

Difference Frequency Laser Spectroscopy of the $v = 1 \leftarrow 0$ Transition of NH

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The $v = 1 \leftarrow 0$ vibration-rotation band of NH was observed with a difference frequency laser and a long-path, Zeeman-modulated discharge cell. The 29 transition wavenumbers (from $P(4)$ to $R(5)$) were measured with an estimated accuracy of 0.003 cm^{-1} . The band origin ($3125.5724 \pm 0.0020 \text{ cm}^{-1}$) as well as the spin-spin, the spin-rotation, and the rotational constants were determined in a least-squares fit.

INTRODUCTION

The direct observation of the high-resolution infrared absorption spectrum of NH has been made using a difference frequency laser and a multiple-reflection discharge cell. The NH radical is well known chemically and spectroscopically. A high-resolution rotational analysis of the $A^3\Pi-X^3\Sigma^-$ electronic transition was made by Dixon (1). The $v = 1 \leftarrow 0$ absorption band of NH was detected in low-temperature matrices by Milligan and Jacox (2). Wayne and Radford (3) observed the far-infrared laser magnetic resonance spectrum for $v = 1$ and $v = 0$ of NH and ND, and $v = 0$ of ^{15}NH .

The infrared vibration-rotation spectrum of NH around $3.2 \mu\text{m}$ has been observed in α -Orionis by Lambert and Beer (4); these lines are useful indicators of nitrogen abundance. The NH radical also has been detected in the atmospheres of many stars by observing the $A^3\Pi-X^3\Sigma^-$ (0-0) bandhead at 3350 \AA (5). Infrared spectroscopy in the $3\text{-}\mu\text{m}$ atmospheric window region is particularly interesting in view of the recent progress in infrared observation of extraterrestrial molecules (6).

EXPERIMENTAL DETAILS

The details of the experimental apparatus are described in Ref. (7). Tunable infrared laser radiation was generated by mixing the output of a cw single-mode dye laser with that of a single-mode argon ion laser in a temperature-controlled LiNbO_3 crystal (8). The infrared beam was passed 16 times through a multiple-reflection discharge cell of effective path length of 1 meter. Around the glass cell was wound a coil for Zeeman modulation at 2.5 kHz with an amplitude of 200 gauss (peak-to-peak). Some of the higher- J transitions were observed with an improved cell that allowed about 500 gauss (peak-to-peak) of modulation. A dc bias current was applied to provide approximately zero-based modulation.

The NH radical was produced in a dc discharge through 0.5 to 0.8 Torr (67 to 106 Pa) of flowing ammonia gas with a discharge current of about 30 mA ($\sim 4 \text{ mA/}$

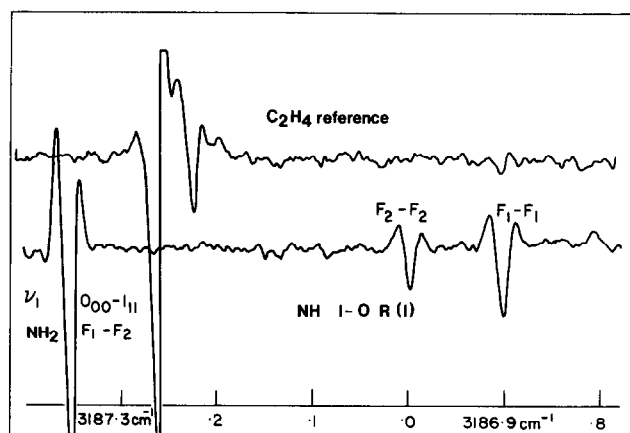


FIG. 1. The lower trace shows the $R(1)$ transitions of NH recorded with Zeeman modulation. The upper trace is a spectrum recorded simultaneously using frequency modulation for frequency calibration.

cm^2). The signal intensity depended very little on the discharge current and the pressure of ammonia, and the same experimental conditions also yielded spectra of NH_2 (7).

The transition wavenumbers were measured by using absorption lines of C_2H_4 (9), N_2O (10), and NH_3 (11) for calibration. A 300-MHz Fabry-Perot etalon provided relative frequency markers. The accuracy of the frequency measurements was estimated to be about 0.003 cm^{-1} . Figure 1 shows a typical example of the NH absorption signals.

ANALYSIS AND DETERMINATION OF THE MOLECULAR CONSTANTS

The Hamiltonian derived in Ref. (12) was used in the analysis¹:

$$H_{\text{rot}} = \frac{2}{3} \lambda (3S_z^2 - S^2) + \gamma(\mathbf{J} - \mathbf{S})\mathbf{S} + \tilde{B}(\mathbf{J} - \mathbf{S})^2. \quad (1)$$

The vibration-rotation energy, including the spin interactions are calculated to the order of κ^6 (κ is the Born-Oppenheimer expansion parameter (13)) of the zeroth-order vibrational energy in a standard perturbation calculation. The matrix is given in terms of the symmetrized Hund's case (a) basis (12, 14):

$$\langle +|H_{\text{rot}}|+ \rangle = T_v^{\text{eff}} + \frac{2}{3} \lambda_v^{\text{eff}} - \gamma_v^{\text{eff}} + \left(\tilde{B}_v - 4D_v'' + \frac{4}{3} \lambda_D - 2\gamma_D \right) J(J+1) - D_v J^2(J+1)^2, \quad (2)$$

$$\langle -|H_{\text{rot}}|- \rangle = T_v^{\text{eff}} + \frac{2}{3} \lambda_v^{\text{eff}} - \gamma_v^{\text{eff}} + \left(\tilde{B}_v + \frac{4}{3} \lambda_D - 2\gamma_D \right) J(J+1) - D_v J^2(J+1)^2, \quad (3)$$

¹ In Ref. (12), the term in S^2 was excluded to avoid the introduction of an additional parameter λ' . The Hamiltonian used in this paper includes the S^2 term to be consistent with most of the more customary formulations. See also under Discussions in Ref. (12).

$$\langle 0|H_{\text{rot}}|0\rangle = T_v^{\text{eff}} - \frac{4}{3}\lambda_v^{\text{eff}} - 2\gamma_v^{\text{eff}} + 2\tilde{B}_v + \left(\tilde{B}_v - 4D_v - 4D_v'' - \frac{8}{3}\lambda_D - 4\gamma_D\right)J(J+1) - D_v J^2(J+1)^2, \quad (4)$$

$$\langle +|H_{\text{rot}}|0\rangle = 2\left\{B_v - \frac{1}{2}\gamma_v^{\text{eff}} - (2D_v + \gamma_D)J(J+1)\right\}[J(J+1)]^{1/2},$$

$$\text{where } |\pm\rangle = \frac{1}{2^{1/2}}[|\Sigma = 1\rangle \pm |\Sigma = -1\rangle] \quad \text{and} \quad |0\rangle = |\Sigma = 0\rangle. \quad (5)$$

In these equations, the effective constants T_v^{eff} , λ_v^{eff} , and γ_v^{eff} are defined by²

$$T_v^{\text{eff}} = T_v - \frac{8}{9}\epsilon^2 \frac{\lambda_{(1)}^2}{\tilde{B}_e} + 2\epsilon^2 \frac{\gamma_{(1)}^2}{\tilde{B}_e}, \quad (6)$$

$$\lambda_v^{\text{eff}} = \lambda_v + \frac{2}{3}\epsilon^2 \frac{\lambda_{(1)}^2}{\tilde{B}_e} + 3\epsilon^2 \frac{\lambda_{(1)}\gamma_{(1)}}{\tilde{B}_e}, \quad (7)$$

$$\gamma_v^{\text{eff}} = \gamma_v + \frac{2}{3}\epsilon^2 \frac{\lambda_{(1)}\gamma_{(1)}}{\tilde{B}_e} + 3\epsilon^2 \frac{\gamma_{(1)}^2}{\tilde{B}_e}, \quad (8)$$

where $\epsilon = \tilde{B}_e/\omega_e$. The Hamiltonian given here is the same as that given by Tischer and in Ref. (12) except for the vibrational term value. The centrifugal terms λ_D and γ_D are defined by

$$\lambda_D = 2\epsilon^2\lambda_{(1)}, \quad (9)$$

$$\gamma_D = 2\epsilon^2\gamma_{(1)} \quad (10)$$

(note that these differ by a factor of 2 from those of Mizushima (15)). The hyperfine interactions were not taken into consideration, because the hyperfine structure was not resolved.

The least-squares fit was performed with \tilde{B}_v , λ_v^{eff} , γ_v^{eff} , D_v , λ_D , and γ_D ($D_v'' = D_v + \gamma_D^2/4D_v$) for both the ground and the excited states and T_v^{eff} as the variable parameters. A preliminary least-squares fit yielded λ_D and γ_D to be $(1.7 \pm 2.7) \times 10^{-4}$ and $(8 \pm 9) \times 10^{-6} \text{ cm}^{-1}$ for the ground state, and the corresponding values for the excited state were $(-0.6 \pm 2.7) \times 10^{-4}$ and $(11 \pm 15) \times 10^{-6} \text{ cm}^{-1}$, respectively. The fit in which λ_D for the ground and the excited states were set equal gave $\lambda_D = (-1.3 \pm 3.3) \times 10^{-4} \text{ cm}^{-1}$. In view of these changes in λ_D and the present experimental accuracy, λ_D and γ_D were neglected in the final fit, and the values λ_0^{eff} and γ_0^{eff} were fixed at the values determined by Wayne and Radford (3). Table I lists the observed wavenumbers together with the residuals of the fit. The molecular constants determined from the fit are shown in Table II.

DISCUSSIONS AND CONCLUSION

The values of the molecular constants in Table II agree very well with those determined by Wayne and Radford (3). The constants are also consistent with, but

² In these equations, $\lambda_{(1)}$ and $\gamma_{(1)}$ are the first-order coefficients in the power series expansion of λ and γ in terms of $\xi (= (r - r_e)/r_e)$, respectively.

TABLE I

Observed Wavenumbers of the $v = 1 \leftarrow 0$ Transitions of NH ($X^3\Sigma^-$)

$J'N'+J$	N	$\nu_{\text{obs}}/\text{cm}^{-1}$	$(o-c)/10^{-4} \text{ cm}^{-1}$
3 4	4 5	2949.9649	8
5 4	6 5	2950.1391	-14
2 3	3 4	2987.3873	28
4 3	5 4	2987.5844	12
1 2	2 3	3023.6314	-12
2 2	3 3	3023.8086	-32
3 2	4 3	3023.9015	-28
2 1	2 2	3058.1111	-13
0 1	1 2	3058.2778	-14
1 1	2 2	3058.9563	1
2 1	3 2	3059.0700	16
1 0	1 1	3092.2161	-6
1 0	2 1	3093.0694	26
1 0	0 1	3094.0010	-4
0 1	1 0	3155.8448	5
2 1	1 0	3156.7883	16
1 1	1 0	3157.6311	7
3 2	2 1	3186.9088	-16
2 2	1 1	3187.0067	-2
1 2	0 1	3187.6786	8
2 2	2 1	3187.8596	27
4 3	3 2	3215.6142	-4
3 3	2 2	3215.6842	-11
2 3	1 2	3215.8502	-19
5 4	4 3	3242.8934	-5
3 4	2 3	3243.0478	14
4 5	3 4	3268.8368	7
7 6	6 5	3293.0534	16
5 6	4 5	3293.1478	-25

more accurate than, those reported by Dixon (1) and Murai and Shimauchi (16). After our work was completed we learned of the Fourier-transform spectra of NH measured by Sakai *et al.* (17). Their measurements are much more extensive but less accurate than those reported here.

The equilibrium molecular constants are also given in Table II. The largest correction term to B_e is given by

$$\delta B = 4 \sum_{n'=\Pi} \tilde{B}_e^2 \langle n|L_x|n'\rangle^2 / \Delta E_{nn'}^0 = g_r^e \tilde{B}_e = (g_r - g_r^n) \tilde{B}_e. \quad (11)$$

This term can be estimated from the rotational g factor, g_r^e , which, unfortunately, was not determined from the magnetic resonance spectra (3). If we assume, as Wayne and Radford (3) did, $g_r = -0.000100$, the g_r^e is calculated to be -6.3×10^{-4}

TABLE II
Molecular Constants of NH ($X^3\Sigma^-$) (in cm^{-1})

	v=0	v=1
\tilde{B}_v	16.34333(33) ^a	15.69634(33)
D_v	0.001702(8)	0.001674(12)
λ_v	0.9197 ^b	0.9189(20)
γ_v	-0.05466 ^b	-0.05171(72)
ν_0	3125.5724(20)	
α_e^B	0.64699(32)	
α_e^λ	0.0008(20)	
α_e^γ	-0.00296(72)	
\tilde{B}_e	16.66683(16)	
B_e	16.656(2) ^c	
D_e	0.001715(11)	
γ_e	1.03756(6) ^c $\overset{\circ}{\text{A}}$	

^aThree times the standard error.

^bFixed to the values in Ref. (3).

^cEstimated uncertainty. See text.

by correcting for the nuclear contribution $g_r^n = 5.3 \times 10^{-4}$. Using this estimate, we obtain

$$\delta B = -1.1 \times 10^{-2} \text{ cm}^{-1}.$$

The equilibrium rotational constant B_e thus obtained is listed in Table II, and the resulting equilibrium internuclear distance is $r_e = 1.03756 \pm 0.00006 \text{ \AA}$.

The vibrational dependence of λ_v could not be determined from our data. Although λ_1 obtained in the present work agrees with that of Wayne and Radford (3) within three standard deviations, fixing λ_1 at their value increased the standard deviation. The centrifugal distortion constant D_e agrees very well with the calculated value of 0.001717 cm^{-1} obtained using the relation

$$D_e = 4\tilde{B}_e^3/\omega_e^2.$$

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