NOTE

Rotational and Hyperfine Constants of Vibrationally Excited NH $(a^1\Delta; v = 1)$[1]

In a recent study (*1*) we examined the electronic structure of NH and ND in the $v = 0$ level of their $a^1\Delta$ state from an analysis of their far-infrared (FIR) laser magnetic resonance (LMR) spectra. In that work, the magnetic hyperfine constants were readily interpreted in terms of a distribution of orbitally degenerate electrons located in nonbonding p orbitals on the nitrogen atom. In this note we report an observation of the lowest rotational transition of NH $(a^1\Delta)$ in its first excited vibrational state.

The radical was produced by the reaction of fluorine atoms with ammonia as in Ref. (*1*), although in most experiments somewhat different pressures were used. Typically, measurements were taken with 5.3 Pa (40 mTorr) of a mixture of 10% F_2 in He combined with 1 Pa (8 mTorr) of Ar and passed through a 2450-MHz microwave discharge to produce atomic fluorine. A trace amount of NH_3 (<1 mTorr) was introduced immediately prior to passage through the far-infrared lasing cavity, adjusted to optimize the signal. Under these conditions, the resulting flame was white with only a tinge of orange, in contrast with the bright orange flame used previously. On the strongest transition, a signal-to-noise ratio of ~40 was typically observed using a 300-ms instrumental time constant. The LMR spectrometer was the same as that used in Ref. (*1*).

Spectra arising from the $J = 3 \leftarrow 2$ transition were recorded using the 105.5-μm lasing line (*2*) of CH_2F_2 ($\nu_L = 2\,841\,142.9$ MHz). Transitions were observed in both the σ and π polarizations, and, under the conditions given above, many exhibited well-resolved saturated absorption features (see Fig. 1). In addition to the usual pattern of allowed transitions characteristic of a molecule in $a^1\Delta$ state, a number of weak transitions corresponding to $\Delta M_I(N) = \pm 1$ were also observed. These transitions, which have zero intensity when the nuclear spins are completely decoupled from the molecular rotation, are observable here due to the particularly low magnetic field strengths required to tune the molecular transition into resonance with the far-infrared lasing line used. A summary of the observed transitions and magnetic field strengths is given in Table I.

Table II presents the results of a least-squares fit of the data to the Hamiltonian used in Ref. (*1*) and compares the constants for the $v = 1$ state with those for $v = 0$. The residuals given in the last column of Table I are consistent with uncertainties resulting from magnetic field measurements and the resettability
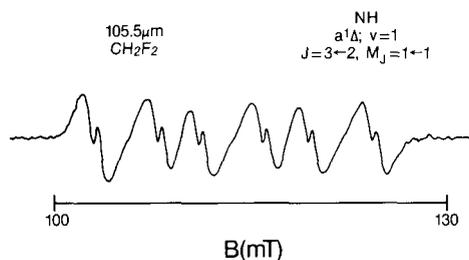
FIG. 1. Part of the 105.5-μm laser magnetic resonance spectrum of NH $(a^1\Delta; v = 1)$ in π polarization showing clearly resolved Lamb dips. The six-line pattern results from the nitrogen and hydrogen nuclear hyperfine structure.

0022-2852/87 $3.00   242

TABLE I

Laser Magnetic Resonance Spectrum of the $J' = 3 \leftarrow J'' = 2$ Transition of NH ($a^1\Delta; v = 1$)
at 105.5 μm ($\nu_L = 2\,841\,142.9$ MHz)

M_J''	$M_I(N)''$	$M_I(H)''$	M_J''	$M_I(N)''$	$M_I(H)''$	B(mT)	((obs-calc)(MHz))
σ polarization							
1	+1	+1/2	2	+1	+1/2	23.22	0.4
1	+1	-1/2	2	+1	-1/2	28.11	-0.2
0	0	+1/2	2	-1	+1/2	30.12*	1.2
1	0	+1/2	2	0	+1/2	32.12	0.0
0	0	-1/2	2	-1	-1/2	34.62*	-1.1
1	0	-1/2	2	0	-1/2	36.67	-1.3
2	0	+1/2	2	+1	+1/2	38.31*	-0.8
1	-1	+1/2	2	-1	+1/2	43.56	0.8
0	+1	+1/2	1	+1	+1/2	46.02	0.3
1	-1	-1/2	2	-1	-1/2	48.76	-0.3
0	+1	-1/2	1	+1	-1/2	50.89	-0.5
0	0	+1/2	1	0	+1/2	53.80	0.2
0	0	-1/2	1	0	-1/2	58.60	-0.4
0	-1	+1/2	1	-1	+1/2	62.16	0.9
0	-1	-1/2	1	-1	-1/2	67.05	1.1
2	0	+1/2	2	-1	+1/2	68.85*	2.0
2	0	-1/2	2	-1	-1/2	73.69*	-0.4
-1	+1	+1/2	0	+1	+1/2	104.20	-0.3
3	+1	+1/2	2	+1	+1/2	105.03	0.4
-1	+1	-1/2	0	+1	-1/2	108.86	-0.3
3	+1	-1/2	2	+1	-1/2	109.75	0.1
-1	0	+1/2	0	0	+1/2	111.56	0.0
3	0	+1/2	2	0	+1/2	112.34	0.5
-1	0	-1/2	0	0	-1/2	116.28	0.1
3	0	-1/2	2	0	-1/2	117.06	0.3
-1	-1	+1/2	0	-1	+1/2	118.80	-0.7
3	-1	+1/2	2	-1	+1/2	120.29	0.2
-1	-1	-1/2	0	-1	-1/2	123.72	0.4
3	-1	-1/2	2	-1	-1/2	125.05	0.0
π polarization							
2	+1	+1/2	2	+1	+1/2	44.30	0.8
2	+1	-1/2	2	+1	-1/2	49.33	0.2
2	0	+1/2	2	0	+1/2	52.59	0.6
2	0	-1/2	2	0	-1/2	57.46	0.1
2	-1	+1/2	2	-1	+1/2	63.05	1.0
2	-1	-1/2	2	-1	-1/2	68.22	0.2
3	0	+1/2	2	+1	+1/2	83.74*	0.1
3	0	-1/2	2	+1	-1/2	88.71**	0.1
3	-1	+1/2	2	0	+1/2	88.71**	-0.9
3	-1	-1/2	2	0	-1/2	93.39*	1.0
1	+1	+1/2	1	+1	+1/2	103.79	0.3
1	+1	-1/2	1	+1	-1/2	108.63	-0.2
1	0	+1/2	1	0	+1/2	111.74	0.1
1	0	-1/2	1	0	-1/2	116.58	-0.4
1	-1	+1/2	1	-1	+1/2	120.05	0.2
1	-1	-1/2	1	-1	-1/2	124.92	-0.2

* indicates unresolved pair   • indicates nuclear spin forbidden

of the FIR laser to the top of its gain curve. As expected, the magnetic hyperfine parameter for the nitrogen atom, a_N, is identical in both states since the nonbonding p electrons (located primarily on the nitrogen atom) remain unaffected by vibrational excitation. The corresponding constant for the proton, a_H, exhibits a weak but significant vibrational dependence since it is proportional to the quantity $\langle 1/r_H^3 \rangle$, where r_H is the distance between the proton and the electrons carrying the angular momentum.

Table II also compares the values of $\langle 1/r_H^3 \rangle^{-1/3}$ computed from the measured values of a_H with the N–H bond length, $\langle 1/R^2 \rangle^{-1/2}$, determined from the rotational constants. In the $v = 0$ state, the agreement is within the experimental uncertainties since, for a p orbital on the nitrogen atom, r_H is approximately equal to the N–H bond distance. While undoubtedly the spatial distribution of the p orbitals is such that r_H cannot identically equal R for all values of r_H, the agreement for $v = 0$ indicates that the differences between them

TABLE II

Molecular Constants for NH $(a^1\Delta)^{(a)}$

	$v=0$ [b]	$v=1$ [c]
$B_v(N^2)$ (MHz)	493043.182(95)	474503.281(29)
$D_v(N^2)$ (MHz)	50.45(11) [d]	49.520(96) [d]
a_N (MHz)	109.65(85)	109.71(22)
a_H (MHz)	70.9(14)	68.20(54)
g_r	-0.00158(6)	-0.00156(16)
$\langle 1/R^2\rangle^{-1/2}$ (Å) [e]	1.0442	1.0644
$\langle 1/r_H^3\rangle^{-1/3}$ (Å) [f]	1.037(9)	1.050(3)

(a) Quoted uncertainties in the spectroscopic constants are
one standard deviation in the fit
(b) Reference (1)
(c) This work; the values $D_1(N^2)$ = 49.520 MHz (taken from
Reference(3)), g_L = 1.00103, and eqQ(N) = -4.0 MHz (from
reference (1)) were constrained in the fit
(d) From Reference (3)
(e) From B_v
(f) From a_H

at least approximately cancel during the averaging over electronic coordinates. For the $v = 1$ state, however, the agreement between $\langle 1/R^2\rangle^{-1/2}$ and $\langle 1/r_H^3\rangle^{-1/3}$ is somewhat poorer, but it seems unlikely that the cancellation occurring in the electronic averaging would be altered significantly by the 2% change in bond length upon excitation to $v = 1$. Instead, it seems more plausible that the discrepancy between "R" derived from B_v and "R" derived from a_H reflects a subtle difference in the manner in which the quantities $\langle 1/R^2\rangle$ and $\langle 1/R^3\rangle$ are *vibrationally* averaged. That such an effect is of the correct magnitude may be checked by computing the quantity $\Delta \equiv \{\langle 1/R^2\rangle^{-1/2} - \langle 1/r_H^3\rangle^{-1/3}\}$ in a harmonic approximation. Following Gordy and Cook (4), we express $\langle 1/R^2\rangle$ and $\langle 1/R^3\rangle$ in terms of the expectation values $\langle \xi\rangle$ and $\langle \xi^2\rangle$, where $\xi = (R - R_e)/R_e$:

$$\langle 1/R^2\rangle = [1 - 2\langle\xi\rangle + 3\langle\xi^2\rangle + \cdots]/R_e^2$$

and

$$\langle 1/R^3\rangle = [1 - 3\langle\xi\rangle + 6\langle\xi^2\rangle + \cdots]/R_e^3.$$

Forming the quantity Δ and retaining only the first term in the series expansion for $f(x) = 1/(1 + ax)^n$ yields the simple result that

$$\Delta = (\tfrac{1}{2})R_e\sqrt{(D_e/B_e)}(v + \tfrac{1}{2})$$

where $\langle\xi\rangle$ and $\langle\xi^2\rangle$ have been replaced by their harmonic oscillator values. Substituting R_0, B_0, and D_0 for R_e, B_e, and D_e, respectively, gives $\Delta(v = 0) = 0.003$ Å and $\Delta(v = 1) = 0.008$ Å compared with the observed values of 0.007(9) and 0.014(3) Å, respectively. In view of the approximations implicit in this expression, the agreement in both sign and magnitude appears reasonable and supports a vibrational averaging effect as at least the major source of the observed discrepancy.

REFERENCES

1. K. R. LEOPOLD, K. M. EVENSON, AND J. M. BROWN, *J. Chem. Phys.* **85**, 324–330 (1986).
2. F. R. PETERSON, A. SCALABRIN, AND K. M. EVENSON, *Int. J. Infrared Millimeter Waves* **1**, 111–115 (1980).

3. J. L. HALL, H. ADAMS, J. V. V. KASPER, R. F. CURL, AND T. K. TITTEL, *J. Opt. Soc. Amer. B* **2**, 781–784 (1985).

4. W. GORDY AND R. L. COOK, "Microwave Molecular Spectra," p. 518, Wiley–Interscience, New York, 1970.

E. C. C. VASCONCELLOS

Instituto de Fisica
Departimento Eletronica Quantica
UNICAMP
13100 Campinas, SP Brasil

STEVEN A. DAVIDSON

Department of Physics
University of Colorado
Boulder, Colorado 80309

JOHN M. BROWN

Physical Chemistry Laboratory
Oxford University
South Parks Road
Oxford OX1 3QZ, England

K. R. LEOPOLD[2]
K. M. EVENSON

National Bureau of Standards
Boulder, Colorado 80303
   Received August 18, 1986

[2] National Research Council Postdoctoral Fellow.