Sub-Doppler Spectroscopy of Ammonia Near 570 GHz

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We have employed the Cologne terahertz spectrometer [1, 2] to observe Lamb dip and crossover phenomena in rotational spectra at 572 GHz. Because of the large power output of the backward wave oscillators used in the system, no special means are required to induce this saturation effect; the coincidentally reflected radiation from the bolometer present in our quasi-optical absorption cell is sufficient to saturate the $v_z = 0$ sub-group. This effect has allowed the observation of the three previously unresolved hyperfine components of the $^{14}NH_3$ A $\leftarrow$ S, $J_K = 1_0 \leftarrow 0_0$ transition, and was also observed for the analogous $^{15}NH_3$ transition in natural abundance (i. e. 0.366 %). These measurements indicate a possible improvement of molecular transition frequencies in the submillimeter region.

The inversion, rotation, and vibration of ammonia has been extensively studied by spectroscopists. Erlandsson and Gordy [3], and Helminger and Gordy [4], reported the first measurements of the rotational spectra for the deuterated and non-deuterated species, respectively. More recently, Magerl et al. [5] measured the ν_2 band quite fully through the microwave modulation of CO_2 laser sidebands. They induced sub-Doppler saturation (Lamb) dips in many of the ν_2 transitions and provided a thorough theoretical explanation of the related hyperfine interaction phenomena, including the related crossover dips which are present in such spectra.

Lamb [6] and Costain [7] described the conditions required for the observation of sub-Doppler absorption features in laser and microwave spectroscopy, respectively. Notably, the radiation must be highly coherent and of sufficient intensity to saturate the absorption; it must also pass through the absorption sample in two beams traveling in opposite directions. Rotational sub-Doppler spectroscopy has therefore historically been performed with resonant cavities which provide the necessary high electric field strengths and fulfill the directional requirements. Work done in this laboratory by Bester et al. [8] and Mittler et al. [9], as well as independent millimeter-wave work by Cazzoli and Dore [10], has shown that the free-space cells are also suitable for Lamb dip measurements.

We have met the Lamb dip requirements in our submillimeterwave laboratory using the backward wave oscillator (BWO)-based spectrometer system described in previous publications [1, 2]. The high power provided by the BWOs employed is sufficient at 570 GHz to saturate rotational transitions of ammonia without the use of resonant cavities. The backward-traveling radiation is caused by reflections from various optical surfaces of the spectrometer, and it seems clear that the majority of the reflected power comes from the detector. This phenomenon is usually a nuisance in the performance of submillimeter wave spectroscopy, but in this case provides sufficient backward-traveling radiation in the standard free-space absorption cell to induce the desired sub-Doppler saturation effects. To observe saturation dips, it is also necessary to operate at fairly low sample pressures, to reduce amplitude of the source modulation, and to ensure, through careful adjustment of the system's lenses, that the forward-traveling wavefronts are highly planar.

The spectrometer system is based on a BWO source (ISTOK Research and Production Co., Fryazino, Russia) operating in the 500 to 700 GHz range with a nominal power output of 5 mW. The BWO is phase-stabilized to a harmonic multiple of a 78-118 GHz synthesizer (Institute of Electronic Measurement, KVARZ, Nizhnii Novgorod, Russia), generated in a planar Schottky diode harmonic mixer employing semi-parabolic optics. The development of these

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components and the phase stabilization electronics is discussed in the recent literature [1, 11, 12, 13]. The resulting radiation is focused through a 3.5 meter absorption cell constructed of Pyrex and wedged Teflon windows, and then detected with a liquid helium-cooled InSb hot-electron bolometer (QMC Inst. Ltd., U. K.). The BWO frequency is modulated and detected digitally at 2f, resulting in second-derivative line shapes. We recorded several spectra of pure ammonia gas at pressures between 2 and 8 mTorr examples of which we present below.

For a three-level system ($E_1 < E_2 \sim E_3$) separated by angular frequencies ω_{12}, ω_{23}, and ω_{13}, and if the Doppler effect causes the $2 \leftarrow 1$ and $3 \leftarrow 1$ transition profiles to overlap, the spectrum can contain Lamb dips at the frequencies ω_{12} and ω_{13}, and a crossover dip at the frequency $(\omega_{12} + \omega_{13})/2$. In this case, the power spectrum $I(\omega)$ contains terms of three types [5]:

$$\frac{(\mu_{12})^4}{(\omega - \omega_{12})^2 + \gamma^2}; \quad \frac{(\mu_{13})^4}{(\omega - \omega_{13})^2 + \gamma^2};$$

$$\frac{(\mu_{12}\mu_{13})^2}{(\omega - (\omega_{12} + \omega_{13})^2 + \gamma^2} \exp[-(v/v_0)^2].$$

Here, the dipole moment matrix element between the state pair (ij) is μ_{ij}, a Maxwellian velocity distribution in v is assumed, $v_0 = (2kT/m)^{1/2}$, and the line width collisional relaxation is γ. The first two types of terms represent the Lamb dips, and the third type generates a crossover dip, where $v \propto (\omega - \omega_{12})$ or $(\omega - \omega_{13})$, respectively. We note that a crossover dip can occur only when the transition pair has a quantum level in common and when the level splitting is comparable with the Doppler width, which in the case of NH_3 ($J_K = 1_0 \leftarrow 0_0$) is 1.7 MHz. For instance, they are not present in the sub-Doppler spectra of H_2S_2 recorded previously in this laboratory [9], since in the case of H_2S_2 the transition pairs arise from two distinct pairs of energy levels.

Figure 1 illustrates the $K = 0$, $J = 0$ and $J = 1$ rotational energy levels of $^{14}NH_3$ in the ground state. The diagram indicates the inversion splitting of the rotational energies, but also shows that every other $K = 0$ level is absent because of nuclear spin statistics, the missing levels being denoted by dotted lines in the figure. The $J = 1$ levels are split into a triplet by the $I = 1$ spin of the ^{14}N nucleus, so that the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$ takes on the values 0, 1, and 2 in the $J = 1$ rotational state. The allowed transitions
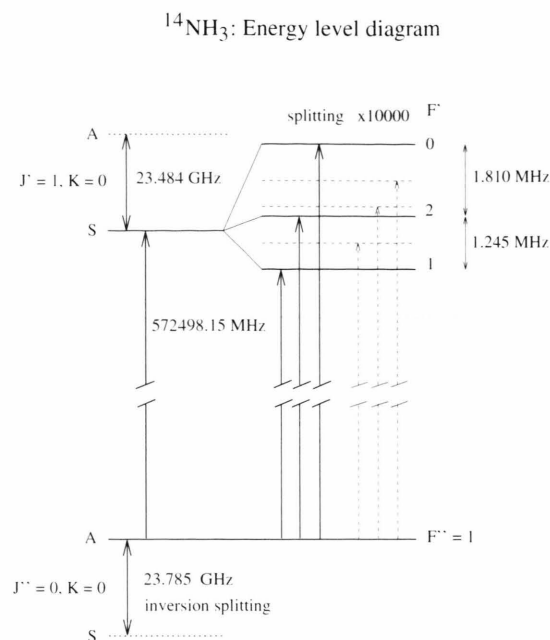

$^{14}NH_3$: Energy level diagram

Fig. 1. Diagram of the rotation-inversion energy levels of $^{14}NH_3$ ($J = 0$, 1; $K = 0$) in the ground state. For $K = 0$ only one of the inversion levels occurs because of nuclear spin statistics. The missing levels are indicated by dotted lines. The hyperfine splitting of the $J' = 1$ level caused by the ^{14}N nuclear spin ($I = 1$) is displayed on the right. The allowed transitions are indicated by bolt arrows, the energies and transitions for the crossover resonances by dashed lines and arrows.

are from $F'' = 1$ ($J'' = 0$) to $F' = 0$, 1, and 2 ($J' = 1$), as indicated by the solid arrows. The energy differences corresponding to each of the possible crossover features are indicated in Fig. 1 by dashed lines.

The observed $^{14}NH_3$ $J = 1 \leftarrow 0$ transition is illustrated in Figure 2. Five absorption features are evident; the allowed transitions are marked by their the $F' - F''$ values. The two observed crossover features are labeled as $C_{F'_1 F''} - C_{F'_2 F''}$. The absence of the possible $C_{01} - C_{11}$ feature is supported by the apparent Doppler width of the transitions, which is clearly smaller than that of the $F' \leftarrow F'' = 1 \leftarrow 1$ plus $F' \leftarrow F'' = 2 \leftarrow 1$ composite feature. Table I lists the measured frequencies of the observed Lamb dips, as determined by a parabolic least-squares fit to each of the extrema. These frequencies were derived from several spectra recorded at lower pressures and with higher spectral resolutions than the spectrum shown in Fig. 1, which is intended to illustrate the overall transition characteristics.
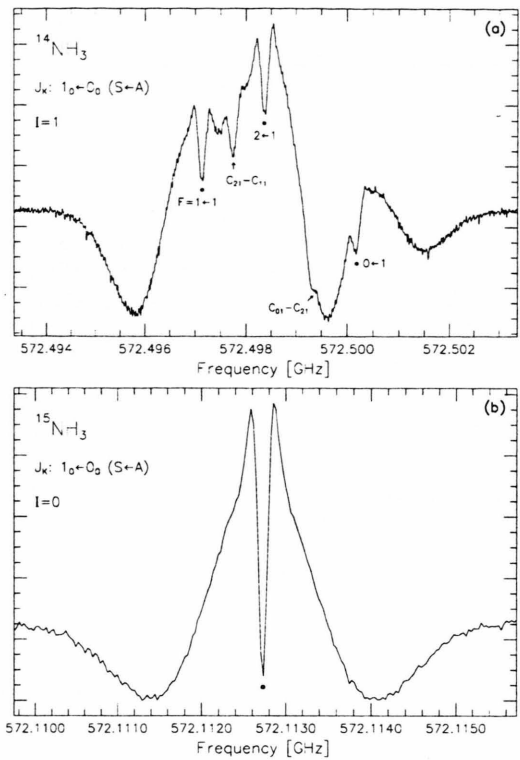
Fig. 2. Observed spectra of ammonia at 572 GHz containing Lamb dips and crossover resonances. In (a) the spectrum of the main isotopomer $^{14}NH_3$ is shown. The hyperfine transitions are marked by filled circles, and the crossover resonances by the $C_{F_1'F''} - C_{F_2'F''}$ notation. In (b) the spectrum of the analogous transition for the $^{15}NH_3$ isotopomer is displayed. Here, the visible Lamb dip feature was observed in natural abundance, i. e. 0.366 %.

Table 1. Measured Lamb dip frequencies of NH_3 for the J_K: $1_0 — 0_0$ transition. In the case of $^{14}NH_3$ the hyperfine components are given, so that X equals F or J for $^{14}NH_3$ or $^{15}NH_3$, respectively.

X'	—	X''	ν_{exp}[a] [MHz]	$\Delta\nu_{exp}$[b] [MHz]
$^{14}NH_3$:				
1	—	1	572 497.137	0.010
2	—	1	572 498.382	0.010
0	—	1	572 500.192	0.025
$^{15}NH_3$:				
1	—	0	572 112.710	0.010

[a] The quoted line positions are shifted to higher frequencies because of the pressure shift of ammonia. For estimation of this shift see text; [b] This column lists the estimated experimental 1σ uncertainties.

The $^{15}NH_3$ sub-Doppler feature (whose frequency is also listed in Table I), observed in natural abundance (i. e. 0.366 %) under similar experimental conditions, consists of a single line (see Figure 2). This derives from the fact that the $I = 1/2$ spin of the ^{15}N nucleus leads in our experiments to no observable hyperfine structure. However, it is clear that the saturation phenomenon made available by the BWO, in conjunction with careful pressure measurements, could lead to a substantial reduction in the estimated uncertainty of this transition frequency over previous measurements [14, 17]. Such measurements were not made in the current qualitative study, so the comments made above concerning the quoted uncertainties in the $^{14}NH_3$ frequencies applies to the $^{15}NH_3$ frequency, as well.

In conclusion, the high coherent power levels of phase-locked BWOs make possible observation of the saturation effects in non-resonant absorption cells at submillimeter wavelengths. This advantage over standard submillimeterwave spectroscopic sources has allowed us to resolve the nuclear hyperfine interactions in the $J = 0$ to 1 transitions of $^{14}NH_3$ in a standard absorption cell, and to measure the analogous Lamb-dip frequency of $^{15}NH_3$. We have also observed similar saturation effects both in the HCl spectrum (near 625 GHz) and in higher transitions of ammonia (above 1 THz); these measurements will be discussed in later publications. For strong, well-isolated lines, the current Doppler-limited frequency accuracy of the Cologne terahertz spectrometer is approximately 5 kHz, as has been shown in the case of CO measurements [18]. The signal to noise ratios

The quoted frequencies have not been corrected for the substantial pressure shift of ammonia which was determined in [14] for this transition to be 6.10(7) MHz/Torr for $^{14}NH_3$ and 5.71(10) MHz/Torr for $^{15}NH_3$. Estimating an upper limit for the pressure of 10 mTorr in our measurements, the line positions are shifted by about 60 kHz to higher frequencies. The experimentally determined uncertainties (1σ) quoted in Table I do not contain this systematic error.

The hyperfine interaction constant eQq for the $J_K = 1_0$ level of $^{14}NH_3$ has been previously measured through molecular beam electric resonance spectroscopy to very high accuracy, and is equal –4.08983(2) MHz (see [15] and [16]). We have determined the value from our data to be –4.098(48) MHz, which is in agreement with the accepted value to within our larger uncertainty. It was assumed that the pressure shift is equal for all hyperfine components.

now obtainable for sub-Doppler features provide only marginal improvement in this figure, but this limitation is at least partly due to spurious signals from the KVARZ synthesizer. The removal of these and other noise sources is currently being pursued in the laboratory. Subsequent measurements could then lead to further improvements in effective molecular determinations, particularly those related to hyperfine interactions, for many important molecular species.

Ammonia is an important interstellar molecule. Its inversion transitions are extensively used for temperature and density determinations of molecular clouds. In cold dark clouds, with kinetic temperatures near 10 K, e. g. TMC1 (NH_3 peak) , the $J = 1 \leftarrow 0$ rotation inversion transition should be observable with its hyperfine structure resolved, provided the interstellar

line width is thermal. At about 10 K we expect a line width of about 300 kHz.

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