Far infrared laser magnetic resonance detection of NH and ND (a $^1\Delta$)

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Rotational spectra of the excited a $^1\Delta$ state of NH and ND have been observed by far infrared laser magnetic resonance spectroscopy. For ND(a $^1\Delta$) the spectroscopic constants are $B_0 = 264\ 750.263(30)$ MHz, $D_0 = 14.383\ 83(91)$ MHz, $a_N = 109.63(22)$ MHz, $a_D = 11.03(23)$ MHz, $eqQ(N) = -4.0(15)$ MHz, $gr = -0.000\ 86(10)$, and $g_L = 1.000\ 506(17)$. For NH (a $^1\Delta$), the constants are $B_0 = 493\ 043.182(95)$ MHz, $D_0 = 50.453$ MHz (constrained in fit), $a_N = 109.65(85)$ MHz, $a_H = 70.9(14)$ MHz, $eqQ(N) = -4.0$ MHz (constrained in fit), $g_r = -0.001\ 58(6)$, and $g_L = 1.001\ 03$ (constrained in fit). Aspects of the electronic structure of the radical as revealed by the magnetic hyperfine constants are discussed in relation to those of chemically similar systems. The Zeeman parameters are interpreted in terms of mixing of the a $^1\Delta$ state with the c $^1\Pi$ state.

INTRODUCTION

The imidogen radical, NH, has been the subject of numerous investigations from a wide variety of perspectives. VUV photolysis of NH_3 has been shown to produce NH in its excited $^3\Pi$ state via a two photon process,[1,2] while photolysis of HN_3[3–6] and $HNCO$[7] produces NH in its excited a $^1\Delta$ state. The ensuing chemistry of the radical in these states, as well as in the ground $^3\Sigma^-$ and excited b $^1\Sigma^+$ state has been the subject of detailed experimental and theoretical study, both with and without the addition of chemical and electronic quenchers.[8–10] Numerous *ab initio* studies[11] of varying scope and accuracy have been performed with the intention of testing computational methods, as well as computing properties of NH per se. NH has been observed in a variety of astrophysical sources including stars[12,13] and comets.[14]

The optical spectrum of NH has been studied over a period of decades. In addition to numerous studies of the c $^1\Pi$–a $^1\Delta$ transition, the d $^1\Sigma^+$–c $^1\Pi$, d $^1\Sigma^+$–b $^1\Sigma^+$ and A $^3\Pi$–X $^3\Sigma^-$ transitions have also been well characterized.[15] The singlet–triplet energy separation remained unknown, however, until the observation of the spin-forbidden b $^1\Sigma^+$–X $^3\Sigma^-$ transition,[16,17] and the value determined (1.56 eV) was later confirmed by negative ion photoelectron spectroscopy.[18] Despite the long radiative lifetime of the metastable a $^1\Delta$ state, however, its high chemical reactivity precluded the observation of its emission to the ground state for a long time, and only recently has the a–X transition been observed in an inert gas matrix[19] and at low resolution in the gas phase.[20]

A number of modern high resolution spectroscopic techniques have been applied to the study of NH in the gas phase. Wayne and Radford[21] have studied pure rotation spectra of the X $^3\Sigma^-$ state of NH ($v = 0,1$), ND ($v = 0,1$), and ^{15}NH ($v = 0$) using the technique of far infrared laser magnetic resonance spectroscopy. The vibrational fundamental of ground state NH has been observed using a difference frequency laser system,[22] while that of the a $^1\Delta$ state has

been studied by color center laser spectroscopy.[23] Emission work on the c $^1\Pi$–a $^1\Delta$ system,[24] and most recently molecular beam LIF studies of the A $^3\Pi$–X $^3\Sigma^-$[25] and c $^1\Pi$–a $^1\Delta$ systems[26] have reexamined these transitions at high resolution. Here, we report a study of pure rotational spectra of NH and ND in the lowest excited (a $^1\Delta$) state using the far infrared laser magnetic resonance technique.

In addition to the rotational and distortion constants, we have determined the magnetic hyperfine constants for the ^{14}N, H, and D nuclei, as well as the rotational and orbital g factors for the radical. The magnetic hyperfine parameters provide detailed information about the radial distribution of orbitally degenerate electrons and the g factor can be interpreted in terms of the mixing of the $^1\Delta$ state with the c $^1\Pi$ state. Thus, the study of this species by far infrared laser magnetic resonance has provided a particularly detailed description of the electronic structure of this excited state of the NH radical.

EXPERIMENTAL

The optically pumped far infrared LMR spectrometer used in the present work has been described in detail elsewhere.[27] Second derivative ($2f$) detection was used in order to eliminate base line drifts which were found to be problematic during broad survey scans. Particular care was necessary in order to operate the laser at 102 μm for the measurement of the $J = 3 \leftarrow 2$ transition of NH. Since this lasing line was found to be quite weak, careful attention to laser alignment, as well as a reduction of the normally 25 μm thick polypropylene beam splitter to 8 μm was necessary for successful operation.

NH and ND ($^1\Delta$) radicals were produced by reaction of fluorine atoms (produced in a 2450 MHz discharge of F_2 in He) with ammonia. The optimum conditions for observation of NH in the $^1\Delta$ state were the same as those for its observation in the X $^3\Sigma^-$ state and corresponded to the maximum orange color of the flame. Typical flame conditions were 0.3% F_2 and 0.3% NH_3 or ND_3, at a total pressure of 40–140 Pa of He (300–1000 mTorr).

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Initial spectral searches for NH ($^1\Delta$) were aided by the spectroscopic constants from classical optical work.[15] These, together with the characteristic hyperfine pattern for ^{14}NH and the characteristic Zeeman pattern for a $^1\Delta$ state enabled the observed spectra to be positively identified as being due to the desired species in the $v = 0$ level.[28] Only the $J = 3 \leftarrow 2$ transition of NH was studied because of a lack of known short wavelength far infrared lasing lines sufficiently near to any other transition of this species.

In a similar manner, the $J = 3 \leftarrow 2$ transition of ND ($^1\Delta$) was readily observed using isotopically substituted ammonia. In this case, the lowest rotational transition occurs at a frequency which allows it to be observed on two distinct far infrared lasing lines (187.8 and 189.7 μm). In addition, the $J = 5 \leftarrow 4$ transition was readily observed using the 113.7 μm line of CH_3OH. All the ND($^1\Delta$) spectra showed well developed saturated absorption features (Lamb dips) which permit a more accurate determination of line position. In the case of the $J = 5 \leftarrow 4$ transition, for which the LMR lines are intrinsically broader, these features were essential to the resolution of the deuterium hyperfine structure.

RESULTS AND ANALYSIS

A summary of the rotational transitions observed and far infrared lasing lines used is given in Table I. Figure 1 shows a single Zeeman component ($M_J = 1 \leftarrow 2$) of the $J = 3 \leftarrow 2$ transition of NH and clearly displays the magnetic hyperfine structure due to the ^{14}N($I = 1$) and H($I = 1/2$) nuclei. Figure 2 shows the deuterium hyperfine structure and saturated absorption features in a single nitrogen spin component ($M_I^N = -1$) of the $J, M_J = 3, -2 \leftarrow 2, -2$ transition of ND ($^1\Delta$). Tables II and III give the observed resonance positions for NH and ND, respectively.

The data have been analyzed using the usual Hamiltonian for a molecule in a $^1\Delta$ state,[29] viz.

$$H = H_{\text{rot}} + H_{\text{hf}} + H_z, \tag{1}$$

$$H_{\text{rot}} = B_0 N^2 - D_0 N^4 + H_0 N^6, \tag{2}$$

$$H_{\text{hf}} = a_N L_z I_z^N + a_{\text{H(D)}} L_z I_z^{\text{H(D)}}$$
$$+ eqQ(N)[3I_z^2 - I^2]/4I(2I - 1), \tag{3}$$

$$H_z = g_L \mu_B \mathbf{B} \cdot \mathbf{L} - g_r \mu_B \mathbf{B} \cdot (\mathbf{J} - \mathbf{L}), \tag{4}$$

where H_{rot}, H_{hf}, and H_z are the rotational, hyperfine, and Zeeman Hamiltonians, respectively, $\mathbf{B}$ is the magnetic field strength, and the other symbols used have their usual meanings. The matrix representation of H, Eqs. (1)–(4), was set up in a nuclear spin decoupled basis, using the matrix elements given in Ref. 29. Since the data for the deuterated species are more abundant, they were the first to be analyzed. The observation of a set of Zeeman components for a single rotational transition allows, in effect, the determina-
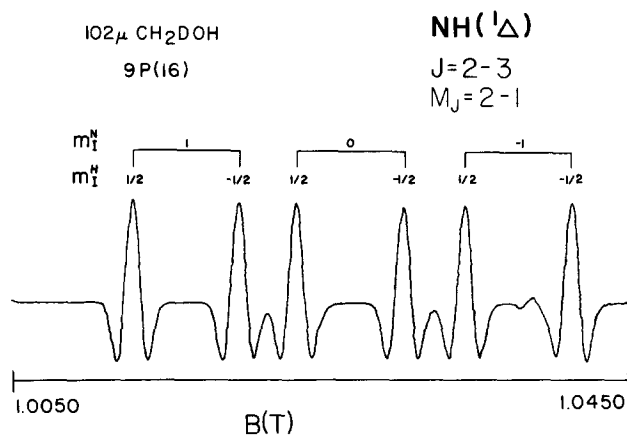
tion of two quantities, a zero-field frequency and a linear combination of g_r and g_L. The observation of two such sets therefore permits, in addition to the determination of B_0 and D_0, a separate determination of g_r and g_L. The observed splittings independently determine the magnetic hyperfine constants, a_N and a_D, while the small asymmetry in the hyperfine multiplets provide a rather poorly determined but statistically significant value for the nuclear electric quadrupole coupling constant of the nitrogen, $eqQ(N)$. Thus, a least squares fit to the ND data, with B_0, D_0, a_N, a_D, g_r, g_L, and $eqQ(N)$ as adjustable parameters, was performed and yielded a satisfactory fit to the observed spectrum. Since the magnetic field measurements are expected to have the quoted accuracy only below 1.7 T, the 1.9 T transitions observed at 187.8 μm were omitted from the fit. The parameters determined are listed in Table IV, and the residuals are given in the last column of Table III. For the purpose of future comparisons, the zero-field frequency of the lowest rotational transition is also tabulated.

Since only a single rotational transition was observed for NH ($^1\Delta$), the data were insufficient to determine all the parameters given in Eqs. (2)–(4). Hence, D_0 was taken from vibrational work[23] and $eqQ(N)$ was constrained to the value obtained from the fit to the ND data. The value of $\Delta g_L = g_L - 0.9999$ (the deviation of g_L from the relativistically cor-

FIG. 1. The $J = 3 \leftarrow 2$, $M_J = 1 \leftarrow 2$ transition of NH($^1\Delta$). The signals were detected at twice the modulation frequency, producing a second derivative line shape.
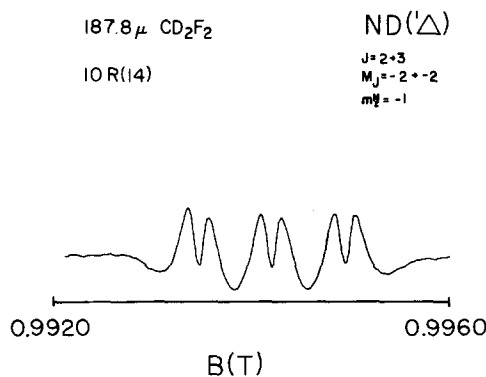
FIG. 2. A deuteron hyperfine triplet of ND($^1\Delta$) clearly showing saturated absorption features.

TABLE I. Summary of observed transitions of NH and ND ($a\ ^1\Delta$).

Species	Transition	$\lambda(\mu m)$	ν(MHz)	Lasing gas	Pump line
NH	$J = 3 \leftarrow 2$	102.2	2938 465.1	CH_2DOH	$9P(16)$
ND	$J = 3 \leftarrow 2$	189.8	1579 250.3	CD_2F_2	$10R(34)$
	$J = 3 \leftarrow 2$	187.8	1596 174.9	CD_2F_2	$10R(14)$
	$J = 5 \leftarrow 4$	113.7	2635 958.0	CH_3OH	$9R(8)$

TABLE II. Observed transitions of NH ($a\ ^1\Delta$) at 102.2 μm.

B(T)[a]	J''	M_J''	$M_I(N)''$	$M_I(H)''$	$-\ J'$	M_J'	$M_I(N)'$	$M_I(H)'$	$(\nu_L - \nu_{calc})$ (MHz)
σ polarization									
1.015 14	2	2	1	$+1/2$	3	1	1	$+1/2$	-2.4
1.020 18	2	2	1	$-1/2$	3	1	1	$-1/2$	-3.1
1.022 98	2	2	0	$+1/2$	3	1	0	$+1/2$	-1.9
1.027 99	2	2	0	$-1/2$	3	1	0	$-1/2$	-3.0
1.030 87	2	2	-1	$+1/2$	3	1	-1	$+1/2$	-3.3
1.035 99	2	2	-1	$-1/2$	3	1	-1	$-1/2$	-2.8
1.533 72	2	1	1	$+1/2$	3	0	1	$+1/2$	2.5
1.538 77	2	1	1	$-1/2$	3	0	1	$-1/2$	2.4
1.541 42	2	1	0	$+1/2$	3	0	0	$+1/2$	0.9
1.546 56	2	1	0	$-1/2$	3	0	0	$-1/2$	1.7
1.549 29	2	1	-1	$+1/2$	3	0	-1	$+1/2$	1.5
1.554 41	2	1	-1	$-1/2$	3	0	-1	$-1/2$	2.0
π polarization									
1.532 07	2	2	1	$+1/2$	3	2	1	$+1/2$	0.4
1.537 17	2	2	1	$-1/2$	3	2	1	-1.2	0.5
1.539 88	2	2	0	$+1/2$	3	2	0	$+1/2$	0.8
1.544 90	2	2	0	$-1/2$	3	2	0	$-1/2$	0.2
1.547 99	2	2	-1	$+1/2$	3	2	-1	$+1/2$	1.9
1.553 06	2	2	-1	$-1/2$	3	2	-1	$-1/2$	1.8

[a] Magnetic field measurements have an estimated absolute accuracy of one part in 10^4.

TABLE III. Observed spectra of ND ($a\ ^1\Delta$).

B(T)[a]	J''	M_J''	$M_I(N)''$	$M_I(D)''$	$-\ J'$	M_J'	$M_I(N)'$	$M_I(D)'$	$(\nu_L - \nu_{calc})$ (MHz)
189.8 μm									
σ polarization									
0.541 70	2	2	1	1	3	1	1	1	-0.7
0.542.48	2	2	1	0	3	1	1	0	-0.9
0.543 27	2	2	1	-1	3	1	1	-1	-0.9
0.549 53	2	2	0	1	3	1	0	1	-2.3
0.550 30	2	2	0	0	3	1	0	0	-1.1
0.551 07	2	2	0	-1	3	1	0	-1	-1.5
0.557 56	2	2	-1	1	3	1	-1	1	-1.6
0.558 34	2	2	-1	0	3	1	-1	0	-1.7
0.559 12	2	2	-1	-1	3	1	-1	-1	-1.8
0.820 34	2	1	1	1	3	0	1	1	1.2
0.821 12	2	1	1	0	3	0	1	0	1.2
0.821 89	2	1	1	-1	3	0	1	-1	1.0
0.828 06	2	1	0	1	3	0	0	1	-0.2
0.828 83	2	1	0	0	3	0	0	0	-0.4
0.829 60	2	1	0	-1	3	0	0	-1	-0.5
0.835 98	2	1	-1	1	3	0	-1	1	0.5
0.836 75	2	1	-1	0	3	0	-1	0	0.3
0.837 53	2	1	-1	-1	3	0	-1	-1	0.2
1.651 58	2	2	1	1	3	3	1	1	0.6
1.652 37	2	2	1	0	3	3	1	0	0.6
1.653 13	2	2	1	-1	3	3	1	-1	0.4
1.659 20	2	2	0	1	3	3	0	1	0.5
1.660 00	2	2	0	0	3	3	0	0	0.5
1.660 76	2	2	0	-1	3	3	0	-1	0.4
1.667 16	2	2	-1	1	3	3	-1	1	0.1
1.667 96	2	2	-1	0	3	3	-1	0	0.2
1.668 73	2	2	-1	-1	3	3	-1	-1	0.1
1.678 49	2	0	1	1	3	-1	1	1	0.1
1.679 26	2	0	1	0	3	-1	1	0	0.0
1.680 05	2	0	1	-1	3	-1	1	-1	0.0
1.686 51	2	0	0	1	3	-1	0	1	0.3
1.687 28	2	0	0	0	3	-1	0	0	0.2
1.688 04	2	0	0	-1	3	-1	0	-1	0.1
1.694 25	2	0	-1	1	3	-1	-1	1	0.8
1.695 01	2	0	-1	0	3	-1	-1	0	0.7
1.695 80	2	0	-1	-1	3	-1	-1	-1	0.7

TABLE III. (*continued*).

$B(T)^a$	J''	M_J''	$M_I(N)''$	$M_I(D)''$	$-J'$	M_J'	$M_I(N)'$	$M_I(D)'$	$(\nu_L - \nu_{calc})$(MHz)
π polarization									
0.818 41	2	2	1	1	3	2	1	1	-1.2
0.819 19	2	2	1	0	3	2	1	0	-1.2
0.819 96	2	2	1	-1	3	2	1	-1	-1.4
0.826 36	2	2	0	1	3	2	0	1	0.4
0.827 13	2	2	0	0	3	2	0	0	0.2
0.827 91	2	2	0	-1	3	2	0	-1	0.1
0.834 34	2	2	-1	1	3	2	-1	1	-0.2
0.835 12	2	2	-1	0	3	2	-1	0	-0.2
0.835 90	2	2	-1	-1	3	2	-1	-1	-0.3
1.678 66	2	1	1	1	3	1	1	1	0.9
1.679 43	2	1	1	0	3	1	1	0	0.8
1.680 21	2	1	1	-1	3	1	1	-1	0.8
1.686 65	2	1	0	1	3	1	0	1	1.1
1.687 43	2	1	0	0	3	1	0	0	1.1
1.688 21	2	1	0	-1	3	1	0	-1	1.0
1.694 28	2	1	-1	1	3	1	-1	1	0.5
1.695 04	2	1	-1	0	3	1	-1	0	0.4
1.695 82	2	1	-1	-1	3	1	-1	-1	0.4
187.8 μm									
σ polarization									
0.649 17	2	-2	1	1	3	-1	1	1	0.2
0.649 93	2	-2	1	0	3	-1	1	0	0.6
0.650 71	2	-2	1	-1	3	-1	1	-1	0.7
0.664 63	2	-2	-1	1	3	-1	-1	1	0.0
0.665 40	2	-2	-1	0	3	-1	-1	0	0.3
0.666 18	2	-2	-1	-1	3	-1	-1	-1	0.4
0.972 88	2	-1	1	1	3	0	1	1	-0.5
0.973 65	2	-1	1	0	3	0	1	0	-0.4
0.974 43	2	-1	1	-1	3	0	1	-1	-0.3
0.980 51	2	-1	0	1	3	0	0	1	0.4
0.981 28	2	-1	0	0	3	0	0	0	0.5
0.982 05	2	-1	0	-1	3	0	0	-1	0.7
0.988 46	2	-1	-1	1	3	0	-1	1	-0.4
0.989 23	2	-1	-1	0	3	0	-1	0	-0.3
0.990 00	2	-1	-1	-1	3	0	-1	-1	-0.1
1.912 39	2	0	1	1	3	1	1	1	4.0
1.913 18	2	0	1	0	3	1	1	0	4.0
1.913 95	2	0	1	-1	3	1	1	-1	4.0
1.920 07	2	0	0	1	3	1	0	1	4.2
1.920 86	2	0	0	0	3	1	0	0	4.2
1.921 62	2	0	0	-1	3	1	0	-1	4.1
1.928 16	2	0	-1	1	3	1	-1	1	4.5
1.928 95	2	0	-1	0	3	1	-1	0	4.5
1.929 71	2	0	-1	-1	3	1	-1	-1	4.2
1.968 95	2	-2	1	1	3	-3	1	1	4.9
1.969 75	2	-2	1	0	3	-3	1	0	4.9
1.970 53	2	-2	1	-1	3	-3	1	-1	4.9
1.977 10	2	-2	0	1	3	-3	0	1	5.3
1.977 88	2	-2	0	0	3	-3	0	0	5.3
1.978 66	2	-2	0	-1	3	-3	0	-1	5.2
π polarization									
0.977 87	2	-2	1	1	3	-2	1	1	0.3
0.978 65	2	-2	1	0	3	-2	1	0	0.3
0.979 42	2	-2	1	-1	3	-2	1	-1	0.5
0.985 76	2	-2	0	1	3	-2	0	1	-0.2
0.986 55	2	-2	0	0	3	-2	0	0	-0.3
0.987 32	2	-2	0	-1	3	-2	0	-1	-0.1
0.993 54	2	-2	-1	1	3	-2	-1	1	-0.9
0.994 31	2	-2	-1	0	3	-2	-1	0	-0.7
0.995 09	2	-2	-1	-1	3	-2	-1	-1	-0.6
1.923 81	2	-1	1	1	3	-1	1	1	4.9
1.924 61	2	-1	1	0	3	-1	1	0	4.9
1.925 38	2	-1	1	-1	3	-1	1	-1	4.8
1.931 35	2	-1	0	1	3	-1	0	1	4.0
1.932 13	2	-1	0	0	3	-1	0	0	3.9
1.932 90	2	-1	0	-1	3	-1	0	-1	3.9
1.939 34	2	-1	-1	1	3	-1	-1	1	4.4

TABLE III. (*continued*).

$B(T)^a$	J''	M_J''	$M_I(N)''$	$M_I(D)''$	$-J'$	M_J'	$M_I(N)'$	$M_I(D)'$	$(\nu_L - \nu_{calc})(MHz)$
1.940 12	2	−1	−1	0	3	−1	−1	0	4.3
1.940 90	2	−1	−1	−1	3	−1	−1	−1	4.3

113.7 μm

σ polarization

$B(T)^a$	J''	M_J''	$M_I(N)''$	$M_I(D)''$	$-J'$	M_J'	$M_I(N)'$	$M_I(D)'$	$(\nu_L - \nu_{calc})(MHz)$
0.770 12	4	4	1	1	5	3	1	1	− 0.3
0.771 01	4	4	1	0	5	3	1	0	0.2
0.771 90	4	4	1	−1	5	3	1	−1	0.8
0.778 15	4	4	0	1	5	3	0	1	− 0.6
0.779 00	4	4	0	0	5	3	0	0	− 0.2
0.779 89	4	4	0	−1	5	3	0	−1	0.3
0.786 13	4	4	−1	1	5	3	−1	1	− 0.5
0.786 96	4	4	−1	0	5	3	−1	0	− 0.3
0.787 83	4	4	−1	−1	5	3	−1	−1	0.2
0.925 04	4	3	1	1	5	2	1	1	− 1.4
0.925 91	4	3	1	0	5	2	1	0	− 1.0
0.926 77	4	3	1	−1	5	2	1	−1	− 0.6
0.933 43	4	3	0	1	5	2	0	1	0.5
0.934 19	4	3	0	0	5	2	0	0	0.4
0.935 03	4	3	0	−1	5	2	0	−1	0.6
0.941 30	4	3	−1	1	5	2	−1	1	0.4
0.942 10	4	3	−1	0	5	2	−1	0	0.5
0.942 95	4	3	−1	−1	5	2	−1	−1	0.8
1.157 70	4	2	1	1	5	1	1	1	0.7
1.158 50	4	2	1	0	5	1	1	0	0.8
1.159 28	4	2	1	−1	5	1	1	−1	0.8
1.165 61	4	2	0	1	5	1	0	1	0.7
1.166 45	4	2	0	0	5	1	0	0	0.9
1.167 24	4	2	0	−1	5	1	0	−1	0.9

π polarization

$B(T)^a$	J''	M_J''	$M_I(N)''$	$M_I(D)''$	$-J'$	M_J'	$M_I(N)'$	$M_I(D)'$	$(\nu_L - \nu_{calc})(MHz)$
1.164 13	4	4	1	1	5	4	1	1	− 0.3
1.164 93	4	4	1	0	5	4	1	0	− 0.3
1.165 71	4	4	1	−1	5	4	1	−1	− 0.3
1.172 07	4	4	0	1	5	4	0	1	− 0.4
1.172 84	4	4	0	0	5	4	0	0	− 0.5
1.173 67	4	4	0	−1	5	4	0	−1	− 0.4
1.179 92	4	4	−1	1	5	4	−1	1	− 0.7
1.180 73	4	4	−1	0	5	4	−1	0	− 0.6
1.181 51	4	4	−1	−1	5	4	−1	−1	− 0.7
1.555 20	4	3	1	1	5	3	1	1	0.0
1.555 96	4	3	1	0	5	3	1	0	0.0
1.556 74	4	3	1	−1	5	3	1	−1	− 0.1
1.563 06	4	3	0	1	5	3	0	1	− 0.2
1.563 84	4	3	0	0	5	3	0	0	− 0.2
1.564 63	4	3	0	−1	5	3	0	−1	− 0.2
1.571 03	4	3	−1	1	5	3	−1	1	0.1
1.571 80	4	3	−1	0	5	3	−1	0	0.1
1.572 60	4	3	−1	−1	5	3	−1	−1	0.1

^{a} Magnetic field measurements have an estimated absolute accuracy of one part in 10^4 below 1.7 T. Transitions observed above 1.7 T were omitted from the fit due to uncertain calibration of the magnetic field.

rected free electron value) was appropriately scaled[30] from the measured ND ($^1\Delta$) value and was also held fixed in the fit. The resulting constants, which similarly produced a satisfactory fit to the observed spectrum, are also given in Table IV.

DISCUSSION

Table IV also compares the spectroscopic constants obtained here with those determined from previous work. For comparison of the NH constants, those of Ubachs *et al.*[26] have been chosen, since they are the most accurate reported, and since that work appears to contain the only other measurement of the hyperfine constants for this species. For ease

of comparison, the rotational and centrifugal distortion constants, B_0 and D_0, of Ref. 26 have been converted from the $\mathbf{R}^2$ formulation to the $\mathbf{N}^2$ formulation adopted here by use of Eq. (2). The ND constants have been compared with those of Hanson *et al.*[31] which are already given in the $\mathbf{N}^2$ formalism.

Where comparison is possible, it may be seen from the table that agreement for the magnetic and electric quadrupole hyperfine constants is within the estimated uncertainties. The rotational constants, however, differ by more than the experimental uncertainties. For NH, the quoted uncertainty in the value of B_0 is one standard deviation in a fit in which the value of D_0 was constrained to that determined by the vibrational work of Ref. 23. Since that value is, in fact,

TABLE IV. Spectroscopic constants of NH and ND ($a\,^1\Delta$).[a]

Constant	This work[b]	Reference 26[c]	This work	Reference 31
$\nu_0(J = 3\leftarrow 2)$	2952 816.7(6)	2952 715(45)	1586 949.1(4)	1587 241(36)
B_0	493 043.182(95)	493 017.8(60)	264 750.263(30)	264 801(6)
D_0	50.45(11)[c,d]	49.968(78)	14.383 83(91)	14.504(2)
a_N	109.65(85)	110.0(5)	109.63(22)	...
$a_{H(D)}$	70.9(14)	69.6(12)	11.03(23)	...
$eqQ(N)$	-4.0^e	$-8.0(26)$	$-4.0(15)$	...
g_r	$-0.001\,58(6)$	...	$-0.008\,6(10)$	...
g_L	1.001 03[f]	...	1.000 506(17)	...

[a] All values (except g factors) in MHz.
[b] Quoted errors are one standard deviation in the fit.
[c] Values have been converted from the $\mathbf{R}^2$ to the $\mathbf{N}^2$ formalism using the relations
$B(\mathbf{N})^2 = B(\mathbf{R}^2) + 8D(\mathbf{R}^2) + 48H(\mathbf{R}^2)$ and $D(\mathbf{N}^2) = D(\mathbf{R}^2) + 12H(\mathbf{R}^2)$.
[d] Constrained to value of Ref. 23.
[e] Constrained to value determined from fit of the ND data.
[f] Computed from measured value for ND and constrained in the fit.

uncertain by as much as 0.1 MHz, and since the zero-field frequency (ignoring H_0) is $6B_0$–$108D_0$, the *absolute* uncertainty in B_0 may actually be as much as 2 MHz. This, however, is not enough to account for the observed discrepancy. Nonetheless since the Zeeman extrapolation of the LMR data gives $\nu(J = 3\leftarrow 2)$ independently of the relative contributions from the B_0 and D_0 terms, the zero-field frequency is a more appropriate quantity to compare with that computed from the optical work. It may be seen from Table IV, however, that the values of the $J = 3\leftarrow 2$ transition computed from the optical constants and that computed from the constants given here still differ by an amount larger that the estimated uncertainties. The same conclusion may be drawn using the spectroscopic constants determined from the optical work of Ramsay and Sarre.[24] Interestingly, however, the value computed from the constants of Hall *et al.*[23] is 2952 823(64) MHz, which, despite the rather large uncertainty, would appear to be closer to our value. This result would imply a slight but detectable contamination of the optically determined constants by those for the upper ($c\,^1\Pi$) state. Similar discrepancies between the optical work of Hanson *et al.*[31] and the rotational work presented here may be seen for ND($^1\Delta$).

Values of $\langle 1/r^3 \rangle$ derived from the magnetic hyperfine constants have been computed using the relation

TABLE V. Comparison of $\langle r^{-3} \rangle$ for related systems.[a]

	$\langle r_{N,P}^{-3} \rangle_o$	$\langle r_{N,P}^{-3} \rangle_s$	$\langle r_H^{-3} \rangle_o$
$N(^2D)$[b]	20.21(2)	22.22(2)	...
$NH(^3\Sigma)$[c]	...	20.1(9)	...
$NH(^1\Delta)$[d]	19.3(2)	...	0.89
$NF(^1\Delta)$[e]	19.29(2)	...	...
$PH(^3\Sigma)$[f]	...	23.7(19)	...
$PH(^1\Delta)$[f]	24.0(11)	...	0.35
$PF(^3\Sigma)$[g]	...	26.180(5)	...

[a] All values in Å^{-3}; subscripts o and s denote orbital and spin averages, respectively.
[b] Reference 32.
[c] Reference 21.
[d] This work.
[e] Reference 29.
[f] Reference 33(a).
[g] Reference 33(b).

$$a_i\,(in\,J) = \frac{2\mu_0 \mu_N g_I}{4\pi\epsilon_0 c^2}\,\langle 1/r^3 \rangle, \qquad (5)$$

where μ_0 and μ_N are the Bohr and nuclear magnetons, respectively, g_I is the g factor for the nucleus under consideration, and r is the distance between the nucleus and the electron carrying the angular momentum. The results are presented in Table V and are compared with those of a number of related systems. For the nitrogen or phosphorus atoms, both spin and orbital averages have been tabulated and are denoted by the subscripts "s" and "o" respectively. Values of the spin average for the $^3\Sigma$ states have been calculated assuming the p-orbital angular expectation value $\langle 3\cos^2\theta - 1 \rangle_o = \langle 3\cos^2\theta - 1 \rangle_s = -2/5$. This approximation appears justified for NH ($X\,^3\Sigma$) and PH ($X\,^3\Sigma$) on the basis of a comparison of the experimental hyperfine constants for the $^1\Delta$ and $^3\Sigma$ states. Specifically, examination of the constants a_N determined for the $^1\Delta$ states and β_N (the electron spin-nuclear spin dipole–dipole interaction parameter determined for the $^3\Sigma$ states) reveals that the ratio $2\beta_N/a_N = \langle (3\cos^2\theta - 1)/r^3 \rangle_s /\langle 1/r^3 \rangle_o$. If the distinction between the spin and orbital averaging may be ignored, this ratio is $-2/5$ for a pure p orbital. Using the hyperfine data from Refs. 21 and 33 as well as that from this work, this ratio is computed to be $-0.416(22)$ for the N atom in NH, and $-0.396(51)$ for the P atom of PH. Thus, to within the experimental uncertainties, the electrons carrying the angular momentum appear to be in p-type orbitals, and the above approximation should provide reasonable estimates of $\langle 1/r^3 \rangle$. Values of $\langle 1/r^3 \rangle$ are not given for the H nuclei of the $^3\Sigma$ states since the approximation is not expected to be valid in this case.

It is readily seen from Table V that the values of $\langle 1/r^3 \rangle$ for the nitrogen atom of $^1\Delta$ and $^3\Sigma$ NH as well as $^1\Delta$ NF are very nearly equal and that the values are comparable to but somewhat smaller than the corresponding averages determined for $N(^2D)$. The small but significant differences among these numbers are undoubtedly subtle effects of core polarization and configuration interaction and are, of course, difficult to interpret at a simplistic level. The general constancy, however, amounts to an experimental quantifica-

tion of chemical intuition that the angular momentum carrying electrons are p-type (nonbonding) orbitals on the nitrogen. A similar argument may be made for the phosphorus systems listed. Although the increase in $\langle 1/r^3 \rangle$ upon going from the nitrogen to the phophorus systems may at first seem surprising it must be recognized that intuition based on $\langle r \rangle$ is not expected to be reliable for $\langle 1/r^3 \rangle$. Indeed the increase in $\langle 1/r^3 \rangle$ going down a group in the Periodic Table is well known for free atoms,[34] and it is at least gratifying to see that the results for the hydrides parallel this trend. Finally, we note that the values of $\langle 1/r^3 \rangle^{-1/3}$ for the hydrogen atom in NH and PH ($^1\Delta$) are 1.039 and 1.419 Å, respectively, which are quite close to the bond lengths for these species (1.045 Å for NH and 1.431 Å for PH). For the proton, the values of $\langle 1/r^3 \rangle$ are more intuitive since r_H is relatively insensitive to the radial electron distribution about the phosphorus or nitrogen atom.

The Zeeman parameters of the radical may also be interpreted in a satisfying way. For both isotopic species, a value of g_r has been determined, and it may be seen from Table IV that g_r scales properly with inverse reduced mass for the two isotopes. Using the standard expression[30] for g_r^N, the nuclear contribution to g_r, the value of the electronic contribution, g_r^e may be computed from the experimental g_r, viz. $g_r^e = g_r^N - g_r$, and gives the result $g_r^e = 0.001\ 13(10)$ for ND ($^1\Delta$). The absolute magnitude of this number may be interpreted in terms of the electronic structure of the system by reduction of Eq. (12) of Ref. 35 using atomic matrix elements of the angular momentum operators (i.e., pure precession) and assuming that only the $c\ ^1\Pi$ state contributes appreciably. The resulting expression

$$g_r^e = \frac{4B_0(g_L + g_r^N)}{E_\Pi - E_\Delta} \qquad (6)$$

yields $g_r^e = 0.001\ 13$ when the energy separation $E_\Pi - E_\Delta = 31\ 190\ \text{cm}^{-1}$ is taken from Ref. 15. The agreement with experiment is clearly remarkable. Thus, the value of g_r^e and hence g_r may be interpreted entirely in terms of mixing of the $a\ ^1\Delta$ state with the $c\ ^1\Pi$ state. Under this condition, moreover, the value of $\Delta g_L = g_L - 0.9999$ will be given theoretically[35] by $\Delta g_L = g_r^e/2$, and hence is expected to be 0.000 57 for ND ($^1\Delta$). The experimental value, 0.000 61, is seen to agree well with this prediction.

Finally, we consider the possible astrophysical significance of the accurate spectroscopic constants now available for NH ($^1\Delta$). Although VUV photolysis of NH_3 produces NH in the $^3\Pi$ state, the singlet manifold is known to be excited in electric discharges.[31,36] Yet, due to the doubly forbidden nature of the $a\ ^1\Delta - X\ ^3\Sigma$ transition and the reactive nature of the $^1\Delta$ state, it does not seem likely that astrophysical NH ($^1\Delta$), if formed by electron or particle collisions, would be detectable by emission. The observation of the pure rotational spectrum, however, provides electric dipole allowed transitions which might be used to monitor the molecule in this state.

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