ROTATIONAL HYPERFINE SPECTRUM OF THE NH RADICAL AROUND 1 THz

F.C. VAN DEN HEUVEL, W.Leo MEERTS and A. DYMANUS

Katholieke Universiteit, Fysisch Laboratorium, 6525 ED Nijmegen, The Netherlands

The rotational transitions $N = 1 - 0, J = 2 - 1$ and $N = 1 - 0, J = 1 - 1$ of the NH radical in the $^3\Sigma^-$ electronic and vibrational ground state have been observed around 1 THz with resolved hyperfine structure. Spectra were recorded at zero magnetic field, using a tunable laser-sideband spectrometer. Analysis yielded improved values of the magnetic hyperfine parameters and the rotational constants.

1. Introduction

For a long time the rotational spectrum of the NH radical has been inaccessible to high-resolution spectroscopy because the spectrum lies beyond the frequency range of conventional microwave spectrometers. A few years ago the radical was studied with the technique of laser magnetic resonance (LMR) [1,2]. These investigations permitted the first determination of the Frosch and Foley [3] magnetic hyperfine parameters b and c, for both the nitrogen and hydrogen nuclei. The experiments demonstrated the power of the LMR technique in the far-infrared region, in particular with respect to sensitivity.

However, with the LMR technique molecular zero-field constants are deduced from a fit of (generally) complex magnetic spectra which also depend on first- and second-order Zeeman parameters. These features, and field inhomogeneities, often limit the accuracy of the constants derived. In this communication we report the pure (zero-field) rotational spectrum of the normal isotopic species [14]NH in the ground electronic and vibrational state X $^3\Sigma^-$, $v = 0$. The transitions $N = 1 \leftarrow 0, J = 2 \leftarrow 1$ and $N = 1 \leftarrow 0, J = 1 \leftarrow 1$ have been recorded with the spectrometer used for the successful investigation of the CF radical [4].

Experimental details

Tunable far-infrared radiation has been produced

by mixing the radiation of a hydrogen cyanide discharge laser (frequency 890.7603 GHz) with that of a klystron, using a Schottky barrier diode as non-linear element. An outline of the spectrometer has been given [4]. The frequencies required for the present experiments, 974 GHz ($J = 2 \leftarrow 1$) and 1000 GHz ($J = 1 \leftarrow 1$), were obtained with klystrons operating at 83 and 109 GHz, respectively.

The method of producing NH radicals was different from the one applied in LMR studies [1,2]. Instead of repetitive hydrogen abstraction from ammonia by fluorine atoms (produced in a microwave discharge through CF_4), a dc glow discharge through pure ammonia was chosen for the production. The discharge was struck in a water-cooled 1 m cell with a diameter of 5 cm. Strongest absorption signals were observed at a discharge current of ≈ 200 mA with a signal-to-noise ratio of ≈ 50 at $RC = 1$ s. A recording is reproduced in fig. 1. Total pressure of the continuously flowing discharge medium was 25 Pa. Zeeman modulation has been applied for detection. A coil wrapped around the cell produced a biased magnetic field that oscillated sinusoidally between 0 and 0.7 mT.

While searching for NH an unexpected line was recorded which could originate neither from a paramagnetic species nor from the ammonia molecule. The resonance appeared at 974488.4(8) GHz, at a distance of only a few MHz from the hyperfine-free frequency of the $J = 2 \leftarrow 1$ transition of NH. Observation of the line was prohibited using Zeeman modulation, but ab-
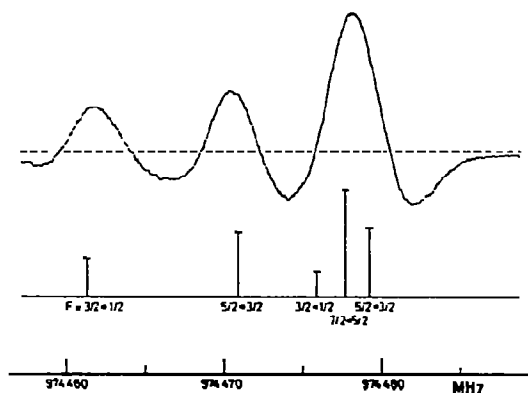

Fig. 1. Central part of the $N = 1 - 0$, $J = 2 - 1$ rotational hyperfine spectrum recorded at 974 GHz and the best-fit spectrum with the relative intensities

sorption was clearly visible by monitoring the power of laser-sideband radiation. At low pressure of the order of 1 Pa the absorption intensity was equal to 100%. The line was identified as the $J = 11 \leftarrow 10$ rotational transition of the hydrogen cyanide (HCN) molecule. Probably the molecule has been produced at low pressure in the presence of carbon atoms sputtered from the electrodes. It is possible that the presence of carbon atoms has been detrimental to NH production efficiency

3. Analysis and results

The effective hamiltonian is composed of a rotational and rotational fine structure term, a term associated with magnetic hyperfine interactions and a quadrupole term.

$$H = H_{rfs} + H_{mhf} + H_Q .$$

In the case of NH, the rotational levels with $\Delta N = \pm 1$ are separated by at least 950 GHz, the $N = 1$ ($J = 0, 1, 2$) fine structure levels by 25–30 GHz, which is large compared to the hyperfine splittings ($\leqslant 0.085$ GHz). Consequently, the hyperfine and rotational fine structure have been analyzed separately hyperfine interaction can be treated as a small perturbation on the widely spaced rotational (N,J) levels. We used the explicit formulas of Miller and Townes [5] to describe the pure rotational spectrum, including fine structure effects. These formulas contain the rotational constant (B), the spin—spin constant (λ) and the spin—

rotation constant (γ). An expression for the magnetic hyperfine term H_{mhf} was derived by Frosch and Foley [3]. These authors introduced the magnetic hyperfine parameters b and c. We used the tensorial form of their hamiltonian, which was given by Wayne and Radford [2]

Calculation of the hyperfine matrix elements has been performed in the representation $|NSJI_1F_1I_2FM_F\rangle$ corresponding to the coupling scheme $J = N + S$, $F_1 = J + I_1$, $F = F_1 + I_2$. Matrix elements of the type

$$\langle N'SJ'I_1F_1'I_2F'M_F'|(H_{mhf} + H_Q)|NSJI_1F_1I_2FM_F\rangle$$

were calculated with the aid of spherical tensor methods [6]. Explicit formulas can be found elsewhere [7]. The number J is an approximate quantum number. We estimated by second-order perturbation calculation that the effects of matrix elements of the type $\Delta J = 0$, $\Delta N \neq 0$ and of the type $\Delta J \neq 0$ are smaller than 0.01 and 0.3 MHz, respectively. As the full Doppler linewidth is 5 MHz, contributions from these matrix elements can be neglected.

As a first step we compared our recorded spectra with prediction based on the four hyperfine constants (b_H, c_H, b_N, c_N) determined by Wayne and Radford [2]. Like these authors we neglected at this stage the small influence of the quadrupole interaction term in the hamiltonian. The calculated and observed spectra showed resemblance, but many lines were shifted by an amount close to or slightly beyond the limits set by the accuracy of the constants (we allowed the constants to vary within their quoted error limits). Although the calculated spectra facilitated identification of the observed lines, some parts of the recordings consisted of closely spaced, sometimes unresolved, lines.

Relative intensities have been calculated to make identifications unambiguous. Dipole moment matrix elements were calculated with standard formulas [8], using the eigenfunctions of the hyperfine hamiltonian. In a preliminary fit we included only the frequencies corresponding to the center of singular absorption lines and obtained the position of lines that were not yet included in the fit. In the case of closely spaced lines we weighted the frequencies according to the intensity and calculated the centre of the composite line corresponding to such a cluster. In this way we were able to include in the fit the frequencies of four

Table 1
The observed $N = 1 \leftarrow 0$ rotational hyperfine spectra

	Identification [a]		$\nu_{obs.} - \nu_0$ [b]	$\nu_{obs.} - \nu_{calc.}$
	ΔF	F		
$J = 2 \leftarrow 1$	1	5/2, 3/2, 1/2	3.47(80)	0 22
	1	3/2	−4.26(40)	−0 44
	1	1/2	−12.99(40)	0.50
	0	5/2, 3/2	−38.28(60)	−0 34
	0	1/2	−24.53(150)	0 42
$J = 1 \leftarrow 1$	1,0	3/2	34.97(60)	0 43
	1	1/2	52.94(60)	−0.35
	1	1/2	−28.97(40)	−0.07
	0	5/2	−0.62(40)	−0 20
	0	3/2	60.27(60)	0.24
	0,1	1/2	79.94(120)	0.45
	−1	5/2	26.41(40)	0 03
	−1	3/2	−66.11(60)	0.52
	−1	3/2	72.35(120)	−1.54

[a] The F value is given for the lower $(N = 0, J = 1)$ level, note that the total F momentum may have different (F_1, I_2) parentages. A line with more than one identification consisted of overlapping hyperfine components and was treated as described in the text.

[b] Position of the lines in MHz referred to the center of the hyperfine spectra. Values of the hyperfine-free rotational frequencies $\nu_0(J = 2 \leftarrow 1)$ and $\nu_0(J = 1 \leftarrow 1)$ are given in the text.

observed composite lines. The procedure converged by iteration to the final fit, in which we included 14 experimental frequencies and determined the four hyperfine parameters. The positions of the two centres of the rotational $J = 2 \leftarrow 1$ and $J = 1 \leftarrow 1$ hyperfine spectra were regarded as floating parameters. Consequently the final fit yielded both the hyperfine constants and the following hyperfine-free rotational frequencies·

$$\nu_0(J = 2 \leftarrow 1) = 974474\ 85(80)\ \text{MHz},$$

$$\nu_0(J = 1 \leftarrow 1) = 999974.03(80)\ \text{MHz}.$$

A comparison between observed and best-fit spectra is presented in table 1; the best-fit hyperfine constants are given in table 2. Inclusion of the quadrupole term in the hamiltonian neither improved the fit, nor yielded a significant value for eqQ. Therefore this term was left out of the final fit. The values of our hyperfine parameters and those obtained by Wayne and Radford [2] are in good agreement within two standard deviations. Our analysis confirms the choice made by Wayne and Radford for the absolute sign of

Table 2
Molecular parameters of NH (in MHz)

	This work	Ref. [2]
B [a]	489959 26(68)	489960(6)
λ	27581.1(43)	27572(6)
γ	−1642.4(17)	−1638 7(24)
b_H	−96 80(57)	−100.2(26)
c_H	91.70(160)	88 8(48)
$b_H + c_H/3$	−66.23(32)	−70.6(10)
b_N	41 86(33)	42 8(16)
c_N	−67.94(61)	−68.4(30)
$b_N + c_N/3$	19 22(18)	20.0(6)

[a] In this work the distortion parameter D was constrained to the value 51 384(90) MHz [9], while it was held fixed to 16 85 × 10^{-4} cm^{-1} (50 515 MHz, [10]) in ref. [2].

the b and c constants, which they made in agreement with ab initio calculation.

Above we determined the hyperfine-free frequencies ν_0 corresponding to the $N = 1 \leftarrow 0, J = 2 \leftarrow 1$ and $N = 1 \leftarrow 0, J = 1 \leftarrow 1$ transition. A third transition $(N = 1 \leftarrow 0, J = 0 \leftarrow 1)$, predicted at 946 GHz, was not searched for, but even if this transition was recorded

as well, the number of experimental fine structure data would have been insufficient to determine both the rotational constants B, the fine structure constants λ and γ and the centrifugal distortion parameter D.

However, the values of $\nu_0(J = 2 \leftarrow 1)$ and $\nu_0(J = 1 \leftarrow 1)$ given above have an accuracy which is much better than the accuracy of prediction (≈ 15 MHz) based on the values of B, λ and γ determined by Wayne and Radford [2] and the value of D of Dixon [10]. We therefore determined the parameters B, D, λ and γ in a least-squares analysis with our frequencies ν_0, while constraining the parameters to their known values within the quoted limits of accuracy.

The values of B, λ and γ were taken from ref. [2], the value $D = 17.14(3) \times 10^{-4}$ cm^{-1} from Bollmark et al. [9]. As part of their investigation the latter authors reanalyzed the optical spectra obtained by Dixon [10]. We followed the method of Bollmark et al. to introduce the centrifugal distortion parameter D in the formulas of Miller and Townes. The fit yielded the values of the parameters given in table 2. The accuracy of the value of B is significantly improved.

4. Concluding remarks

The current work demonstrates the capability of a far-infrared laser-sideband spectrometer to obtain high-resolution spectra of light radicals which cannot be studied in the microwave region. The laser-sideband spectrometer may become a serious competitor of the LMR technique which was the only powerful method in the far-infrared to study radicals and ions. The present spectrometer can be used to study non-magnetic molecules and states and produces spectra at zero magnetic field. Recently [11], for example, we obtained rotational spectra of ions in the ground electronic and vibrational state: $HCO^+(^1\Sigma)$ and $HN_2^+(^1\Sigma)$.

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