

*Letter to the Editor***Laboratory measurement of the $N = 1 \leftarrow 0$ rotational transition of NH at 1 THz**

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Abstract. The $N = 1 \leftarrow 0$ pure rotational transition of the NH radical ($X^3\Sigma^-$), located at 1 THz, was measured with the Cologne terahertz spectrometer using a frequency stabilized backward wave oscillator as radiation source. The NH radical was produced in a dc discharge of a flowing mixture of ammonia and helium. Transition frequencies of all three fine structure transitions with associated hyperfine components were precisely measured and analyzed to determine accurate molecular constants, including hyperfine coupling constants for both nuclei. As a result, the accuracy of the molecular constants has been improved by one to two orders of magnitude. The nuclear spin-rotation coupling constant for the nitrogen nucleus has been determined for the first time. The precise frequencies reported in this work are of importance to astronomical applications.

Key words: Molecular data – Methods: laboratory – Techniques: spectroscopic – ISM: clouds – ISM: molecules

1. Introduction

The NH radical is one of the fundamental hydrides, and its spectroscopic properties have been studied extensively. The electronic spectrum of NH has been measured by various researchers since 1935, as compiled by Huber & Herzberg (1979). From the electronic spectrum, molecular constants for the ground electronic state have been obtained by Dixon (1959), Murai & Shimauchi (1966), Malicet et al. (1970), Ubachs et al. (1984), and Brazier et al. (1986). Notably, the investigation by Brazier et al. (1986) of the $A^3\Pi_i - X^3\Sigma^-$ band near 3360 Å with a high-resolution Fourier transform (FT) spectrometer yielded relatively precise molecular constants, while the investigation of Ubachs et al. (1984) determined hyperfine coupling constants from molecular beam experiments. The vibration-rotation spectrum of NH has been measured and analyzed by Bernath &

Amano (1982) and Sakai et al. (1982). Hyperfine coupling constants were also determined from rotational spectra recorded by Radford & Litvak (1975) and Wayne & Radford (1976) with a far infrared laser magnetic resonance (LMR) spectrometer. In addition, van den Heuvel et al. (1982) measured the rotational spectrum at zero magnetic field using a tunable laser-sideband spectrometer. They observed two transitions ($J = 2 \leftarrow 1$ and $1 \leftarrow 1$) between the fine structure levels of the $N = 1 \leftarrow 0$ rotational transition and determined molecular constants including hyperfine coupling constants. A measurement of the $J = 0 \leftarrow 1$ fine structure transition has not been reported so far.

The NH radical has also been well studied in interstellar space. It has been observed in absorption toward stars (e.g. Schmitt 1969, Lambert & Beer 1972, Lambert et al. 1984, Ridgway et al. 1984), including the Sun (Grevesse et al. 1990, Geller et al. 1991), and towards comets (e.g. Feldman et al. 1993) via its electronic, vibration-rotation, and high- N rotational transitions. The NH radical has also been detected in diffuse interstellar clouds toward ζ Per and HD 27778 from its electronic absorption spectra (Meyer & Roth 1991). The obtained column density toward ζ Per is $9.0 \times 10^{11} \text{ cm}^{-2}$. This value is 20–40 times larger than the one obtained by gas-phase chemical model calculations for ζ Per (van Dishoeck & Black 1988; van Dishoeck 1992; Wagenblast et al. 1993). Accordingly, a significant contribution to the NH formation rate must occur on grain surfaces, as has already been considered by Mann & Williams (1984), and strongly suggested by Wagenblast et al. (1993).

Unlike the case of diffuse clouds, no detection of NH has been reported in dark clouds. One reason for this is that the $N = 1 \rightarrow 0$ transition falls in the 900–1000 GHz region, and is difficult to observe from ground-based observatories owing to the enhanced atmospheric opacity. A knowledge of the abundance of NH is important for the study of nitrogen chemistry in dark clouds, because it is one of the probable intermediate species in the production of NH_3 from the nitrogen ion by successive hydrogenation reactions (e.g. Herbst, DeFrees, & McLean 1987; Galloway & Herbst 1989). The abundance of NH_3 is high in many dark clouds, and the detection of NH

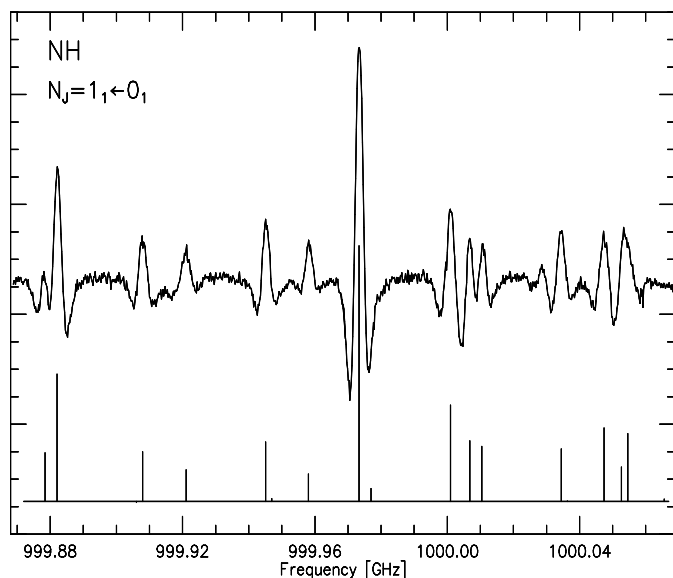


Fig. 1. The $N_J = 1_1 \leftarrow 0_1$ rotational spectrum of the NH radical ($X^3\Sigma^-$) recorded at 1000 GHz. Relative intensities and calculated line positions of the hfs components (Table 1) are shown below the spectrum. This 200 MHz scan consists of 887 data points with a total integration time of about 140 seconds.

can be expected in these sources. The NH_2 radical, another intermediate in the formation of ammonia, has been detected in absorption towards SgrB2 (van Dishoeck et al. 1993).

In this *Letter*, we report extended frequency measurements of the pure rotational transition $N = 1 \leftarrow 0$ of NH carried out with the Cologne terahertz spectrometer. These measurements yielded precise transition frequencies from which accurate molecular constants including hyperfine coupling constants were obtained. The results are of importance to future radioastronomical observations.

2. Experiment

The NH radical was produced in a dc discharge of ammonia (NH_3) and helium at partial pressures of about 2 Pa and 5 Pa, respectively. The absorption cell was 2 m long with an inner diameter of 10 cm. The optimum discharge current was 200 mA, and the cell temperature was kept at about -80°C by cooling with liquid nitrogen. The radiation source used was a backward wave oscillator (BWO OB-83-1) with a frequency range of 874–1100 GHz supplied by the ISTOK Research and Production Company (Fryazino, near Moscow). The BWO was frequency stabilized by phase-locking its output to a KVARZ synthesizer, which uses a 5 MHz reference signal from a rubidium atomic clock providing a short term relative accuracy of better than 10^{-11} . Further details of the experimental setup can be found in Winnewisser (1995) and Belov et al. (1995). Table 1 lists the 25 observed frequencies together with their experimental uncertainties, which were estimated according to the obtained signal-to-noise ratios. For single lines with a good signal-to-noise ratio the uncertainties were estimated to be 50 kHz. For some weak or blended lines the uncertainties were increased

Table 1. Observed frequencies for the $N = 1 \leftarrow 0$ rotational transition of NH

J'	F'_1	$F' \leftarrow$	J''	F''_1	F''	Frequency ^a [MHz]	O–C [kHz]	Rel. Int. ^b	
0	0.5	0.5	←	1	0.5	1.5	946 380.790(50)	-9^c	1.3
0	0.5	1.5	←	1	0.5	1.5	946 380.790(50)	-9^c	1.1
0	0.5	1.5	←	1	0.5	0.5	946 419.975(50)	26	1.0
0	0.5	1.5	←	1	1.5	2.5	946 475.820(50)	-28	3.6
0	0.5	0.5	←	1	1.5	1.5	946 509.244(50)	-5^c	1.1
0	0.5	1.5	←	1	1.5	1.5	946 509.244(50)	-5^c	1.4
0	0.5	0.5	←	1	1.5	0.5	946 527.481(100)	63	1.0
2	1.5	1.5	←	1	0.5	1.5	974 436.846(200)	-154^c	2.0
2	2.5	2.5	←	1	1.5	2.5	974 436.846(200)	-154^c	2.4
2	2.5	1.5	←	1	1.5	1.5	974 444.044(50)	-8	1.9
2	1.5	0.5	←	1	0.5	0.5	974 450.438(50)	38	2.6
2	2.5	1.5	←	1	1.5	0.5	974 462.216(100)	-88	5.4
2	2.5	2.5	←	1	1.5	1.5	974 470.832(300)	-215	9.0
2	2.5	3.5	←	1	1.5	2.5	974 478.612(500)	$172^{c,d}$	14.8
2	1.5	2.5	←	1	0.5	1.5	974 478.612(500)	$172^{c,d}$	9.6
2	1.5	1.5	←	1	0.5	0.5	974 478.612(500)	$172^{c,d}$	3.6
2	1.5	2.5	←	1	1.5	2.5	974 574.428(100)	28	1.3
1	1.5	2.5	←	1	0.5	1.5	999 878.056(500)	-357^d	1.5
1	0.5	1.5	←	1	0.5	1.5	999 882.089(50)	14	3.9
1	1.5	0.5	←	1	0.5	1.5	999 907.929(50)	19	1.5
1	0.5	1.5	←	1	0.5	0.5	999 921.020(200)	-124	1.0
1	1.5	1.5	←	1	0.5	0.5	999 945.056(50)	-55	1.8
1	0.5	0.5	←	1	0.5	0.5	999 958.242(50)	20	0.8
1	1.5	2.5	←	1	1.5	2.5	999 973.385(50)	4	7.8
1	1.5	1.5	←	1	1.5	2.5	1 000 001.018(50)	7	3.0
1	1.5	2.5	←	1	1.5	1.5	1 000 006.822(100)	-25	1.9
1	0.5	1.5	←	1	1.5	1.5	1 000 010.521(100)	11	1.7
1	1.5	1.5	←	1	1.5	1.5	1 000 034.490(50)	13	1.6
1	0.5	0.5	←	1	1.5	1.5	1 000 047.436(200)	-152	2.3
1	1.5	0.5	←	1	1.5	0.5	1 000 053.885(300)	-35^c	2.0
1	1.5	1.5	←	1	1.5	0.5	1 000 053.885(300)	-35^c	1.1

^aIn brackets: estimated experimental uncertainty.

^bRelative intensity of the hyperfine structure (hfs) in percent of the total intensity.

^cHfs not resolved. Treated as described in the text.

^dOverlapped line. Not included in the fit.

up to 500 kHz. Figure 1 displays the recorded spectrum of the $N_J = 1_1 \leftarrow 0_1$ transition at 1000 GHz.

3. Analysis

The electronic ground state of NH is $^3\Sigma^-$, so that the rotational energy levels for $N > 0$ exhibit a fine structure leading to a triplet system in the observed spectrum. For the lowest pure rotational transition, this fine structure triplet is located at 946, 974, and 1000 GHz. Furthermore, the nonzero nuclear spins of nitrogen and hydrogen give rise to magnetic dipole hyperfine structure, which is further subdivided into Fermi contact (b_F), dipole-dipole (t), and nuclear spin-rotation (C_I) interactions. In addition, the ^{14}N nucleus has nuclear spin $I = 1$ and hence causes an electric quadrupole interaction governed by the parameter eQq . The Hamiltonian matrix elements needed to determine the energy levels were calculated according to the

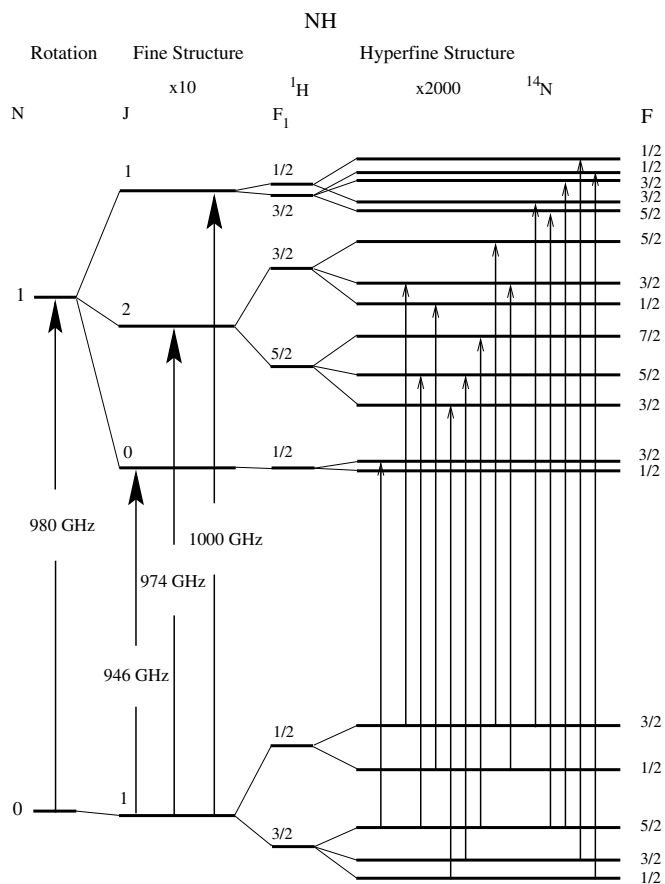


Fig. 2. Energy level diagram of the $N = 0$ and 1 states of NH. The energy scale for the fine structure splitting is enlarged 10 times and the scale for the hyperfine structure is enlarged 2000 times with respect to the rotational energy levels. Transitions with relative intensities of 2% or more are indicated as listed in Table 1 (frequencies increase from left to right).

coupling scheme $\mathbf{J} = \mathbf{S} + \mathbf{N}$, $\mathbf{F}_1 = \mathbf{I}_H + \mathbf{J}$, and $\mathbf{F} = \mathbf{I}_N + \mathbf{F}_1$. Figure 2 shows the energy level diagram of the $N = 1 \leftarrow 0$ transition. We used the same computer program as previously employed by Saleck et al. (1994a) and Klaus et al. (1994, 1996), where the explicit matrix elements can be found. The calculated spectral frequencies were varied in the standard manner to determine the best molecular constants. In the fitting procedure, the observed frequencies were weighted proportionally to the inverse square of their experimental uncertainties. For unresolved hyperfine splittings, the frequencies were calculated as the weighted average of the individual hyperfine components. The transitions already reported by van den Heuvel et al. (1982) were replaced by our remeasured frequencies, which were expected to be more reliable. The observed-minus-calculated (O–C) values given in Table 1 show that the experimental frequencies are reproduced very well within their uncertainties, the σ value of the fit being 46 kHz.

In Table 2, the obtained constants are listed together with their 1σ uncertainties. In the analysis, D_0 , the centrifugal distortion constant, was fixed at 51.307 MHz. This value was derived from D_0 of ND after measurement of its $N = 2 \leftarrow 1$ transition

in the 1 THz region (to be published). A value for $C_I(N)$, the spin-rotation constant involving the nitrogen nucleus, was determined for the first time for NH by this study. The inclusion of $C_I(H)$ yielded no significant improvement to the fit.

4. Discussion

The experimental uncertainties of our frequency measurements at 1 THz are 50 kHz in the best cases, a number which is about 10 times better than the uncertainties obtained by van den Heuvel et al. (1982). This frequency accuracy is sufficiently high for a radioastronomical identification of NH and the determination of velocities in molecular clouds, because the corresponding uncertainty in velocity, 0.015 km s^{-1} , is much smaller than the linewidths of molecular lines in quiescent clouds (typically $0.3\text{--}1.0 \text{ km s}^{-1}$).

The newly determined molecular constants are compared in Table 2 with those obtained by tunable laser-sideband spectroscopy (van den Heuvel et al. 1982), by FT spectroscopy (Brazier et al. 1986), and by a molecular beam, laser-induced fluorescence experiment (Ubachs et al. 1984). They agree well with each other, but an improvement of one to two orders of magnitude was achieved in the present work. Van den Heuvel et al. (1982) included results from LMR measurements (Wayne & Radford 1976) in the fit, since not all three fine structure components had been observed at that time. In our analysis, only the frequencies listed in Table 1 were used to determine the molecular constants presented in Table 2. Brazier et al. 1986 reported slightly different values for B_0 and D_0 , because they included the higher terms H_0 , L_0 , and M_0 in their analysis.

The value of $eQq(N)$ obtained here is $-3.02 \pm 0.11(1\sigma)$ MHz. Ubachs et al. (1984) reported a value of $-5.0 \pm 1.2(1\sigma)$ MHz, whereas our value is found to be larger than the corresponding value, $-2.256 \pm 0.146(3\sigma)$ MHz, obtained for ND (Saito & Goto 1993, Saito 1996). Further measurements are necessary to obtain a more precise quadrupole coupling constant.

The value of $C_I(N)$ can be calculated by a second order perturbation method using the formula (Townes & Schawlow 1975):

$$C_I(N) = 4hB \sum_{n \neq 0} \frac{a_{0n} | \langle 0 | L_x | n \rangle |^2}{E_n - E_0},$$

where a_{0n} is the matrix element of the nuclear spin-orbit interaction between the electronic state concerned, $|0\rangle$, and other electronic states, $|n\rangle$. A possible electronic state which can interact with the ground state of NH is the $A^3\Pi_i$ state, which exists at $29\,776.76 \text{ cm}^{-1}$ above the ground state (Dixon 1959). We employ a value of 138.8 MHz calculated by Morton & Preston (1978) for the value of a_{0n} . The value of $| \langle 0 | L_x | n \rangle |^2$ is difficult to estimate, but, if we assume it to be of the order of one, the calculated value of $C_I(N)$ is about 0.3 MHz. This agrees roughly with our value of 0.180(27) MHz. In addition, the ratio $C_I(N)/B_0$ is comparable to the corresponding values from other molecules, e.g. NO (Saleck et al. 1994b). This indicates that, besides the second order perturbation between the

Table 2. Molecular constants for NH ($X^3\Sigma^-$) in its vibrational ground state^a

Constant	This Work	v. d. Heuvel et al. 1982	Brazier et al. 1986	Ubachs et al. 1984
B_0	489 959.613 (12)	489 959.26 (68)	489 959.16 (13)	
D_0	51.307 ^b	51.384 ^c (90)	51.0482 (10)	
$H_0 \times 10^3$			3.7007 (34)	
$L_0 \times 10^7$			-4.189 (49)	
$M_0 \times 10^{11}$			1.25 (24)	
λ_0	27 577.859 (14)	27 581.1 (43)	27 582.8 (44)	
λ_{D_0}			-0.273 (43)	
γ_0	-1 643.564 (18)	-1 642.4 (17)	-1 644.18 (66)	
γ_{D_0}			0.4526 (22)	
$\gamma_{H_0} \times 10^5$			4.10 (27)	
b_F (N)	18.832 (10)	19.22 (18)		19.6 (4)
t (N)	-22.665 (16)	-22.65 (20)		-22.1 (2)
eQq (N)	-3.02 (11)			-5.0 (12)
C_I (N)	0.180 (27)			
b_F (H)	-66.126 (16)	-66.23 (32)		-66.3 (12)
t (H)	30.087 (33)	30.57 (53)		30.2 (6)

^aAll values in MHz. In brackets: 1σ uncertainties in units of the last quoted digits.

^bFixed value. See text. ^cConstrained value. See van den Heuvel et al. 1982.

$X^3\Sigma^-$ and $A^3\Pi_i$ states, the relatively large value of C_I (N) in NH is mainly caused by the large rotational constant.

5. Conclusion

In summary, extended and more precise frequency measurements performed with the Cologne terahertz spectrometer have led to an improved set of molecular constants for the NH radical in its vibrational ground state. An additional hyperfine coupling constant, C_I , could be determined for the ^{14}N nucleus in NH for the first time.

The frequencies reported in this work may be useful for an interstellar detection of the $N = 1 \rightarrow 0$ rotational transition, though a ground-based observation will be difficult because of the reduced atmospheric transmission in the terahertz region. However, this frequency range is accessible to airborne or spaceborne observatories. For ground-based observations, the newly observed transitions at 946 GHz, located 41 GHz lower than the atmospheric water line, are most suitable for further interstellar investigations on NH.

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