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The Pure Rotational Absorption Spectrum of Hydrazoic Acid in the Far-Infrared Region

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The pure rotational absorption spectrum of HN_3 gas has been measured in the wavenumber region 20 to 400 cm^{-1}. The observed spectrum shows irregularities which may be ascribed to higher order *c*-type Coriolis interaction and centrifugal distortion interactions between the ground state and the ν_5 state. The present resolution and wavenumber accuracy allows the interaction to be observed for levels with $K_a = 6$–9. The determination of the ground state parameters has been performed using wavenumbers for transitions involving $K_a \leqslant 5$ only. In addition to the pure rotational transitions in the ground state, some pure rotational transitions in the ν_5 and ν_6 states are identified.

INTRODUCTION

The absorption of radiation by HN_3 in the far-infrared region has previously been measured by Krakov *et al.* (*1*). In their investigation they measured the region 20 to 250 cm^{-1} with a resolution of 0.2–0.5 cm^{-1}. The analysis of their data yielded values for A, B, C, and D_K. The rotational constants B and C and the centrifugal distortion constants D_J, D_{JK}, H_{JJK}, and H_{JKK} had been determined earlier with much higher accuracy by means of microwave spectroscopy by Kewley *et al.* (*2*). Later, the A constant was determined by means of microwave spectroscopy (*3*) through the measurement of *b*-type transitions. Still D_K and H_{KKK} could not be determined, and D_K was constrained to previously determined values (*1, 4*) whereas $H_{KKK} = 0$. Through the measurement and analysis of the pure rotational Raman spectrum (*5*), D_K and H_{KKK} were determined more precisely. The microwave data were then reanalyzed and the result for the value of the A constant is given in Ref. (*5*).

In order to determine a complete set of ground state parameters without constraints and especially to improve the *K*-dependent parameters, the present investigation was performed.

EXPERIMENTAL DETAILS

The HN_3 gas was made by heating a mixture of stearic acid and NaN_3 under vacuum. The gas was collected in glass vessels at about 300 Torr pressure. The spectra were

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TABLE I

Assignments, Wavenumbers (in cm^{-1}), and Residuals of the Pure Rotational Absorption Spectrum of HN_3

J'	K_a'	K_c'	J"	K_a''	K_c''	Wavenumbers	10^4(O-C)
7	1	7	6	0	6	25.4155	-12
9	1	9	8	0	8	26.9315	-15
10	1	10	9	0	9	27.6888	41
11	1	11	10	0	10	28.4313	-10
12	1	12	11	0	11	29.1747	-10
13	1	13	12	0	12	29.9146	-2
14	1	14	13	0	13	30.6475	-23
15	1	15	14	0	14	31.3799	-8
16	1	16	15	0	15	32.1084	10
17	1	17	16	0	16	32.8294	-7
18	1	18	17	0	17	33.5456	-31
19	1	19	18	0	18	34.2630	-3
20	1	20	19	0	19	34.9746	8
21	1	21	20	0	20	35.6810	6
22	1	22	21	0	21	36.3824	-7
23	1	23	22	0	22	37.0835	16
24	1	24	23	0	23	37.7783	14
25	1	25	24	0	24	38.4689	9
26	1	26	25	0	25	39.1547	-7
27	1	27	26	0	26	39.8402	11
28	1	28	27	0	27	40.5202	11
29	1	29	28	0	28	41.1973	18
30	1	30	29	0	29	41.8694	11
31	1	31	30	0	30	42.5396	19
32	1	32	31	0	31	43.2022	-14
33	1	33	32	0	32	43.8681	20
34	1	34	33	0	33	44.5282	29
35	1	35	34	0	34	45.1832	20
36	1	36	35	0	35	45.8344	4
37	1	37	36	0	36	46.4833	-3
38	1	38	37	0	37	47.1312	10
39	1	39	38	0	38	47.7746	9
41	1	41	40	0	40	49.0543	21
42	1	42	41	0	41	49.6900	28
43	1	43	42	0	42	50.3196	0
44	1	44	43	0	43	50.9494	1
45	1	45	44	0	44	51.5731	-35
46	1	46	45	0	45	52.2039	26
47	1	47	46	0	46	52.8224	-14
26	2	25	27	1	26	36.7452	-11
25	2	24	26	1	25	37.6551	-8
24	2	23	25	1	24	38.5664	50
23	2	22	24	1	23	39.4659	32
22	2	21	23	1	22	40.3629	30
21	2	20	22	1	21	41.2558	29
20	2	19	21	1	20	42.1430	13
19	2	18	20	1	19	43.0251	-11
18	2	17	19	1	18	43.9071	5
17	2	16	18	1	17	44.7825	-3
16	2	15	17	1	16	45.6541	-6
15	2	14	16	1	15	46.5227	4
14	2	13	15	1	14	47.3856	-1
13	2	12	14	1	13	48.2463	15
12	2	11	13	1	12	49.0965	-32
11	2	10	12	1	11	49.9501	-1
10	2	9	11	1	10	50.7968	3
9	2	8	10	1	9	51.6392	7
8	2	7	9	1	8	52.4761	0
7	2	6	8	1	7	53.3098	3
6	2	5	7	1	6	54.1383	-2
5	2	4	6	1	5	54.9657	26
4	2	3	5	1	4	55.7813	-22
3	2	2	4	1	3	56.6023	28
7	2	6	7	1	7	59.9375	41
8	2	7	8	1	8	59.9654	-5
9	2	8	9	1	9	60.0039	15
10	2	9	10	1	10	60.0432	3
11	2	10	11	1	11	60.0870	-6
12	2	11	12	1	12	60.1374	11
13	2	12	13	1	13	60.1887	-4
14	2	13	14	1	14	60.2451	-8
15	2	14	15	1	15	60.3062	-6
16	2	15	16	1	16	60.3730	12
17	2	16	17	1	17	60.4417	8
18	2	17	18	1	18	60.5134	-6
19	2	18	19	1	19	60.5912	-1
20	2	19	20	1	20	60.6726	0
21	2	20	21	1	21	60.7577	-3
22	2	21	22	1	22	60.8473	-2
23	2	22	23	1	23	60.9414	2
24	2	23	24	1	24	61.0397	8
25	2	24	25	1	25	61.1416	9
26	2	25	26	1	26	61.2469	3
27	2	26	27	1	27	61.3572	5

J'	K_a'	K_c'	J"	K_a''	K_c''	Wavenumbers	10^4(O-C)
2	2	1	1	1	0	61.4065	27
28	2	27	28	1	28	61.4715	7
29	2	28	29	1	29	61.5886	-5
30	2	29	30	1	30	61.7110	-5
31	2	30	31	1	31	61.8382	2
32	2	31	32	1	32	61.9679	-8
33	2	32	33	1	33	62.1033	-2
3	2	2	2	1	1	62.1887	-6
34	2	33	34	1	34	62.2426	1
35	2	34	35	1	35	62.3855	-1
36	2	35	36	1	36	62.5325	-4
37	2	36	37	1	37	62.6846	3
38	2	37	38	1	38	62.8396	-3
4	2	3	3	1	2	62.9708	5
41	2	40	41	1	41	63.3301	-15
42	2	41	42	1	42	63.5026	-13
43	2	42	43	1	43	63.6775	-29
5	2	4	4	1	3	63.7479	9
46	2	45	46	1	46	64.2329	-21
6	2	5	5	1	4	64.5186	-6
51	2	50	51	1	51	65.2427	-7
7	2	6	6	1	5	65.2871	0
8	2	7	7	1	6	66.0508	2
9	2	8	8	1	7	66.8106	10
10	2	9	9	1	8	67.5648	5
11	2	10	10	1	9	68.3154	8
12	2	11	11	1	10	69.0608	4
13	2	12	12	1	11	69.8021	2
14	2	13	13	1	12	70.5389	0
15	2	14	14	1	13	71.2723	7
16	2	15	15	1	14	72.0007	9
17	2	16	16	1	15	72.7234	-3
18	2	17	17	1	16	73.4435	4
19	2	18	18	1	17	74.1578	-3
20	2	19	19	1	18	74.8690	2
21	2	20	20	1	19	75.5739	-11
22	2	21	21	1	20	76.2784	15
23	2	22	22	1	21	76.9738	-5
24	2	23	23	1	22	77.6676	2
25	2	24	24	1	23	78.3562	2
26	2	25	25	1	24	79.0384	-19
27	2	26	26	1	25	79.7201	-1
28	2	27	27	1	26	80.3962	5
29	2	28	28	1	27	81.0684	15
30	2	29	29	1	28	81.7332	-5
31	2	30	30	1	29	82.3956	-5
32	2	31	31	1	30	83.0540	-2
33	2	32	32	1	31	83.7071	-8
34	2	33	33	1	32	84.3581	8
36	2	35	35	1	34	85.6419	-12
37	2	36	36	1	35	86.2786	-9
38	2	37	37	1	36	86.9115	-2
39	2	38	38	1	37	87.5394	-1
40	2	39	39	1	38	88.1641	11
41	2	40	40	1	39	88.7814	-9
42	2	41	41	1	40	89.3990	17
43	2	42	42	1	41	90.0074	-6
45	2	44	44	1	43	91.2165	-3
46	2	45	45	1	44	91.8155	7
47	2	46	46	1	45	92.4044	-43
29	2	27	30	1	30	37.9883	-3
28	2	26	29	1	29	38.6459	-19
27	2	25	28	1	28	39.3155	32
26	2	24	27	1	27	39.9806	-14
25	2	23	26	1	26	40.6581	12
24	2	22	25	1	25	41.3357	-12
23	2	21	24	1	24	42.0218	-1
22	2	20	23	1	23	42.7153	34
21	2	19	22	1	22	43.4036	-31
20	2	18	21	1	21	44.1050	-13
19	2	17	20	1	20	44.8133	27
18	2	16	19	1	19	45.5202	6
17	2	15	18	1	18	46.2322	-11
16	2	14	17	1	17	46.9513	-2
15	2	13	16	1	16	47.6739	-3
13	2	11	14	1	14	49.1335	5
12	2	10	13	1	13	49.8678	-12
11	2	9	12	1	12	50.6110	17
10	2	8	11	1	11	51.3533	-6
9	2	7	10	1	10	52.1020	-7
8	2	6	9	1	9	52.8572	14
7	2	5	8	1	8	53.6130	-1
6	2	4	7	1	7	54.3759	13
5	2	3	6	1	6	55.1390	-12

J'	K_a'	K_c'	J"	K_a''	K_c''	Wavenumbers	10^4(O-C)
45	2	43	45	1	44	55.8181	-16
4	2	2	5	1	5	55.9083	-16
44	2	42	44	1	43	55.9721	2
43	2	41	43	1	42	56.1198	-28
42	2	40	42	1	41	56.2718	1
41	2	39	41	1	40	56.4182	-8
40	2	38	40	1	39	56.5614	-31
39	2	37	39	1	38	56.7059	-21
38	2	36	38	1	37	56.8487	-7
37	2	35	37	1	36	56.9873	-14
36	2	34	36	1	35	57.1241	-15
35	2	33	35	1	34	57.2607	6
34	2	32	34	1	33	57.3915	-6
33	2	31	33	1	32	57.5206	-8
32	2	30	32	1	31	57.6477	-4
31	2	29	31	1	30	57.7710	-9
30	2	28	30	1	29	57.8923	-5
29	2	27	29	1	28	58.0096	-11
28	2	26	28	1	27	58.1252	-4
27	2	25	27	1	26	58.2374	2
26	2	24	26	1	25	58.3450	-6
25	2	23	25	1	24	58.4499	-7
24	2	22	24	1	23	58.5515	-8
23	2	21	23	1	22	58.6503	-1
22	2	20	22	1	21	58.7438	-12
21	2	19	21	1	20	58.8361	1
20	2	18	20	1	19	58.9236	3
19	2	17	19	1	18	59.0064	-4
18	2	16	18	1	17	59.0873	8
17	2	15	17	1	16	59.1622	-1
16	2	14	16	1	15	59.2335	-8
15	2	13	15	1	14	59.3026	4
14	2	12	14	1	13	59.3671	10
13	2	11	13	1	12	59.4276	16
12	2	10	12	1	11	59.4826	8
11	2	9	11	1	10	59.5331	-3
10	2	8	10	1	9	59.5823	15
9	2	7	9	1	8	59.6241	0
8	2	6	8	1	7	59.6619	-12
7	2	5	7	1	6	59.6985	7
6	2	4	6	1	5	59.7329	46
2	2	0	1	1	1	61.4065	-58
4	2	2	3	1	3	63.0172	-37
5	2	3	4	1	4	63.8298	-15
6	2	4	5	1	5	64.6463	5
7	2	5	6	1	6	65.4633	-11
8	2	6	7	1	7	66.2869	-1
9	2	7	8	1	8	67.1154	16
10	2	8	9	1	9	67.9460	12
11	2	9	10	1	10	68.7803	5
12	2	10	11	1	11	69.6197	6
13	2	11	12	1	12	70.4650	24
14	2	12	13	1	13	71.3093	-11
15	2	13	14	1	14	72.1642	18
16	2	14	15	1	15	73.0201	13
17	2	15	16	1	16	73.8784	-11
18	2	16	17	1	17	74.7451	5
19	2	17	18	1	18	75.6152	10
20	2	18	19	1	19	76.4886	3
21	2	19	20	1	20	77.3668	-1
22	2	20	21	1	21	78.2499	-3
23	2	21	22	1	22	79.1390	9
24	2	22	23	1	23	80.0319	12
25	2	23	24	1	24	80.9285	4
26	2	24	25	1	25	81.8325	21
27	2	25	26	1	26	82.7368	-7
28	2	26	27	1	27	83.6525	28
29	2	27	28	1	28	84.5668	-1
30	2	28	29	1	29	85.4891	-2
31	2	29	30	1	30	86.4171	3
32	2	30	31	1	31	87.3500	3
33	2	31	32	1	32	88.2865	-14
34	2	32	33	1	33	89.2325	9
35	2	33	34	1	34	90.1802	-6
36	2	34	35	1	35	91.1392	35
37	2	35	36	1	36	92.0962	-1
38	2	36	37	1	37	93.0652	25
39	2	37	38	1	38	94.0339	-11
40	2	38	39	1	39	95.0125	-8
41	2	39	40	1	40	95.9955	-23
42	2	40	41	1	41	96.9907	23
43	2	41	42	1	42	97.9841	-13
39	3	37	40	2	38	67.1990	-39
38	3	36	39	2	37	68.0216	-29

Note. The table includes values for transitions between unperturbed levels only. Double primes refer to the initial states.

TABLE I—*Continued*

J'	K'_a	K'_c	J''	K''_a	K''_c	Wavenumbers	10^4(O-C)
37	3	35	38	2	36	68.8467	22
36	3	34	37	2	35	69.6617	-13
33	3	31	34	2	32	72.1089	-13
32	3	30	33	2	31	72.9213	-21
31	3	29	32	2	30	73.7347	-7
30	3	28	31	2	29	74.5455	-7
29	3	27	30	2	28	75.3552	-8
28	3	26	29	2	27	76.1647	0
26	3	24	27	2	25	77.7777	-16
25	3	23	26	2	24	78.5843	-10
24	3	22	25	2	23	79.3918	13
23	3	21	24	2	22	80.1952	4
22	3	20	23	2	21	80.9976	-9
21	3	19	22	2	20	81.7999	-15
20	3	18	21	2	19	82.6035	-2
19	3	17	20	2	18	83.4132	79
18	3	16	19	2	17	84.2140	76
16	3	14	17	2	15	85.8111	42
15	3	13	16	2	14	86.6103	39
14	3	12	15	2	13	87.4078	23
13	3	11	14	2	12	88.2066	25
12	3	10	13	2	11	89.0035	13
11	3	9	12	2	10	89.8007	7
9	3	7	10	2	8	91.3951	6
8	3	6	9	2	7	92.1939	26
7	3	5	8	2	6	92.9912	35
6	3	4	7	2	5	93.7843	5
5	3	3	6	2	4	94.5797	1
4	3	2	5	2	3	95.3754	2
3	3	1	2	2	0	101.7297	0
4	3	2	3	2	1	102.5221	-6
5	3	3	4	2	2	103.3163	8
6	3	4	5	2	3	104.1085	5
7	3	5	6	2	4	104.8999	-3
8	3	6	7	2	5	105.6942	22
9	3	7	8	2	6	106.4832	-3
10	3	8	9	2	7	107.2750	4
11	3	9	10	2	8	108.0657	4
12	3	10	11	2	9	108.8568	12
13	3	11	12	2	10	109.6453	-2
14	3	12	13	2	11	110.4367	18
15	3	13	14	2	12	111.2261	23
16	3	14	15	2	13	112.0174	52
17	3	15	16	2	14	112.8008	7
18	3	16	17	2	15	113.5911	37
20	3	18	19	2	17	115.1646	46
21	3	19	20	2	18	115.9489	36
22	3	20	21	2	19	116.7297	-2
23	3	21	22	2	20	117.5168	31
24	3	22	23	2	21	118.2956	-11
25	3	23	24	2	22	119.0808	20
26	3	24	25	2	23	119.8611	12
27	3	25	26	2	24	120.6384	-18
28	3	26	27	2	25	121.4175	-19
29	3	27	28	2	26	122.1956	-19
30	3	28	29	2	27	122.9743	-2
31	3	29	30	2	28	123.7493	-10
32	3	30	31	2	29	124.5233	-16
33	3	31	32	2	30	125.2960	-21
34	3	32	33	2	31	126.0683	-17
35	3	33	34	2	32	126.8385	-20
36	3	34	35	2	33	127.6086	-8
37	3	35	36	2	34	128.3754	-14
38	3	36	37	2	35	129.1405	-21
39	3	37	38	2	36	129.9044	-22
40	3	38	39	2	37	130.6649	-40
41	3	39	40	2	38	131.4289	-5
42	3	40	41	2	39	132.1881	2
43	3	41	42	2	40	132.9428	-16
44	3	42	43	2	41	133.6960	-28
45	3	43	44	2	42	134.4506	-4
46	3	44	45	2	43	135.2024	14
47	3	45	46	2	44	135.9455	-32
36	3	33	37	2	36	69.8784	-20
35	3	32	36	2	35	70.6752	0
34	3	31	35	2	34	71.4693	-10
33	3	30	34	2	33	72.2646	-13
32	3	29	33	2	32	73.0601	-16
30	3	27	31	2	30	74.6534	-9
29	3	26	30	2	29	75.4495	-14
28	3	25	29	2	28	76.2439	-39
27	3	24	28	2	27	77.0452	4
26	3	23	27	2	26	77.8424	4
25	3	22	26	2	25	78.6379	-15

J'	K'_a	K'_c	J''	K''_a	K''_c	Wavenumbers	10^4(O-C)
24	3	21	25	2	24	79.4360	-8
23	3	20	24	2	23	80.2342	-1
22	3	19	23	2	22	81.0319	0
47	3	44	47	2	45	98.6595	-17
46	3	43	46	2	44	98.7049	2
45	3	42	45	2	43	98.7466	4
44	3	41	44	2	42	98.7851	-4
43	3	40	43	2	41	98.8202	-27
42	3	39	42	2	40	98.8554	-29
41	3	38	41	2	39	98.8909	-10
40	3	37	40	2	38	98.9239	2
38	3	35	38	2	36	98.9879	57
22	3	19	21	2	20	116.7569	36
24	3	21	23	2	22	118.3314	13
25	3	22	24	2	23	119.1189	6
26	3	23	25	2	24	119.9090	27
27	3	24	26	2	25	120.6920	-23
28	3	25	27	2	26	121.4808	-14
29	3	26	28	2	27	122.2681	-19
30	3	27	29	2	28	123.0552	-25
31	3	28	30	2	29	123.8439	-16
32	3	29	31	2	30	124.6325	-7
33	3	30	32	2	31	125.4190	-19
34	3	31	33	2	32	126.2064	-23
36	3	33	35	2	34	127.7809	-35
38	3	35	37	2	36	129.3595	-11
39	3	36	38	2	37	130.1464	-25
40	3	37	39	2	38	130.9354	-20
41	3	38	40	2	39	131.7296	35
42	3	39	41	2	40	132.5142	-9
43	3	40	42	2	41	133.3025	-19
45	3	42	44	2	43	134.8818	-21
46	3	43	45	2	44	135.6701	-41
47	3	44	46	2	45	136.4643	-6
48	3	45	47	2	46	137.2536	-25
46	4	43	47	3	44	100.6754	29
44	4	41	45	3	42	102.2957	32
43	4	40	44	3	41	103.1041	21
42	4	39	43	3	40	103.9131	21
41	4	38	42	3	39	104.7222	25
40	4	37	41	3	38	105.5271	-9
39	4	36	40	3	37	106.3395	36
38	4	35	39	3	36	107.1456	22
37	4	34	38	3	35	107.9521	15
36	4	33	37	3	34	108.7578	4
35	4	32	36	3	33	109.5657	18
34	4	31	35	3	32	110.3681	-19
33	4	30	34	3	31	111.1789	32
32	4	29	33	3	30	111.9816	5
27	4	24	28	3	25	116.0036	6
26	4	23	27	3	24	116.8023	-40
25	4	22	26	3	23	117.6090	-3
24	4	21	25	3	22	118.4112	-8
23	4	20	24	3	21	119.2129	-14
22	4	19	23	3	20	120.0163	0
21	4	18	22	3	19	120.8170	-10
20	4	17	21	3	18	121.6182	-11
19	4	16	20	3	17	122.4176	-27
18	4	15	19	3	16	123.2204	-6
17	4	14	18	3	15	124.0200	-13
16	4	13	17	3	14	124.8186	-27
15	4	12	16	3	13	125.6191	-18
14	4	11	15	3	12	126.4196	-6
13	4	10	14	3	11	127.2174	-17
12	4	9	13	3	10	128.0160	-17
11	4	8	12	3	9	128.8143	-17
10	4	7	11	3	8	129.6133	-6
9	4	6	10	3	7	130.4098	-17
8	4	5	9	3	6	131.2074	-13
7	4	4	8	3	5	132.0039	-16
6	4	3	7	3	4	132.7998	-22
5	4	2	6	3	3	133.5971	-11
4	4	1	5	3	2	134.3943	3
4	4	1	3	3	0	141.5375	-15
5	4	2	4	3	1	142.3289	-21
6	4	3	5	3	2	143.1192	-34
7	4	4	6	3	3	143.9084	-53
8	4	5	7	3	4	144.7008	-36
9	4	6	8	3	5	145.4916	-32
10	4	7	9	3	6	146.2805	-42
11	4	8	10	3	7	147.0723	-18
12	4	9	11	3	8	147.8587	-45
13	4	10	12	3	9	148.6507	-11
14	4	11	13	3	10	149.4390	-9

J'	K'_a	K'_c	J''	K''_a	K''_c	Wavenumbers	10^4(O-C)
15	4	12	14	3	11	150.2287	10
16	4	13	15	3	12	151.0147	-2
17	4	14	16	3	13	151.8024	7
18	4	15	17	3	14	152.5872	-9
19	4	16	18	3	15	153.3701	-38
20	4	17	19	3	16	154.1584	-9
21	4	18	20	3	17	154.9429	-13
22	4	19	21	3	18	155.7283	-3
23	4	20	22	3	19	156.5105	-21
24	4	21	23	3	20	157.2931	-29
25	4	22	24	3	21	158.0784	-5
26	4	23	25	3	22	158.8607	-5
27	4	24	26	3	23	159.6432	1
28	4	25	27	3	24	160.4239	-5
29	4	26	28	3	25	161.2054	2
30	4	27	29	3	26	161.9854	0
31	4	28	30	3	27	162.7656	5
32	4	29	31	3	28	163.5437	-5
33	4	30	32	3	29	164.3223	-4
34	4	31	33	3	30	165.1015	9
35	4	32	34	3	31	165.8791	11
36	4	33	35	3	32	166.6573	26
37	4	34	36	3	33	167.4326	18
38	4	35	37	3	34	168.2079	16
39	4	36	38	3	35	168.9830	19
40	4	37	39	3	36	169.7582	29
41	4	38	40	3	37	170.5305	16
42	4	39	41	3	38	171.3035	17
43	4	40	42	3	39	172.0753	14
44	4	41	43	3	40	172.8484	30
45	4	42	44	3	41	173.6185	23
46	4	43	45	3	42	174.3893	30
47	4	44	46	3	43	175.1590	34
48	4	45	47	3	44	175.9310	68
51	4	48	50	3	47	178.2317	64
52	4	49	51	3	48	179.0002	94
53	4	50	52	3	49	179.7588	34
54	4	51	53	3	50	180.5257	65
38	5	34	39	4	35	145.4153	-10
37	5	33	38	4	34	146.2265	0
31	5	27	32	4	28	151.0782	-15
30	5	26	31	4	27	151.8862	-10
29	5	25	30	4	26	152.6934	-8
27	5	23	28	4	24	154.3068	-3
26	5	22	27	4	23	155.1132	3
25	5	21	26	4	22	155.9186	2
24	5	20	25	4	21	156.7240	6
23	5	19	24	4	20	157.5304	25
22	5	18	23	4	19	158.3320	-1
21	5	17	22	4	18	159.1362	4
20	5	16	21	4	17	159.9387	-4
19	5	15	20	4	16	160.7425	5
18	5	14	19	4	15	161.5453	9
17	5	13	18	4	14	162.3470	6
16	5	12	17	4	13	163.1481	2
15	5	11	16	4	12	163.9494	4
14	5	10	15	4	11	164.7506	9
13	5	9	14	4	10	165.5510	11
12	5	8	13	4	9	166.3509	12
11	5	7	12	4	8	167.1501	12
10	5	6	11	4	7	167.9486	8
9	5	5	10	4	6	168.7471	10
8	5	4	9	4	5	169.5454	14
6	5	2	7	4	3	171.1397	13
5	5	1	6	4	2	171.9344	-5
5	5	1	4	4	0	180.6628	-7
6	5	2	5	4	1	181.4541	2
7	5	3	6	4	2	182.2437	-2
8	5	4	7	4	3	183.0330	-3
9	5	5	8	4	4	183.8223	2
10	5	6	9	4	5	184.6111	7
11	5	7	10	4	6	185.3986	4
12	5	8	11	4	7	186.1862	8
13	5	9	12	4	8	186.9728	7
14	5	10	13	4	9	187.7578	-4
15	5	11	14	4	10	188.5399	-39
16	5	12	15	4	11	189.3296	8
17	5	13	16	4	12	190.1149	17
18	5	14	17	4	13	190.8967	-4
19	5	15	18	4	14	191.6811	8
20	5	16	19	4	15	192.4639	9
21	5	17	20	4	16	193.2466	15
22	5	18	21	4	17	194.0265	-2
23	5	19	22	4	18	194.8095	19

TABLE I—*Continued*

$J'\ K'_a\ K'_c$	$J''\ K''_a\ K''_c$	Wavenumbers	10^4(O-C)	$J'\ K'_a\ K'_c$	$J''\ K''_a\ K''_c$	Wavenumbers	10^4(O-C)	$J'\ K'_a\ K'_c$	$J''\ K''_a\ K''_c$	Wavenumbers	10^4(O-C)
24 5 20	23 4 19	195.5880	1	34 5 30	33 4 29	203.3576	5	44 5 40	43 4 39	211.0599	-13
25 5 21	24 4 20	196.3678	2	35 5 31	34 4 30	204.1296	-10	45 5 41	44 4 40	211.8251	-27
26 5 22	25 4 21	197.1479	12	36 5 32	35 4 31	204.9017	-16	47 5 43	46 4 42	213.3545	-44
27 5 23	26 4 22	197.9259	7	37 5 33	36 4 32	205.6760	6	50 5 46	49 4 45	215.6536	34
28 5 24	27 4 23	198.7048	17	38 5 34	37 4 33	206.4485	16	51 5 47	50 4 46	216.4131	6
29 5 25	28 4 24	199.4810	6	39 5 35	38 4 34	207.2172	-4	52 5 48	51 4 47	217.1707	-34
30 5 26	29 4 25	200.2580	10	40 5 36	39 4 35	207.9877	0	53 5 49	52 4 48	217.9299	-50
31 5 27	30 4 26	201.0345	15	41 5 37	40 4 36	208.7570	-1	54 5 50	53 4 49	218.6903	-47
32 5 28	31 4 27	201.8085	2	42 5 38	41 4 37	209.5241	-17	55 5 51	54 4 50	219.4496	-47
33 5 29	32 4 28	202.5854	23	43 5 39	42 4 38	210.2927	-11				

recorded on a Bruker 113V FTIR instrument. The spectral resolution was measured to be 0.03 cm^{-1} in close agreement to the theoretical limit set by the maximum optical path difference of 32 cm. The wavenumbers of the absorption lines were determined by means of a peak-finder program, and the calibration was performed by means of the wavenumbers for selected water vapor lines measured by Kauppinen *et al.* (*6*). The appearance of water vapor lines is due to residual air in the instrument. To cover the whole spectral region where pure rotational transitions could be detected, two experiments were performed. The low-wavenumber range 20–130 cm^{-1} was measured using a 28-cm cell with Teflon windows and filled to 3 Torr pressure. The total scan time was 13 hr. To measure the high-wavenumber region (100–400 cm^{-1}), the total scan time was 12 hr using a 20-cm cell equipped with polyethylene windows and filled to 10 Torr pressure.

The results of the measurements are wavenumbers for about 1100 absorption lines. Nearly all lines were assigned to pure rotational transitions for HN_3 in the ground state or in the vibrationally excited states ν_5 and ν_6. For reasons explained later, not all lines were used in the analysis and only the wavenumbers used in the analysis are given in Table I.

Selected parts of the observed spectrum are shown in Figs. 1, 3, and 4.

ASSIGNMENTS

The HN_3 molecule is a slightly asymmetric rotor. The quantum number K_a for the limiting prolate top may then be used to identify the transitions. The spectrum appears as a number of subbands each corresponding to a value of K''_a (lower state) and the selection rules $\Delta K_a = 1$, $\Delta K_c = \pm 1$, and $\Delta J = 0, \pm 1$. The asymmetry of the molecule is observed through the splitting of the transitions starting from the $K''_a = 1$ and 2 levels (see Fig. 1). Using the previously determined values for the ground state parameters (*3, 5*), the assignments of the ground state transitions were straightforward. Thus 860 observed ground state transitions were identified, but only the assignments for the wavenumbers listed in Table I are given.

In addition to the pure rotational transitions in the ground state, about 250 pure rotational transitions in the ν_5 and ν_6 states were observed. The assignments were straightforward using the constants for these levels given in Ref. (*6*). Q and R branches for $K''_a = 2$ through 7 in the ν_5 state were identified whereas the P branches were too weak to be observed. In the ν_6 state Q and R branches for $K''_a = 2$, 4, and 5 were assigned.

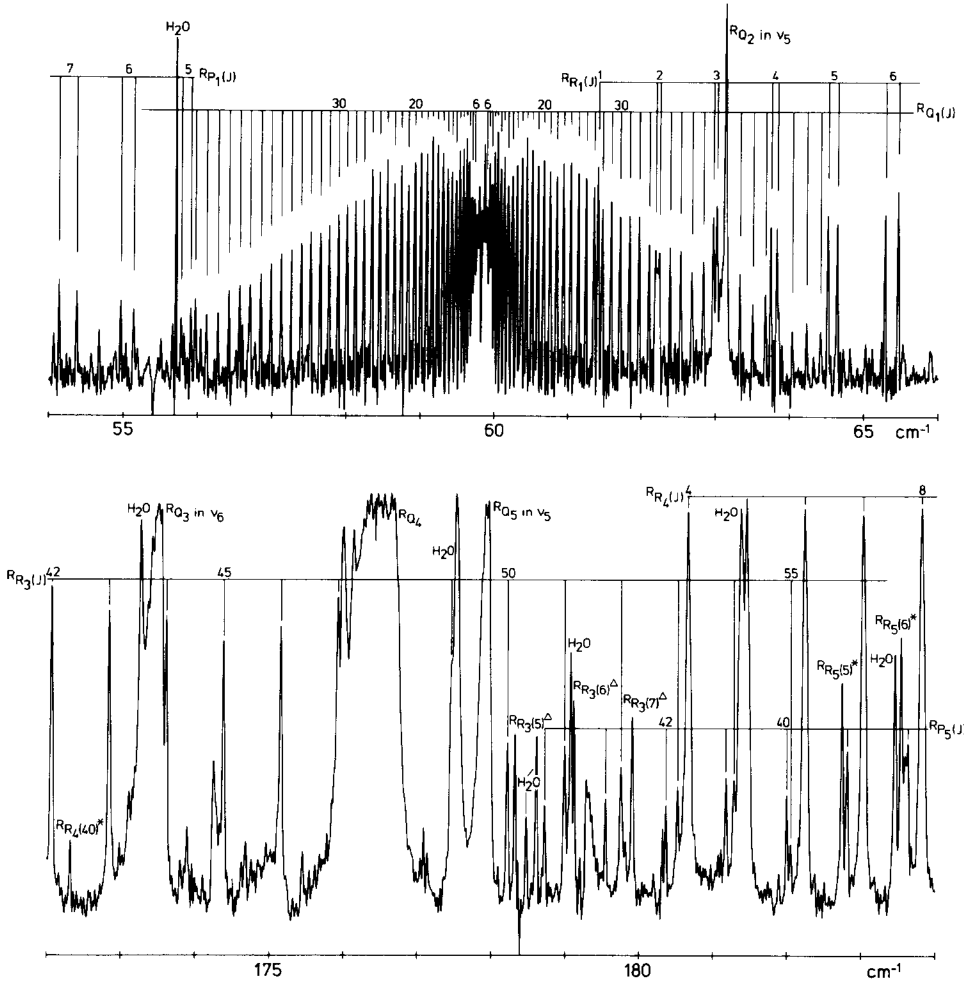

FIG. 1. The upper trace shows the region of the ${}^{R}Q_1(J)$ branch. The effect of the asymmetry of the molecule is clearly observed by the degradation to opposite wavenumbers of the two series of lines which constitute the Q branch. The lower trace shows the region of the unresolved ${}^{R}Q_4(J)$ branch, the ${}^{R}Q_5(J)$ branch in ν_5, and the ${}^{R}Q_3(J)$ branch in ν_6. Asterisks refer to the ν_5 state and Δ's refer to the ν_6 state.

GROUND STATE ANALYSIS

Each subband was subjected to a least-squares analysis using a fourth-order polynomial in the J-quantum number in order to determine the subband origins ν_{sub} and to check the assignments. The subband origins are given in Table II.

By means of the values for ν_{sub}, the energies for the K_a rotational levels of the ground state have been calculated, and the results are given in Table III.

Next, a least-squares analysis was performed on the assigned wavenumbers of the pure rotational spectrum using the Hamiltonian given by Watson (7). During the

TABLE II

Subband Origins (in cm^{-1})

K_a	Pure rotation in $\nu_5(\Delta K_a=1)$	$\nu_5(\Delta K_a=0)$	Pure rotation Gr.st.($\Delta K_a=1$)
0	(2.639)	537.2642(7)	19.977(7)
1	(26.919)	519.9259(5)	59.8196(7)
2	63.155(5)	487.0256(6)	99.3481(8)
3	101.466(1)	450.8227(4)	138.3649(3)
4	139.97(1)	413.9196(8)	176.7038(3)
5	177.989(1)	377.161(1)	214.2136(2)
6	215.12(1)	(340.936)	250.7705(3)
7	252.52(2)	(305.286)	286.323(2)
8		(271.483)	321.05(2)
9			353.37(4)
10			387.5(2)*

Note. The values have been obtained by analyzing each subband separately using the wavenumber expression for a diatomic molecule. The errors are standard deviations representing the quality of the fit only. Numbers in parentheses are calculated values.

* *Q*-branch maximum estimated from the spectrum.

TABLE III

Values (in cm^{-1}) for the K_a Rotational Energy Levels in the Ground State and in the ν_5 State of HN_3 Calculated from the Numbers Given in Table II

K_a	Ground state	ν_5 state
0	0	537.26
1	19.98	539.90
2	79.80	566.82
3	179.14	629.97
4	317.51	731.43
5	494.21	871.37
6	708.43	1049.36
7	959.20	1264.48
8	1245.52	1517.00
9	1566.57	
10	1919.94	
11	2307.4	

TABLE IV

Ground State Parameters (in cm^{-1}) for HN_3

		Far IR	Microwave/ Far IR	Microwave (Ref. 3)	Raman (Ref. 5)
	A	20.38166(7)	20.38193(2)	20.3806(2)	20.382(3)
	B	0.401437(9)	0.4014441(2)	0.4014158(2)	0.39718(2)
	C	0.392955(9)	0.3929588(2)	0.3929869(2)	
10^7	Δ_J	1.67(5)	1.56(2)	1.55(2)	1.97(7)
10^5	Δ_{JK}	2.632(9)	2.647(2)	2.639(4)	2.5(2)
10^3	Δ_K	8.955(6)	8.955*	7.7*	8.71(9)
10^9	δ_J	2.7(3)	2.97(8)	2.96(8)	0*
10^6	δ_K	3.5(3)	3.5*	0*	-
10^{13}	H_{JJJ}	2(15)	45(17)	29(12)	-
10^{10}	H_{JJK}	1.5(4)	19(6)	14(3)	-
10^8	H_{JKK}	-4.0(2)	-3.8(2)	-4.0(1)	-
10^5	H_{KKK}	1.28(2)	1.28*	0	0.74(9)

* Constrained.

analysis it turned out that only wavenumbers assigned to $K_a'' \leqslant 4$ would fit the analysis. This may be explained by c-type Coriolis interaction and centrifugal distortion interactions (8) between the ground state levels and the ν_5 levels. The lack of fit for wavenumbers assigned to $K_a'' \geqslant 5$ are K_a dependent as well as J dependent.

The final analysis therefore includes the 533 lines of the five lowest subbands only. The results of the analysis are given in Table IV.

To get an impression of the magnitude of the perturbation, the following transitions were calculated by means of the constants given in the first column of Table IV and compared to the observed wavenumbers:

Transition	Observed wavenumbers	Obs. − Calc.
$39_{6,33} \rightarrow 40_{7,34}$	281.569	−0.267
$40_{7,33} \rightarrow 41_{8,34}$	315.397	−2.662
$38_{8,30} \rightarrow 39_{9,31}$	356.450	5.387
$28_{9,19} \rightarrow 29_{10,20}$	375.535	−1.703

HOT BAND ANALYSIS

Each subband of the hot bands was analyzed similarly to the ground state subbands. The calculated subband origins are included in Table II for the ν_5 state, and in addition,

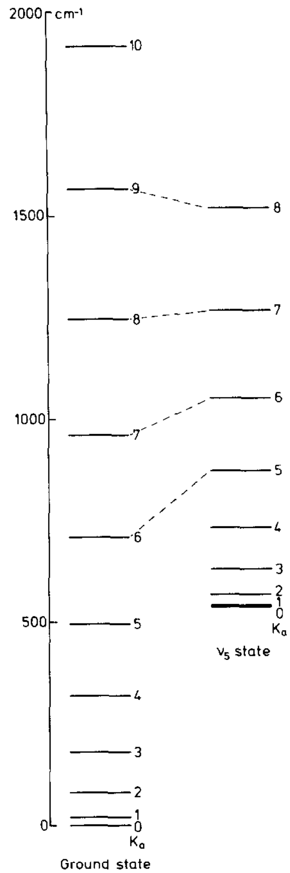

FIG. 2. Plot of the rotational energy levels in the ground state and in the ν_5 state (see text).

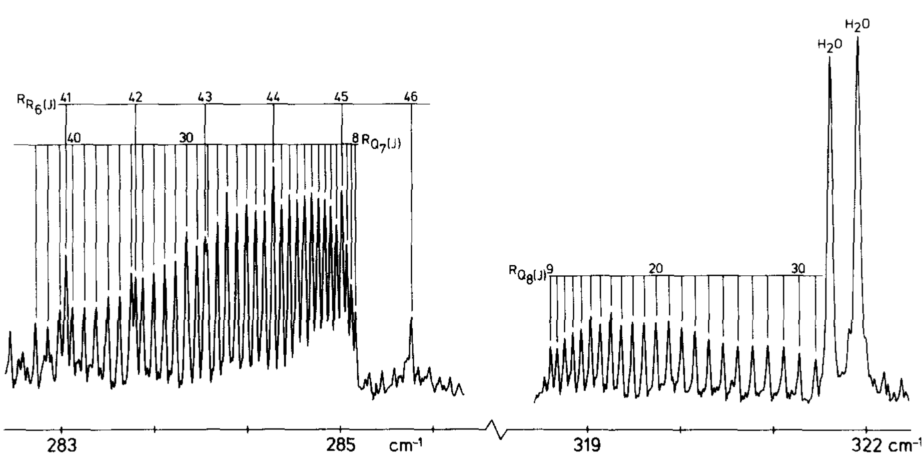

FIG. 3. Traces showing the degradation of the $^{R}Q_7(J)$ and the $^{R}Q_8(J)$ branches in the ground state.

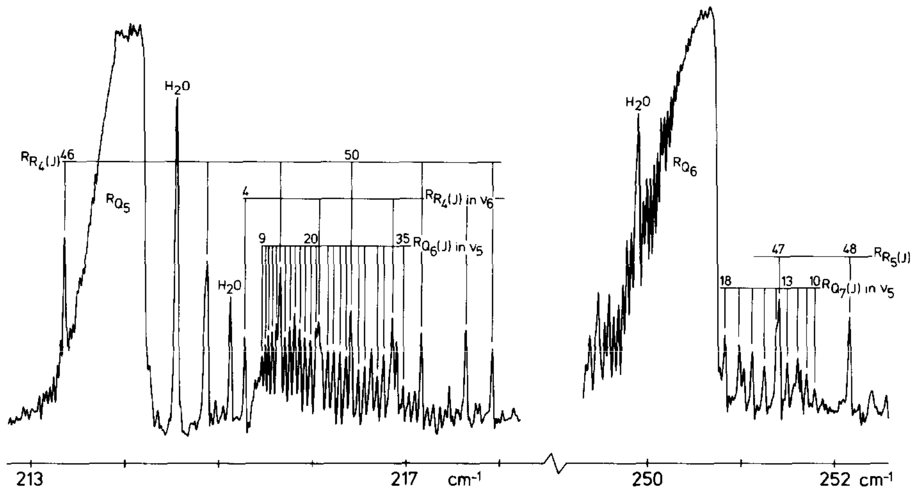

FIG. 4. Traces showing the degradation of the ${}^{R}Q_6(J)$ and ${}^{R}Q_7(J)$ branches in the ν_5 state.

the values for the subband origins for the ν_5 band are given. These last mentioned values are calculated from the observed ν_5 lines with $\Delta K_a = 0$ given in Ref. (*9*).

From these data, five additional subband origins (which are not directly observed) may be determined. The values are given in parentheses in Table II.

Combining all values given in Table II, the K_a-dependent part of the energy levels with $K_a'' = 0$ through 10 and 8 may be determined for the ground state and the ν_5 state, respectively. The results are given in Table III and the values are used for Fig. 2.

The hot bands of the ν_6 fundamental do not contribute any new information of this band, and therefore the values for the subband origins are not included in Table II.

TABLE V

Reduced Frequencies (in MHz) Evaluated as Described in Ref. (*3*)

J"	K_a''	K_c''	J'	K_a'	K_c'	Frequency	Obs.-Calc.
2	0	2	3	0	3	71446.069	0.081
2	1	2	3	1	3	71062.607	0.146
2	1	1	3	1	2	71820.772	0.244
12	1	12	12	1	11	19705.890	0.053
23	0	23	22	1	22	19792.439	0.045

DISCUSSION

As mentioned, there might be a c-type Coriolis interaction and centrifugal distortion interactions between the ground state levels and the ν_5 levels. Levels differing in K_a by ± 1, ($\pm 3 \cdots$) are interacting. Looking at the energy level diagram in Fig. 2, it is seen that the ground state levels with $K_a = 6$, 7, 8, and 9 are very close to the levels of ν_5 that have $K_a = 5$, 6, 7, and 8, respectively. For the ground state $K_a = 8$ and 9, a crossing occurs. The effect of the crossing would be expected to be a lowering of the $K_a = 8$ levels and a pushing up of the $K_a = 9$ levels. This is experimentally verified by the appearance of the $^RQ_7(J)$ and $^RQ_8(J)$ branches which are degraded to lower and higher wavenumbers, respectively. The spectra of these two Q branches are shown in Fig. 3.

The Coriolis resonance may have a similar effect on the $^RQ_6(J)$ and $^RQ_7(J)$ pure rotational branches in the ν_5 state. Through the interaction where $^RQ_7(J)$ (ground state) lines are degraded to lower wavenumbers, the $^RQ_6(J)$ (ν_5) lines must be pushed upward and vice versa for $^RQ_8(J)$ (ground state) and $^RQ_7(J)$ (ν_5). The two hot band Q branches are shown in Fig. 4. The $^RQ_6(J)$ is clearly degraded to higher wavenumbers. The $^RQ_7(J)$ branch is partly obscured by the $^RQ_6(J)$ ground state branch, but the few lines on the high-wavenumber side of the $^RQ_6(J)$ ground state branch clearly indicate a series of lines degrading to lower wavenumbers.

The present determination of ground state parameters are based on those transitions which are unaffected by the Coriolis resonance as measured with the present resolution and wavenumber accuracy. The results are given in the first column of Table IV together with previously determined values (columns 3 and 4). When comparable, it is seen that the agreement between the values obtained by the different types of experiments is satisfactory. However, the values obtained from the microwave data are dependent of the values for Δ_K, δ_K, and H_{KKK}. During the time the microwave data were analyzed, the value for Δ_K was taken as the value of D_K given in Ref. (*4*), and δ_K and H_{KKK} had to be constrained to zero because no values for these constants were available.

In the present work, a value for δ_K has been determined and the accuracy of the values of Δ_K and H_{KKK} have been improved considerably compared to the values obtained by Raman spectroscopy. Consequently, the microwave data have been reanalyzed, constraining Δ_K, δ_K, and H_{KKK} to the values obtained in this investigation. In addition, frequencies measured later for other transitions than those given in Ref. (*3*) have been included in the reanalysis of the microwave data. The additional microwave frequencies are given in Table V. The results of this analysis are given in column 2 of Table IV. Comparing columns 1 and 2, it is seen that the agreement between the values obtained is excellent.

The model used does not account for the interaction between the ground state and the ν_5 and ν_6 states. In the analyses of the spectra of ν_5 and ν_6, the interaction between these two bands were taken into account. The next step is to take into account the mutual interaction of all three states, and work is in progress to develop a program by which all three bands may be analyzed simultaneously.

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