe that the discrepancy between the calculated and observed results at $T_{\mathrm{kin}} = 50$ K can be largely attributed to uncertainties in the calculated rate constants, estimated to be 50% for individual state-to-state rates [17]. These uncertainties are due almost entirely to inaccuracies in the potential surface. Furthermore, recent experimental results suggest that the rates used here overestimate the propensity for parity changing [15]. While new rate constants have been calculated using more reliable NH_3–He surfaces, the only sufficiently complete set is that of Green [17].

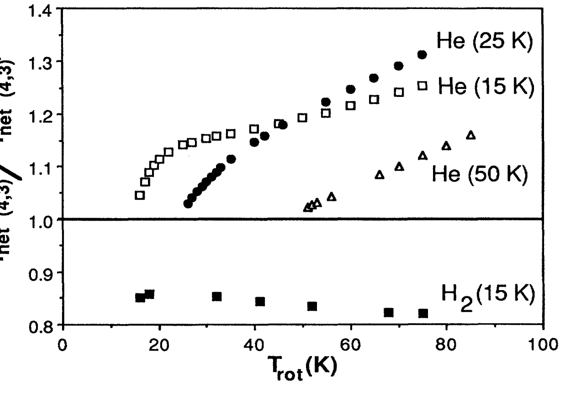

FIG. 4. Ratio of net collisional rates out of the lower and upper (4,3) inversion states versus rotational temperature, T_{rot}, calculated using state-to-state rate constants of Ref. [17] for He and Ref. [19] for H_2(para). Numbers in parentheses on plot labels are kinetic temperatures.

A second consideration which may also impact the reliability of the calculated ratios is the use of a rotational temperature to describe a system which is not in thermal equilibrium. Strictly speaking, in order to do an accurate comparison of our results with the theoretical rates it would be necessary to replace the Boltzmann factors used to calculate the net rates between (4,3) and other levels with the actual, experimentally measured relative populations of the levels.

The ratios for NH_3-H_2 in Fig. 4 suggest that at a kinetic temperature of 15 K emission should not be observed for any rotational temperature. While this is consistent with our observations, it should be noted that the NH_3-H_2 rate constants were only available up to, and including, the (4,3) level (165 cm^{-1}) as compared to the NH_3-He rates which included states through (7,0) (557 cm^{-1}). Also, since the only appropriate theoretical rates available were for para-H_2, contributions from collisions with ortho-H_2 are ignored. However, recent experimental studies [14] suggest that a propensity for parity changing is substantially stronger for para-H_2 than for ortho-H_2. If this is the case, then inclusion of NH_3–ortho-H_2 rates in our analysis would not increase the theoretical likelihood of a population inversion in the (4,3) doublet.

In summary, we have observed the (4,3) ammonia inversion line in maser emission in a collisionally cooled cell at temperatures of 10–27 K. The same line was seen in absorption for cell temperatures >27 K. The population inversion in the (4,3) inversion levels is apparently produced through a propensity for parity changing in collisions with helium, coupled with the fact that the $K = 0$ levels have only one inversion level, the net result being that more molecules are placed into the upper rather than the lower (4,3) inversion level. Emission was not observed on any inversion line for cooling by H_2 collisions. We are continuing our investigations into this system and plan to make extensive measurements of NH_3 rotational temperatures at various kinetic temperatures, which we hope will prove useful for the interpretation of radioastronomical data. In addition, we plan to instigate experiments in which the temperature at which the ammonia enters the cell is increased in order to see if this would cause other inversion lines, particularly at high J, to go into maser emission. We also hope that this Letter will motivate other investigators, both experimental and theoretical, to expand upon our work.

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