Fourier Transform Infrared Emission Spectroscopy of ND and PH

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The infrared vibration–rotation bands of ND in the $X^3\Sigma^-$ state were recorded using a Fourier transform spectrometer. The bands were observed in a microwave discharge of a mixture of N_2 and D_2 in the presence of He. The rotational structure of six bands, 1–0, 2–1, 3–2, 4–3, 5–4, and 6–5, has been observed in the $1800–2600$ cm^{-1} region. The analysis of these bands provides an independent determination of the ground state vibrational constants in addition to an improved set of rotational constants. The principal molecular constants for the ground state are

$$\omega_e = 2399.1255(299)\ cm^{-1}, \quad \omega_e x_e = 42.1064(212)\ cm^{-1}, \quad \omega_e y_e = 0.1203(54)\ cm^{-1}$$

$$B_e = 8.908665(146)\ cm^{-1}, \quad \alpha_e = 0.254570(192)\ cm^{-1}, \quad r_e = 1.036651(9)\ \text{Å}.$$

The molecular constants for PH have also been refined by combining the previous infrared [*J. Mol. Spectrosc.* **122,** 275–281 (1987)] and the recent submillimeter-wave [*Chem. Phys. Lett.* **211,** 443–448 (1993)] measurements. © 1996 Academic Press, Inc.

INTRODUCTION

NH is one of the most studied free radicals because of its importance in astrophysics (*1–9*), atmospheric sciences (*10*), and chemistry (*11–18*). NH has been observed in the spectra of sun (*1, 2*), cool stars (*3–6*), interstellar medium (*7*), and comets (*8, 9*) and has tentatively been identified in the earth's atmosphere (*10*). This radical is frequently observed in flames (*11–14*) and is readily made by photodissociation or electron impact (*15–18*). The laboratory spectra of NH date from 1893, when Eder (*19*) initially observed the $A^3\Pi–X^3\Sigma^-$ transition near 3360 Å. Since then there have been many investigations of this radical from the submillimeter to the vacuum ultraviolet regions of the spectrum. Most of the previous work on NH has been summarized in our previous papers (*20, 21*).

There have been numerous recent theoretical calculations of the properties of NH including the dissociation energy (*22*), dipole moments (*23*), radiative properties, and the rates of predissociation (*17, 18, 23–26*). Most of the recent experiments on NH and ND have concentrated on the laser spectroscopy of highly excited Rydberg states (*27–31*).

In spite of so much interest in NH, only limited spectroscopic data are available for the ND molecule. This molecule has previously been studied by Shimauchi (*32, 33*) and Kopp and co-workers (*34, 35*). These authors measured the 0–0,

1–1, and 2–2 bands of the $A^3\Pi–X^3\Sigma^-$ transition at grating resolution, but the analysis of these bands does not provide the sufficient data to determine the equilibrium vibrational constants. Recently, Patel-Misra *et al.* (*36*) observed the spectrum of this molecule in the $\Delta v = +1$ sequence of the $A^3\Pi–X^3\Sigma^-$ transition using a molecular beam source. They measured the lines in the 1–0, 2–1, and 3–2 bands of this transition with a precision of ± 0.3 cm^{-1}. They combined these measurements with the previous data on the 0–0, 1–1, and 2–2 bands (*32–35*) and reported the equilibrium vibrational and rotational constants for ND. These constants have relatively large uncertainty because of limited resolution.

The high-resolution vibration–rotation spectra of the ground state of NH have been measured by Boudjaadar *et al.* (*37*) and Chackerian *et al.* (*38*), and the far-infrared laser magnetic resonance spectra of the $a^1\Delta$ state of NH and ND have been studied by Leopold *et al.* (*39*). In the most recent work on ND, Saito and Goto (*40*) have observed the submillimeter-wave spectrum and reported precise rotational constants including the hyperfine parameters for the $v = 0$ vibrational level of the $X^3\Sigma^-$ state.

In the present work, we report the observation of six vibration–rotation bands of ND at 0.01 cm^{-1} resolution using a Fourier transform spectrometer. From the analysis of these bands, we have characterized the first seven vibrational levels of the ground $X^3\Sigma^-$ state. The present results provide a significant improvement in the molecular constants of ND.

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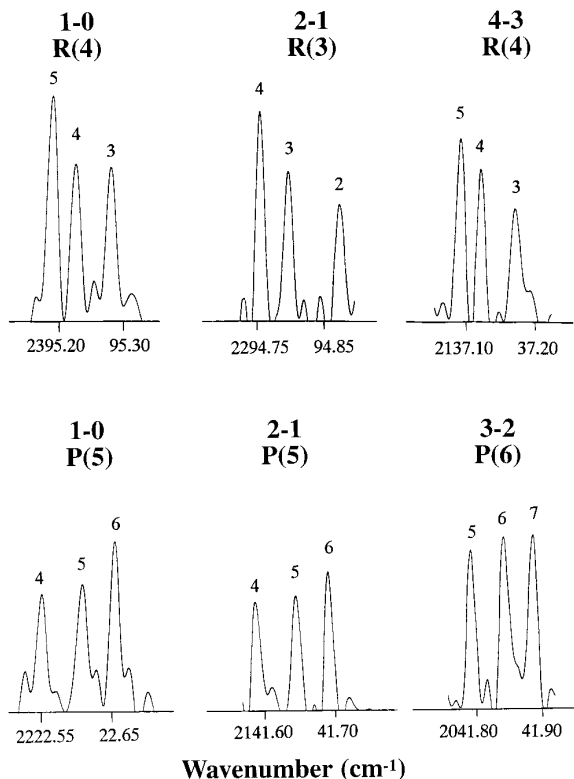
FIG. 1. A part of the spectrum of ND showing some $R(N'')$ and $P(N'')$ lines in different vibration-rotation bands. The J quantum numbers associated with each transition have also been provided.

EXPERIMENTAL

The vibration–rotation bands of ND were produced in an electrodeless microwave discharge through a flowing mixture of 0.13 Torr of N_2, 0.13 Torr of D_2, and 0.8 Torr of He. The discharge tube was made of quartz and had a diameter of about 12 mm. The emission from the lamp was focussed on the entrance aperture of the 1-m Fourier transform spectrometer associated with the McMath–Pierce telescope of the National Solar Observatory. The spectrometer was equipped with a KCl beam splitter and liquid-nitrogen-cooled InSb detectors. The use of a Ge filter limited the observation of the spectra to the 1800–5000 cm^{-1} spectral region. A total of 20 scans were coadded in about 1 hr at a resolution of 0.01 cm^{-1}.

In addition to ND bands, this spectrum also contained molecular lines of the $w^1\Pi–a^1\Delta$ transition of N_2 and many atomic lines of the He, N, and D atoms. Because of a lack of strong CO lines in this spectrum, we decided to use some strong atomic lines as transfer standards for wavenumber calibration. For this purpose, we chose a separately recorded spectrum in which both CO and the atomic lines were strong. The atomic lines were first calibrated using the CO lines

(*41*), then the calibration was transferred to the spectrum of ND. The spectra were measured using a program called PC-DECOMP developed at Kitt Peak. The measurements of the strong and unblended lines, which are observed with a maximum signal-to-noise ratio of 15:1 are expected to be accurate to ±0.001 cm^{-1}.

In the 2240–2390 cm^{-1} spectral region the lines of ND are overlapped with strong atmospheric CO_2 absorption. The lines located under the absorption lines of CO_2 could not be measured. The lines of ND falling at the edge of the CO_2 absorption features are not as accurate as the unblended lines and were therefore given lower weights in the final fit.

RESULTS AND DISCUSSION

(a) Analysis of ND Vibration–Rotation Bands

The structure of each band consists of three R and three P branches. The low N lines of the R and P branches could be easily identified by their characteristic triplet pattern. For a particular value of N, the three spin components of the $^3\Sigma^-$ state have J values $J = N + 1$, N, and $N - 1$ for the F_1, F_2, and F_3 spin components, respectively. This triplet pattern is clearly illustrated in Fig. 1, in which the three components of several $R(N'')$ and $P(N'')$ lines have been marked with the corresponding J'' quantum numbers. The splitting in the lines decreases rapidly with increasing J, and the components become unresolved at a J value ranging from 8 to 15 in the different bands. The R branches of each of these bands form a head at relatively high N values. For example, in the 1–0 band the R head is formed at $R(N = 26)$. After the head, the returning lines again show signs of
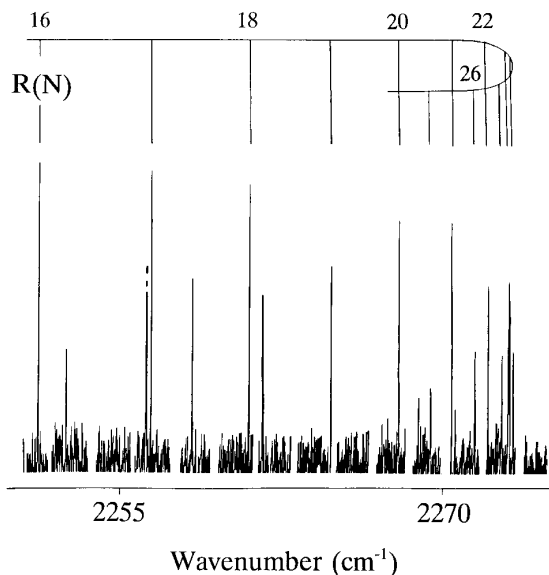

FIG. 2. A part of the R branch of the 4–3 band near the head.

TABLE 1
Line Positions (in cm^{-1}) in the Vibration–Rotation Bands of ND

1 - 0

J	R1	O-C	R2	O-C	R3	O-C	P1	O-C	P2	O-C	P3	O-C
0	2298.8263	-13										
1			2348.8303	4	2364.9843	9	2331.1404	9				
2	2348.7515	-24	2364.8384	-9	2380.3857	16	2297.8236	8	2279.6198	0	2260.9327	-15
3	2364.7879	11	2380.3088	1	2395.2783	-5	2279.7012	-2	2261.0816	-8	2241.9964	36
4	2380.2667	-9	2395.2270	1	2409.6232	-2	2261.1419	-9	2242.0733	-14	2222.5495	14
5	2395.1928	2	2409.5834	4	2423.4004	6	2242.1259	-2	2222.6083	-5	2202.6408	-43
6	2409.5537	5	2423.3670	9	2436.5943	-4	2222.6554	-4	2202.6964	-3	2182.3038	4
7	2423.3398	1	2436.5669	12	2449.1973	3	2202.7430	16	2182.3510	4	2161.5403	26
8	2436.5420	-2	2449.1726	11	2461.1978	20	2182.3942	2	2161.5848	23	2140.3615	3
9	2449.1499	-5	2461.1719	-13	2472.5820	11	2161.6246	-9	2140.4054	7	2118.7855	-11
10	2461.1529	-14	2472.5626	17	2483.3451	25	2140.4469	-6	2118.8294	-0	2096.8235	-27
11	2472.5436	-4	2483.3265	17	2493.4700	-12	2118.8757	35	2096.8693	6	2074.4962	39
12	2483.3090	-10	2493.4550	-5	2502.9565	-11	2096.9130	15	2074.5331	-16	2051.7974	4
13	2493.4424	-1	2502.9422	-16	2511.7882	-42	2074.5807	30	2051.8385	-10	2028.7491	-34
14	2502.9353	28	2511.7772	-32	2519.9654	-16						
15	2511.7708	-2	2519.9562	-7	2527.4726	-4						
16	2519.9500	9	2527.4646	1	2534.3021	2						
17	2527.4577	-6	2534.2965	15	2540.4455	-2						
18	2534.2904	1	2540.4413	10	2545.8920	-47						
19	2540.4361	-10	2545.8920	-6	2550.6456	-17						
20	2545.8920	13	2550.6456	12	2554.6908	6						
21	2550.6456	20	2554.6908	25	2558.0188	6						
22	2554.6908	24	2558.0188	17	2560.6236	-10						
23	2558.0188	8	2560.6236	-4	2562.5034	8						
24	2560.6236	-18	2562.5034	11	2563.6459	1						
25	2562.5034	-4	2563.6459	6	2564.0468	-10						
26	2563.6459	-7	2564.0468	-1	2563.7027	2						
27	2564.0468	-7	2563.7028	21	2562.6042	3						
28	2563.6970	-32	2562.6016	10	2560.7457	-4						
29	2562.5959	-27	2560.7422	16	2558.1253	21						
30	2560.7353	-11	2558.1149	0	2554.7335	41						
31	2558.1049	-29	2554.7187	10	2550.5637	46						
32			2550.5398	-32	2545.6069	7						
33	2550.5253	-23	2545.5816	-33	2539.8622	-30						
34	2545.5702	61	2539.8335	-40								
35	2539.8155	53										

2 - 1

J	R1	O-C	R2	O-C	R3	O-C	P1	O-C	P2	O-C	P3	O-C
1			2264.3218	-7	2279.9734	-4						
2	2264.2474	-9	2279.8301	-0	2294.8744	2	2214.8259	-21	2197.1355	29		
3	2279.7796	3	2294.8004	13	2309.2702	2	2197.2126	-10	2179.1047	18	2160.5255	15
4	2294.7597	0	2309.2190	5			2179.1637	10	2160.6041	4	2141.5883	0
5	2309.1888	29			2336.3987	6	2160.6533	-12	2141.6457	-12	2122.1941	-6
6			2336.3670	22	2349.0987	-3	2141.6931	-2	2122.2413	-30	2102.3576	-51
7	2336.3395	-7	2349.0724	20			2122.2872	-12	2102.4077	-1	2082.1073	6
8	2349.0524	37					2102.4509	0	2082.1480	-16	2061.4392	-5
9	2361.1639	-6			2383.6131	10	2082.1935	14	2061.4821	8	2040.3740	-1
10			2383.5910	-16	2393.8874	18	2061.5232	-5			2018.9227	6
11	2383.5761	-18	2393.8695	10	2403.5271	-1	2040.4585	8			1997.0937	-19
12	2393.8559	3	2403.5099	-24	2412.5299	24	2019.0073	16				
13	2403.5003	-11	2412.5157	12	2420.8755	-18	1997.1796	1				
14	2412.5047	-9	2420.8664	3	2428.5634	-39	1974.9898	-11				
15	2420.8563	-27	2428.5554	-26	2435.5856	-32						
16	2428.5485	-41	2435.5808	-5	2441.9329	-5						
17	2435.5771	-4	2441.9272	-2	2447.5892	-33						
18	2441.9232	-19	2447.5858	-21	2452.5555	-24						
19	2447.5858	-12	2452.5537	-9	2456.8192	-25						
20	2452.5537	-11	2456.8192	-1	2460.3745	-15						
21	2456.8192	-13	2460.3745	1	2463.2128	-5						
22	2460.3745	-17	2463.2128	8	2465.3267	7						
23	2463.2128	-14	2465.3267	18	2466.7092	20						
24	2465.3267	-3	2466.7092	36	2467.3517	21						
25	2466.7092	19	2467.3486	15	2467.2581	118						
26	2467.3486	9	2467.2423	0	2466.4009	103						
27	2467.2432	19	2466.3844	-1	2464.7808	49						
28	2466.3844	32	2464.7643	-26								
29	2464.7643	38			2459.2485	46						
30			2459.2234	-30	2455.3116	-25						
31	2459.2092	-20	2455.2882	-25								
32	2455.2682	-13										

Note. The observed minus calculated wavenumbers are in 10^4 cm^{-1}.

TABLE 1—*Continued*

					3 - 2							
J	R1	O-C	R2	O-C	R3	O-C	P1	O-C	P2	O-C	P3	O-C
1			2179.8951	12								
2	2179.8207	-2	2194.8967	-3	2209.4329	-13			2114.7234	13		
3	2194.8479	5	2209.3625	10	2223.3274	17	2114.7998	-19	2097.1983	19	2079.1207	-4
4	2209.3236	1	2223.2765	-2	2236.6712	23	2097.2571	20	2079.1991	-16	2060.6872	-10
5	2223.2473	19	2236.6315	2	2249.4486	30	2079.2497	-8	2060.7471	3	2041.7984	18
6	2236.6042	-6	2249.4145	-3	2261.6440	16	2060.7922	-1	2041.8473	11	2022.4636	-19
7	2249.3908	-10	2261.6180	16	2273.2513	31	2041.8885	-10	2022.5074	-34	2002.7087	-6
8	2261.5962	-1	2273.2268	11	2284.2550	31	2022.5536	6	2002.7499	-24	1982.5354	-52
9	2273.2077	-3	2284.2290	-33	2294.6443	11	2002.7934	-5	1982.5807	-16	1961.9707	-7
10	2284.2143	-26	2294.6230	-31	2304.4115	-4	1982.6264	25	1962.0112	-15		
11	2294.6108	-19	2304.3952	-18	2313.5517	36	1962.0533	-9				
12	2304.3880	25	2313.5363	11	2322.0425	6	1941.0966	-0				
13	2313.5267	11	2322.0297	-14	2329.8797	-44	1919.7651	24				
14	2322.0260	28	2329.8717	-33	2337.0603	-48						
15	2329.8717	28	2337.0557	-21	2343.5712	-45						
16	2337.0557	24	2343.5712	11	2349.4038	-32						
17	2343.5712	39	2349.4038	7								
18	2349.4038	20										
19												
20					2365.7684	46						
21			2365.7684	22								
22	2365.7684	-26			2369.6504	73						
23			2369.6504	20								
24	2369.6504	-58			2370.5702	4						
25			2370.5784	4								
26	2370.5857	-29										

					4 - 3							
J	R1	O-C	R2	O-C	R3	O-C	P1	O-C	P2	O-C	P3	O-C
1					2109.9030	-18						
2			2109.7604	-26	2123.7901	-2						
3	2109.7168	8	2123.7165	-3	2137.1713	17			2015.0945	3	1997.5182	-35
4	2123.6813	-0	2137.1202	4	2150.0003	12	2015.1510	-19	1997.5992	14	1979.5724	-133
5	2137.0905	-5	2149.9606	-1	2162.2608	3	1997.6467	-9	1979.6380	-29		
6	2149.9361	-4	2162.2316	28	2173.9408	4	1979.6857	-7	1961.2361	9		
7	2162.2078	-2	2173.9136	4	2185.0278	6	1961.2791	7				
8	2173.8957	4	2185.0004	-31	2195.5117	19						
9	2184.9866	-13	2195.4875	-15	2205.3787	10						
10	2195.4772	17	2205.3571	-22	2214.6207	2						
11	2205.3468	-10	2214.6025	-17	2223.2242	-36						
12	2214.5968	24	2223.2119	-14	2231.1891	-5						
13	2223.2046	-8	2231.1768	-2	2238.4909	-50						
14	2231.1708	3	2238.4839	-10	2245.1346	-23						
15	2238.4839	38	2245.1249	-26	2251.0987	-43						
16	2245.1249	7	2251.0952	1	2256.3801	-43						
17	2251.0952	20	2256.3801	21	2260.9675	-41						
18	2256.3801	27	2260.9675	9	2264.8530	-25						
19	2260.9675	1	2264.8530	12	2268.0269	3						
20	2264.8530	-10	2268.0269	27	2270.4771	15						
21	2268.0269	-7	2270.4771	26	2272.1967	32						
22	2270.4771	-20	2272.1967	31	2273.1701	-10						
23	2272.1967	-27	2273.1701	-23	2273.4001	7						
24	2273.1772	-21	2273.4001	-17								
25	2273.4131	33										

					5 - 4							
J	R1	O-C	R2	O-C	R3	O-C	P1	O-C	P2	O-C	P3	O-C
2			2024.1035	25	2037.6106	24						
3	2024.0574	3	2037.5313	-32	2050.4595	-42					1915.4021	-32
4	2037.5009	-12	2050.4131	-5	2062.7660	4	1932.5362	-25	1915.4763	-21	1897.9635	32
5	2050.3871	-8	2062.7288	20	2074.4962	7	1915.5260	-26	1898.0126	-1		
6	2062.7055	-4	2074.4652	17	2085.6414	16	1898.0591	4	1880.0917	-22	1861.6917	-24
7	2074.4463	4	2085.6118	-8	2096.1880	11	1880.1357	-22				
8	2085.5978	1	2096.1615	-15	2106.1275	21	1861.7755	-8				
9	2096.1534	28	2106.1012	-30	2115.4433	-9	1842.9841	-8				
10	2106.0970	32	2115.4208	-46	2124.1319	-8						
11	2115.4167	-2	2124.1126	-33	2132.1815	14						
12	2124.1126	35	2132.1618	-33	2139.5745	-14						
13	2132.1618	19	2139.5602	-24	2146.3076	-18						
14	2139.5585	-2	2146.2974	-2	2152.3676	-26						
15	2146.2974	22	2152.3597	-1	2157.7430	-50						

TABLE 1—*Continued*

| | | | | | 5 - 4 | | | | | | | |
J	R1	O-C	R2	O-C	R3	O-C	P1	O-C	P2	O-C	P3	O-C
16	2152.3597	10	2157.7384	-6	2162.4297	-27						
17	2157.7384	-7	2162.4251	6	2166.4084	-45						
18	2162.4251	-7	2166.4084	23	2169.6766	-26						
19	2166.4084	-0	2169.6766	31	2172.2202	-7						
20	2169.6766	-1	2172.2202	41	2174.0281	6						
21	2172.2202	-0	2174.0281	46	2175.0896	9						
22	2174.0281	-4	2175.0896	41	2175.3964	26						
23	2175.0896	-15	2175.3964	51								
24	2175.3964	-12	2174.9297	-8								
25			2173.6921	-2								

| | | | | | 6 - 5 | | | | | | | |
J	R1	O-C	R2	O-C	R3	O-C	P1	O-C	P2	O-C	P3	O-C
4	1950.3796	-36	1962.7543	14	1974.5606	19						
5	1962.7283	-12	1974.5186	-18	1985.7376	14						
6	1974.5009	-7	1985.7062	16	1996.3223	9						
7	1985.6892	-1	1996.2921	-23	2006.3051	31						
8	1996.2823	5	2006.2782	-2	2015.6688	25						
9	2006.2700	19	2015.6427	-28	2024.4006	-24						
10	2015.6354	-19	2024.3790	-54	2032.5007	3						
11	2024.3790	10	2032.4808	-32	2039.9485	9						
12	2032.4808	14	2039.9308	-21	2046.7326	-6						
13	2039.9308	10	2046.7183	-18								
14	2046.7183	-2	2052.8339	-3	2058.2686	-54						
15	2052.8339	-1	2058.2686	48	2063.0043	-24						
16	2058.2686	37	2063.0043	65	2067.0269	-52						
17	2063.0043	42	2067.0269	25	2070.3349	-42						
18	2067.0269	-9	2070.3349	24	2072.9133	-24						
19	2070.3349	-20	2072.9133	32	2074.7506	4						
20	2072.9133	-22	2074.7506	50	2075.8311	3						
21	2074.7506	-13	2075.8311	41								
22	2075.8311	-30										

spin-splitting but only a small number of returning lines could be picked-out because of their very weak intensity. A part of the 4–3 band showing the formation of the *R* head is presented in Fig. 2. The observed rotational lines are reported in Table 1, labeled with their J'' values (not N'').

In the fundamental 1–0 band, lines have been observed up to $R(N = 34)$ and $P(N = 13)$. The *P*-branch lines are weak in intensity because of strong Herman–Wallis effects (*38*). In fact, no *P*-branch lines were identified for the 6–5 band and only a few low-N *P* lines were identified in the 5–4 and 4–3 bands (Table 1).

The observed rotational lines of the individual bands were initially fitted separately using the customary $^3\Sigma^-$ Hamiltonian. An explicit listing of the matrix elements for the $^3\Sigma^-$ Hamiltonian is provided in our previous paper on NH (*20*). The initial constants obtained for the $v = 0$ vibrational level were found to be in reasonable agreement with the constants of Saito and Goto (*40*) obtained from the submillimeter-wave spectrum. The final set of constants were obtained by fitting the data of all of the bands simultaneously to provide a single set of constants (Table 2). In this fit the hyperfine-free submillimeter pure rotational wavenumbers for the $N = 1 \rightarrow 0$ transition of Saito

and Goto (*40*) were also included. The values used were 491 943.2365, 522 069.9217, and 546 150.3924 MHz for $J = 0-1$, $2-1$, and $1-1$ transitions, respectively. For the $v = 2$, 3, 4, 5, and 6 vibrational levels, the constants L_v and γ_{Hv} were not determined and were fixed to zero. The constants of Table 2 were used to determine the equilibrium molecular constants for the ground state, which are provided in Table 3. The ω_e value that we determine is in reasonable agreement with the value obtained by Patel-Misra *et al.* (*36*) but $\omega_e x_e$ differs by 1.25 cm^{-1}. Their ground state $\Delta G(1/2)$ and $\Delta G(3/2)$ values of 2317.52(20) and 2235.77(30) cm^{-1} (*36*) are also considerably different than the present values of 2315.23753(23) and 2231.73836(43) cm^{-1}, respectively. Patel-Misra *et al.*'s B values, however, agree well with the present constants, within experimental error. Not surprisingly, since we used their data, our $v = 0$ rotational constants are also in excellent agreement with the constants of Saito and Goto (*40*).

The equilibrium constants of ND result in the ground state equilibrium bond length of 1.036651(9) Å which can be compared with the bond length $r_e = 1.03675$ Å for the ground state of NH (*20*). The recommended dissociation energy D_0 is 77.7 kcal/mole (27 200 cm^{-1}) for NH (*22*).

<div align="center">

TABLE 2
Rotational Constants (in cm⁻¹) for the $X^3\Sigma^-$ State of ND

</div>

Constants[a]	v=0	v=1	v=2	v=3
T_v	0.0	2315.23753(23)	4546.97589(36)	6695.29463(46)
B_v	8.781588(14)	8.528719(13)	8.276445(15)	8.024129(15)
$10^4 \times D_v$	4.8816(11)	4.8292(10)	4.7827(11)	4.7450(10)
$10^8 \times H_v$	1.883(37)	1.797(31)	1.679(27)	1.558(22)
$10^{13} \times L_v$	1.59(22)	--	--	--
$10^2 \times \gamma_v$	-2.9475(21)	-2.8370(32)	-2.7291(44)	-2.6048(55)
$10^6 \times \gamma_{Dv}$	4.86(53)	5.10(46)	5.79(37)	5.39(34)
$10^9 \times \gamma_{Hv}$	3.86(27)	2.18(22)	--	--
λ_v	0.918811(53)	0.91848(22)	0.91742(38)	0.91690(48)
	v=4	v=5	v=6	
T_v	8760.00356(58)	10740.59149(75)	12636.1566(13)	
B_v	7.771022(16)	7.516144(17)	7.258347(25)	
$10^4 \times D_v$	4.7182(10)	4.7038(10)	4.7068(12)	
$10^8 \times H_v$	1.419(19)	1.243(16)	1.032(17)	
$10^2 \times \gamma_v$	-2.4857(59)	-2.3593(65)	-2.2312(75)	
$10^6 \times \gamma_{Dv}$	4.88(32)	4.08(30)	3.33(30)	
λ_v	0.91472(62)	0.91090(74)	0.90611(88)	

[a]The numbers in parentheses are one standard deviation in the last digit.

Our data for vibration−rotation levels up to $v = 6$, $N = 21$ enable about 55% of the potential well of ND to be mapped.

(b) Redetermination of Molecular Constants of PH

We had some initial difficulty in combining the ND measurements with the pure rotational transitions of Saito and

<div align="center">

TABLE 3
Equilibrium Constants (in cm⁻¹) for the $X^3\Sigma^-$ State of ND

</div>

ω_e	2399.1255(299)[a]	$10^3 \times \gamma_e$	1.032(67)
$\omega_e x_e$	42.1064(212)	$10^4 \times \delta_e$	-1.424(66)
$\omega_e y_e$	0.1203(54)	$10^4 \times D_e$	4.9168(36)
$\omega_e z_e$	-0.01295(44)	$10^6 \times \beta_e$	-6.81(24)
B_e	8.908665(146)	$10^7 \times \gamma_D$	5.42(35)
α_e	0.254570(192)	$r_e(\text{Å})$	1.036651(9)

[a]The numbers in parentheses are one standard deviation in the last digit.

Goto (*40*). As we were checking our computer program it was noticed that the constants reported in our previous work on PH (*42*) do not reproduce the high J lines within the experimental error. In addition, submillimeter-wave measurements have also been reported recently for PH (*43*). We therefore decided to refit our previous vibration−rotation measurements along with the pure rotation lines in order to obtain improved constants for the ground state of PH. The new set of molecular constants for the ground state of PH are provided in Table 4 and the equilibrium constants in Table 5.

CONCLUSION

The infrared emission spectra of six vibration−rotation bands of ND have been observed at high resolution using a Fourier transform spectrometer. The analysis of these bands provides a set of rotational constants for the $v = 0, 1, 2, 3, 4, 5,$ and 6 vibrational levels of the $X^3\Sigma^-$ state. A much improved set of equilibrium vibrational and rotational constants was determined. Improved molecular constants for PH

TABLE 4
Rotational Constants (in cm^{-1}) for the $X^3\Sigma^-$ State of PH

Constants[a]	v=0	v=1	v=2
T_v	0.0	2276.20901(51)	4465.02033(74)
B_v	8.412518(27)	8.160347(25)	7.908062(26)
$10^4 \times D_v$	4.4311(19)	4.3917(17)	4.3578(20)
$10^8 \times H_v$	1.391(33)	1.268(29)	1.072(39)
$10^2 \times \gamma_v$	-7.6916(43)	-7.3409(68)	-6.9940(92)
$10^5 \times \gamma_{Dv}$	1.423(51)	1.421(55)	1.446(56)
λ_v	2.20969(12)	2.21109(67)	2.21070(88)
$10^4 \times \lambda_{Dv}$	1.90(18)	1.75(18)	1.63(18)
	v=3	v=4	v=5
T_v	6566.15898(88)	8578.9443(11)	10502.1949(13)
B_v	7.654863(27)	7.399660(40)	7.140857(51)
$10^4 \times D_v$	4.3413(19)	4.3509(41)	4.3682(60)
$10^8 \times H_v$	0.984(36)	1.24(12)	1.15(19)
$10^2 \times \gamma_v$	-6.633(11)	-6.305(14)	-5.949(18)
$10^6 \times \gamma_{Dv}$	1.335(57)	1.502(87)	1.42(12)
λ_v	2.2082(11)	2.2029(14)	2.1930(18)
$10^4 \times \lambda_v$	1.39(17)	0.93(17)	0.23(19)

[a] The numbers in parentheses are one standard deviation in the last digit.

TABLE 5
Equilibrium Constants (in cm^{-1}) for the $X^3\Sigma^-$ State of PH

ω_e	2363.7735(362)[a]	$10^3 \times \gamma_e$	0.868(116)
$\omega_e x_e$	43.9074(270)	$10^4 \times \delta_e$	-1.85(13)
$\omega_e y_e$	0.1059(73)	$10^4 \times D_e$	4.4618(51)
$\omega_e z_e$	-0.01864(64)	$10^6 \times \beta_e$	-6.10(47)
B_e	8.539040(186)	$10^7 \times \gamma_D$	7.85(92)
α_e	0.253387(284)	r_e(Å)	1.422179(16)

[a] The numbers in parentheses are one standard deviation in the last digit.

have also been provided by combining our previous infrared measurements (42) with the submillimeter-wave measurements of Goto and Saito (43).

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