

## THE ROTATIONAL SPECTRUM OF NITRIC ACID: THE FIRST FIVE VIBRATIONAL STATES

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**Abstract**—With the work reported here, we have completed a series of rotational analyses of the  $\nu_9$ ,  $\nu_7$ ,  $\nu_6$ , and  $\nu_8$  vibrational states of the important atmospheric species nitric acid. In this paper, we report the details of our work on the  $\nu_8$  vibrational state, which arise from the  $\text{NO}_2$  out of plane vibration. For this state, over 210 transitions have been measured in the millimeter and submillimeter spectral region and analyzed with Watson's A reduced centrifugal distortion Hamiltonian. In the course of our work on the excited vibrational states, a number of additional lines of the ground state have been observed and a more complete analysis of the ground state is provided. Also included in this work is a comparison of all these spectra and an overview of the millimeter and submillimeter spectra associated with these states. Although at the high sensitivity available in laboratory experiments, many additional lines are observable, all arise from vibrational states whose populations are more than 100 times lower than the ground state. The most prominent of these are due to the states which give rise to the perturbed  $2\nu_9$  and  $\nu_5$  bands near  $11\mu\text{m}$ . These results provide a significant data base for both atmospheric remote sensing experiments and spectral analyses of data in other spectral regions, especially the infrared (i.r.).

### INTRODUCTION

Nitric acid ( $\text{HNO}_3$ ) is both a common chemical species and an important minor constituent of the terrestrial atmosphere. As a result it has received considerable spectroscopic attention,<sup>1-18</sup> both in the microwave and i.r. spectral regions. As we have shown previously, with the spectral range available to our millimeter and submillimeter (mm/submm) techniques, it is possible to acquire enough data so that all unperturbed thermally populated rotational levels can be calculated with good accuracy from measurements of the pure rotational spectrum.

We have previously analyzed the rotational spectrum of its ground vibrational state,<sup>3,4,6</sup>  $\nu_9$  at  $456\text{ cm}^{-1}$ ,<sup>14</sup>  $\nu_7$  at  $579\text{ cm}^{-1}$ ,<sup>15</sup> and  $\nu_6$  at  $647\text{ cm}^{-1}$ .<sup>16</sup> In this paper we report the measurement and assignment of 215 transitions in the  $\nu_8$  excited vibrational state at  $762\text{ cm}^{-1}$ . Also reported in this paper are 193 newly measured lines, most of which are highly excited, of the ground vibrational state that were measured during the course of this work and an analysis of these data. Finally, we show a comparison among the spectral constants of these states and discuss the general nature of the spectra and their relation to atmospheric remote sensing experiments.

### EXPERIMENTAL STUDIES

The experimental techniques, which we have developed for high-resolution spectroscopy in the mm/submm, have been discussed in detail elsewhere.<sup>15,19-21</sup> In this work, we have used both a broad band mm/submm spectrometer based on YIG oscillator and TWT technology,<sup>15</sup> which was especially useful in the assignment of these spectra, as well as a klystron-driven system with a  $^3\text{He}$  detector which was used for many of the higher frequency transitions.<sup>19-21</sup>

$\text{HNO}_3$  gas was obtained from a mixture of fuming nitric and sulfuric acids. The sulfuric acid, which has very low vapor pressure, was included in the mixture to bind water and thereby increase

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the purity of the  $\text{HNO}_3$  gas. The measurements were carried out in a variety of room-temperature cells, the length of which was typically 1m. Although  $\text{HNO}_3$  is a reactive gas, no extraordinary precautions were required. In a stainless steel and glass system, the sample was stable for long periods. In systems containing copper and brass, it was necessary to renew the sample periodically. Although a very wide range of states was observed, it is clear that the spectroscopy could be extended to much higher energy by the use of longer and/or heated cells.

## THEORY

We have used Watson's reduced centrifugal distortion Hamiltonian in its A form for all of our analyses of the vibrational states of nitric acid.<sup>22</sup> Through terms of the 8th order in the angular momentum, the Hamiltonian is

$$\mathcal{H} = \mathcal{H}_r + \mathcal{H}_d^{(4)} + \mathcal{H}_d^{(6)} + \mathcal{H}_d^{(8)}, \quad (1)$$

$$\mathcal{H}_r = 1/2 (B_y + B_z)P^2 + [B_x - 1/2(B_y + B_z)](P_z^2 - b_p P_z^2), \quad (2)$$

$$\mathcal{H}_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 P_z^2 - \delta_K (P_z^2 P_z^2 + P_z^2 P_z^2), \quad (3)$$

$$\mathcal{H}_d^{(6)} = H_J P^6 + H_{JK} P^4 P_z^2 + H_{KJ} P^2 P_z^4 + H_K P_z^6 + 2h_J P^4 P_z^2 + h_{JK} P^2 (P_z^2 P_z^2 + P_z^2 P_z^2) + h_K (P_z^4 P_z^2 + P_z^2 P_z^4), \quad (4)$$

Table 1. Assignments of observed transitions for  $\nu_8$  (MHz).

J'K'-K'+	J''K''-K''+	Observation	Observed - Calculated	J'K'-K'+	J''K''-K''+	Observation	Observed - Calculated
9 1 8 - 8	1 7	131352.490	0.008	17 5 12 - 16	5 11	281242.382	0.015
9 4 6 - 8	4 5	156271.044	0.001	17 6 11 - 16	6 10	293704.638	0.112
10 0 10 - 9	0 9	131430.908	-0.089	17 9 8 - 16	9 7	331502.247	0.072
10 1 9 - 9	1 8	143871.240	-0.093	17 10 8 - 16	10 7	331449.968	-0.152
10 2 8 - 9	2 7	156315.927	0.009	17 11 7 - 16	11 6	344197.593	0.159
11 2 9 - 10	2 8	168832.051	0.008	18 2 16 - 17	2 15	256440.270	-0.035
11 4 7 - 10	4 6	193767.578	-0.024	18 3 15 - 17	3 14	268872.314	0.096
11 5 7 - 10	5 6	193764.941	-0.053	18 3 16 - 17	3 15	256440.255	-0.050
12 0 12 - 11	0 11	156469.736	-0.044	18 4 14 - 17	4 13	281306.591	0.110
12 1 11 - 11	1 10	168908.302	0.000	18 5 13 - 17	5 12	293746.826	-0.006
12 2 10 - 11	2 9	181348.486	0.070	18 5 13 - 17	5 12	318676.966	-0.045
12 6 7 - 11	6 6	218773.640	0.065	18 7 11 - 17	7 10	343822.705	0.076
13 0 13 - 12	0 12	168988.574	-0.009	18 9 9 - 17	9 8	343816.210	0.180
13 2 11 - 12	2 10	193864.697	-0.020	18 10 9 - 17	10 8	459868.244	-0.034
13 4 9 - 12	4 8	218764.086	-0.069	18 17 1 - 17	16 2	459813.127	-0.009
13 5 8 - 12	5 7	231252.685	0.064	18 17 2 - 17	16 1	256523.095	-0.078
13 9 4 - 12	9 3	287812.150	0.160	19 1 18 - 18	1 17	268953.759	0.044
13 10 3 - 12	10 2	290177.462	-0.007	19 2 17 - 18	2 16	281383.837	-0.065
14 0 14 - 13	0 13	181506.884	-0.064	19 3 16 - 18	3 15	293815.576	-0.035
14 1 13 - 13	1 12	193943.701	-0.046	19 4 15 - 18	4 14	318697.568	-0.023
14 2 12 - 13	2 11	206380.850	0.092	19 6 13 - 18	6 12	368917.197	0.013
14 3 11 - 13	3 10	218820.996	-0.010	19 10 9 - 18	10 8	382005.469	0.017
14 4 10 - 13	4 9	231270.458	0.037	19 11 8 - 18	11 7	368900.579	0.002
14 6 8 - 13	6 7	256262.987	-0.135	19 11 9 - 18	11 8	381748.014	0.078
14 7 8 - 13	7 7	256260.155	-0.250	19 12 8 - 18	12 7	256606.005	-0.095
14 9 6 - 13	9 5	281411.519	0.008	20 0 20 - 19	0 19	269037.255	0.073
15 0 15 - 14	0 14	194024.853	0.011	20 1 19 - 19	1 18	256606.176	0.076
15 1 14 - 14	1 13	206460.742	-0.021	20 1 20 - 19	1 19	281466.357	-0.081
15 3 12 - 14	3 11	231334.243	0.033	20 2 18 - 19	2 17	318757.007	0.032
15 4 11 - 14	4 10	243778.564	-0.021	20 5 15 - 19	5 14	331196.837	-0.062
15 5 10 - 14	5 9	256238.085	-0.081	20 6 14 - 19	6 13	394060.819	-0.110
15 8 7 - 14	8 6	294119.995	0.089	20 11 9 - 19	11 8	281550.390	-0.094
15 10 6 - 14	10 5	306372.247	0.066	21 1 20 - 20	1 19	293978.368	-0.065
16 0 16 - 15	0 15	206542.216	-0.017	21 2 19 - 20	2 18	318832.433	0.004
16 1 15 - 15	1 14	218977.197	-0.054	21 4 17 - 20	4 16	331261.971	0.050
16 2 14 - 15	2 13	231411.620	0.017	21 5 16 - 20	5 15	368607.180	-0.097
16 4 12 - 15	4 11	256287.744	0.079	21 8 13 - 20	8 12	381105.625	0.085
16 5 11 - 15	5 10	268739.111	-0.007	21 9 12 - 20	9 11	450507.963	0.013
16 6 10 - 15	6 9	281213.808	0.018	21 14 7 - 20	14 6	443872.344	-0.028
16 8 8 - 15	8 7	306375.647	0.010	21 15 7 - 20	15 6	470529.270	0.071
16 14 2 - 15	12 3	447382.455	-0.087	21 16 5 - 20	16 4	450926.531	-0.005
17 0 17 - 16	0 16	219059.033	-0.053	21 16 6 - 20	16 5	457842.046	-0.055
17 1 16 - 16	1 15	231493.208	0.035	21 17 4 - 20	17 3	451191.356	-0.041
17 2 15 - 16	2 14	243926.308	0.057	21 17 5 - 20	17 4	448296.276	0.005
17 3 14 - 16	3 13	256359.912	-0.060	21 18 3 - 20	18 2	447387.561	0.006
17 4 13 - 16	4 12	268797.119	0.035	21 18 4 - 20	18 3	443214.733	0.028
				21 19 2 - 20	19 1		

Table 1—continued

J'k'-K'+ J''k''-K''+	Observation	Observed - Calculated	J'k'-K'+ J''k''-K''+	Observation	Observed - Calculated
22 022 -21 021	281634.033	-0.130	29 327 -29 128	341775.937	0.131
22 121 -21 120	294062.988	-0.058	29 623 -28 622	443685.863	0.004
22 418 -21 417	331339.857	-0.033	29 722 -28 721	456095.265	-0.016
22 517 -21 516	343766.438	-0.032	29 821 -28 820	468507.232	0.009
22 1012 -21 1011	406092.441	0.053	29 1118 -28 1117	505787.970	-0.052
22 13 9 -21 13 8	444570.778	0.067	30 030 -29 029	381714.568	0.028
22 14 8 -21 14 7	459130.123	0.088	30 427 -30 228	341645.801	-0.036
22 14 9 -21 14 8	444385.264	-0.033	30 525 -29 524	443774.777	0.003
22 15 7 -21 15 6	477988.882	0.123	30 822 -29 821	480994.901	0.035
22 15 8 -21 15 7	457292.928	0.026	30 723 -29 722	468586.829	-0.082
22 16 7 -21 16 6	468253.552	0.036	30 921 -29 920	493406.689	-0.017
22 17 6 -21 17 5	473581.978	-0.032	31 130 -30 129	406637.337	0.010
22 18 4 -21 18 3	476895.452	0.004	31 427 -30 426	443866.628	-0.013
22 18 5 -21 18 4	472340.032	0.001	31 527 -31 328	341507.832	0.022
22 20 2 -21 20 1	463852.096	-0.027	31 526 -30 525	456271.133	-0.092
22 20 3 -21 20 2	463817.479	-0.035	31 625 -30 624	468674.518	0.027
23 023 -22 022	294147.021	-0.091	31 724 -30 723	481077.522	0.012
23 221 -22 220	319000.142	0.058	31 823 -30 822	493481.618	-0.048
23 320 -22 319	331423.541	-0.109	31 922 -30 921	505888.767	-0.025
23 419 -22 418	343846.711	0.107	32 032 -31 031	406725.337	-0.031
23 617 -22 616	368697.386	-0.046	32 329 -31 328	443959.600	-0.020
23 914 -22 913	406040.328	-0.003	32 428 -31 427	456364.167	-0.091
23 1310 -22 13 9	456600.703	-0.085	32 527 -31 526	468766.428	-0.054
23 14 9 -22 14 8	469997.771	-0.028	32 626 -31 625	481167.084	0.012
23 1410 -22 14 9	456571.990	-0.113	32 627 -32 428	341361.184	-0.159
23 15 9 -22 15 8	469623.976	0.023	33 231 -32 230	444052.458	0.049
23 16 8 -22 16 7	482371.676	0.126	33 330 -32 329	456458.145	-0.012
23 19 5 -22 19 4	493256.693	0.029	33 627 -32 626	493658.453	0.030
23 20 3 -22 20 2	488972.598	-0.009	33 727 -33 528	341206.033	-0.003
23 20 4 -22 20 3	488662.546	-0.055	34 133 -33 132	444143.990	-0.019
23 21 2 -22 21 1	484497.938	-0.045	34 232 -33 231	456551.656	-0.047
23 21 3 -22 21 2	484479.657	0.126	34 331 -33 330	468955.428	-0.044
24 123 -23 122	319085.800	-0.016	34 530 -34 331	378715.161	-0.114
24 222 -23 221	331509.618	-0.050	35 035 -34 034	444233.557	-0.046
24 321 -23 320	343931.578	0.002	35 134 -34 133	456644.007	0.064
24 519 -23 518	368773.876	0.099	35 233 -34 232	469049.801	0.018
24 618 -23 617	381197.301	0.025	35 431 -34 430	493849.601	-0.052
24 1113 -23 1112	443516.076	-0.008	35 630 -35 431	378553.650	-0.019
24 1411 -23 1410	468826.338	-0.050	35 927 -35 728	340867.147	-0.088
25 025 -24 024	319170.731	0.045	36 135 -35 134	469142.689	0.014
25 124 -24 123	331595.970	0.012	36 234 -35 233	481546.584	-0.032
25 223 -24 222	344018.400	0.024	36 333 -35 332	493946.320	0.017
25 421 -24 420	368857.505	-0.025	36 730 -36 531	378383.668	-0.046
25 1015 -24 1014	443459.055	0.025	36 1027 -36 828	340682.793	-0.069
25 1213 -24 1212	468505.238	-0.041	37 037 -36 036	469233.402	0.027
26 125 -25 124	344105.191	-0.036	37 136 -36 135	481640.115	-0.057
26 620 -25 619	406195.161	-0.038	37 235 -36 234	494042.107	-0.062
26 1016 -25 1015	455928.005	0.067	37 1127 -37 928	340487.888	-0.005
26 1115 -25 1114	468405.077	0.014	38 038 -37 037	481731.519	0.071
27 027 -26 026	344190.937	-0.005	38 137 -37 136	494136.404	0.002
27 225 -26 224	369033.100	0.073	38 930 -38 731	378017.405	-0.010
27 819 -26 818	443530.217	0.166	39 138 -38 137	506631.408	0.077
27 1017 -26 1016	468400.014	-0.003	39 1030 -39 831	377820.404	0.039
27 1116 -26 1115	480861.882	0.068	40 040 -39 039	506723.766	-0.039
28 127 -27 126	369121.139	0.125	40 139 -39 138	519125.009	0.082
28 226 -27 225	381538.927	0.026	41 041 -40 040	519217.987	-0.036
28 227 -28 028	341898.064	-0.019	42 736 -42 537	452665.134	0.111
28 424 -27 423	406366.809	-0.052	44 837 -44 638	464814.343	0.034
28 721 -27 720	443602.718	0.003	44 936 -44 737	452228.372	0.059
28 820 -27 819	456018.958	0.069	45 1036 -45 837	451997.265	-0.018
28 1018 -27 1017	480874.145	0.026	46 1037 -46 838	464347.390	-0.042
29 029 -28 028	369207.693	0.071			

$$\mathcal{H}_d^{(8)} = L_J P^8 + L_{JK} P^6 P_z^2 + L_{JK} P^4 P_z^4 + L_{KKJ} P^2 P_z^6 + L_K P_z^8 + 2l_J P^6 P_z^2 + l_{JK} P^4 (P_z^2 P_z^2 + P_z^2 P_z^2) + l_{KJ} P^2 (P_z^4 P_z^2 - P_z^4) + l_K (P_z^6 P_z^2 + P_z^2 P_z^6), \quad (5)$$

where  $\Delta_j$  etc. are the quartic distortion coefficients;  $H_j$  etc. are the sextic distortion coefficients;  $L_j$  etc. are the 8th order distortion coefficients;  $b_p = (B_z - B_y)/(2B_x - B_y - B_z)$  is Wang's asymmetry parameter,  $P^2 = P_x^2 + P_y^2 + P_z^2$ . Here, we have used the definition

$$P_z^2 = P_x^2 - P_y^2. \quad (6)$$

We have previously discussed our implementation of this theory.<sup>23-25</sup> All states have been analyzed using III<sup>1</sup> representation, which identifies the pseudo-oblate top c-axis with the z-axis.

Table 2. Results of analyses (MHz).

Constant	Ground State	$\nu_9$	$\nu_7$	$\nu_6$	$\nu_8$
$B_x$	13011.0363(9)	12998.9857(17)	13028.9751(20)	13006.2313(19)	12998.0750(40)
$B_y$	12099.8672(9)	12015.1109(14)	12098.5694(18)	12057.4635(14)	12005.4674(37)
$B_z$	6260.64550(83)	6255.24152(100)	6201.61605(110)	6282.34695(97)	6260.81793(62)
$\Delta_J$ ( $\times 10^1$ )	0.1411303(118)	0.1376247(173)	0.1455271(227)	0.1450237(233)	0.1398794(266)
$\Delta_{JK}$ ( $\times 10^1$ )	-0.2016851(263)	-0.1898288(582)	-0.2009457(858)	-0.2195221(621)	-0.1900644(1073)
$\Delta_K$ ( $\times 10^2$ )	0.7391763(1958)	0.657399(537)	0.604707(777)	0.969217(586)	0.636145(1014)
$\delta_J$ ( $\times 10^2$ )	0.118207(37)	0.12182(22)	0.12785(46)	0.14689(14)	0.12007(103)
$\delta_K$ ( $\times 10^1$ )	-0.205381(80)	-0.199121(282)	-0.27632(55)	-0.13082(35)	-0.17833(59)
$H_J$ ( $\times 10^7$ )	0.18871(681)	0.1895(193)	0.41398(3140)		0.51047(6505)
$H_{JK}$ ( $\times 10^7$ )	-0.941481(47120)	-2.1043(1288)	-5.32575(23190)	-1.3798(4194)	-2.6373(3024)
$H_{KJ}$ ( $\times 10^7$ )	0.989368(126900)	4.41454(2203)	11.3406(3971)	4.1976(12790)	4.14585(28780)
$H_K$ ( $\times 10^7$ )	-0.23920(8575)	-2.4851(1312)	-6.80644(19780)	-2.5066(8764)	-2.0240(533)
$h_J$ ( $\times 10^8$ )	-0.97610(2926)	-0.955(223)	-1.94(73)		-5.814(1537)
$h_{JK}$ ( $\times 10^8$ )	-0.1102(97)	0.1224(491)	0.6103(1014)	-0.125(89)	0.194(120)
$h_{KJ}$ ( $\times 10^8$ )	0.11170(350)	0.00760(568)	-0.02870(990)	-0.06546(3604)	
$L_J$ ( $\times 10^{12}$ )	-0.1564(1404)				
$L_{JK}$ ( $\times 10^{11}$ )	0.49019(9097)			3.4299(22610)	
$L_{JK}$ ( $\times 10^{10}$ )	-0.367702(27670)		0.01937(343)	-0.94605(68860)	
$L_{KKJ}$ ( $\times 10^{10}$ )	0.750362(37290)			0.59592(46610)	
$L_K$ ( $\times 10^{10}$ )	-0.430728(17730)	-0.00368(232)			
$l_J$ ( $\times 10^{13}$ )	0.998(701)				
$l_{JK}$ ( $\times 10^{11}$ )	-0.500(268)			-6.21(411)	
$l_{KJ}$ ( $\times 10^{10}$ )	0.1337(731)			2.290(1975)	
$l_K$ ( $\times 10^{10}$ )	-0.2552(406)				
rms	0.109	0.124	0.068	0.086	0.066
lines	465	234	148	188	215

THE  $\nu_8$  STATE

The  $\nu_8$  vibrational state, which is derived from the  $\text{NO}_2$  out-of-plane vibration, lies  $762\text{ cm}^{-1}$  above the ground state<sup>8</sup> and results in transition strengths that are reduced by a factor of about 50. Although the mm/submm spectrum of nitric acid is very crowded, our previous analyses of the lower-lying vibrational states allowed us to eliminate the large proportion of stronger lines that did not belong to  $\nu_8$  and greatly simplified the assignment. The rotational spectrum reported here was associated with the band identified in the i.r. as  $\nu_8$  on the basis of its intensity relative to the other vibrational states. Table 1 shows the 215 lines of this state that have been measured and assigned. These cover the range from  $J = 9$  to 46 and from  $K_p = 0$  to 21. The spectral constants that result from analysis of these data are shown in Table 2, along with the rms deviation of the fit, 0.066 MHz. Because of correlations among the constants, it is necessary to retain more digits in the spectral constants than indicated by the uncertainties, so that the spectrum can be accurately calculated from the constants.

## THE GROUND STATE

Although we have published extensive analyses of the ground state of nitric acid, in the course of this work our search for the substantially weaker lines of the excited vibrational states has led us to measure 194 additional lines of the ground-state spectrum. Many of these are at higher energy than those previously measured. This fact allows not only an improved calculation of the ground-state spectrum and its associated spectral constants, but the additional redundancy strengthens our test for misassigned lines and extends the frontier of assignment surety to substantially higher energy.

Table 3 lists the newly-measured transitions; the rest of the data set is not reproduced here but is taken from Refs. 1–6. These range to  $J = 70$  and to  $K_p = 51$ . The constants that result from this analysis are shown in Table 2, along with the deviation of the fit, 0.109 MHz. This deviation is somewhat larger than current measurement uncertainties, estimated to average 0.100 MHz, because of the large number of data sources that have been included in the analysis.

## OVERVIEW OF THE FIRST FIVE VIBRATIONAL STATES OF NITRIC ACID

The strongest features in the nitric acid spectrum are due to  $\Delta J = 1$  transitions that are quadruply degenerate. These transitions are of the form

$$J' - n(n, J' - 2n) \rightarrow J' - 1 - n(n, J' - 1 - 2n), \quad (7)$$

$$J' - n(n + 1, J' - 2n) \rightarrow J' - 1 - n(n + 1, J' - 1 - 2n), \quad (8)$$

$$J' - n(n, J' - 2n) \rightarrow J' - 1 - n(n + 1, J' - 1 - 2n), \quad (9)$$

$$J' - n(n + 1, J' - 2n) \rightarrow J' - 1 - n(n, J' - 1 - 2n), \quad (10)$$

where  $J'$  is the maximum  $J$  value for the branch and where  $n = 0, 1, 2, \dots$ . These values occur in bands of lines which, in the near oblate asymmetric-rotor limit, are separated by  $B_x + B_y - 4B_z$ .<sup>17</sup> For the vibrational states of nitric acid, this number is nearly zero and the bands are closely spaced. The spectra of the several states were assigned by using our broadband spectrometer to record the spectrum around the location of the band head. The different states then appeared as families of equally-spaced lines that were identifiable on the basis of their relative strengths. Identification of the observed spectra with the previously defined vibrational numbering scheme was done by an extensive intercomparison of the relative intensities. For lines of reasonable strength, the intensity ratios agreed with expectations to about 10%.

In addition to their utility in assigning the spectra, transitions of the type discussed have been used for the detection of the ground state of nitric acid in the atmosphere. The near degeneracy of many strong lines in each branch of the ground state provides easily identifiable spectroscopic features;<sup>6</sup> airborne observations of stratospheric emission spectra have detected these features.<sup>26,27</sup> Each excited vibrational state displays a similar near degeneracy of strong transitions, raising the possibility of assigning excited state transitions in atmospheric spectra.

In Table 2 we have collected together the spectral constants of the ground state and the first four vibrational states  $\nu_9$ ,<sup>14</sup>  $\nu_7$ ,<sup>15</sup>  $\nu_6$ ,<sup>16</sup> and  $\nu_8$  of nitric acid. At very high resolution, the torsional motion of the  $\text{NO}_2$  group, which gives rise to the  $\nu_9$  vibrational state, produces a small splitting (about 2MHz) in the observed b-type rotational spectrum.<sup>14</sup> The constants shown in Table 2 for that state are from an analysis of 234 lines of the essentially unperturbed a-type spectrum; these results are representative of all the states that lie below  $1200 \text{ cm}^{-1}$ . Although, for each of these states, a large amount of data was acquired (more than 1000 transitions were measured), the observed data represent only a small fraction of the observable transitions. It was the aim of this work to measure a sufficiently large number of lines in each vibrational state to be able to predict accurately all thermally populated energy levels. Since there is no step function in the thermal population, as a practical matter this work includes levels whose energy was below approx.  $1200 \text{ cm}^{-1}$  (6 kT).

None of these states have shown any evidence of perturbation. In all cases, the theoretical fit to the experimental data has been as expected. In addition, the lower-order distortion constants are relatively constant among the vibrational states. This observation is unlike the well known cases for which there are interactions among different vibrational states; such interactions are often manifested in widely-varying distortion constants since these constants are correlated with the neglected interaction terms.

Because of the extremely crowded nature of this spectrum and the large number of states involved, we have made extensive use of the procedure in which observed lines are removed one at a time from the data set, the remaining lines were analyzed to predict the frequency of the removed line, and comparisons were then made between the predicted frequency, the calculated uncertainty in the predicted frequency, and the observed transition frequency. During the course of these checks, we have found three previously assigned ground-state lines, which are probably incorrectly assigned or blended with another absorption. These are listed in Table 4 and have been removed from the analysis. Although this procedure does not completely ensure against the inclusion of misassigned lines in the analyses of the several vibrational states, the procedure, combined with the substantial redundancy of the data sets, does ensure that any possible misassignments will have no significant effect on the results.

We have also recently reported a systematic study of pressure broadening of nitric acid by both  $O_2$  and  $N_2$ .<sup>18</sup> In that work, 16 transitions in the ground state that are representative of the strong transitions in the mm/submm spectrum of nitric acid were selected for study. Since little variation is expected among the pressure-broadening parameters of the vibrational states, these results should be applicable to all of the spectra reported here, as well as to the vibrational-rotational bands in the infrared. These results, which are significantly different from earlier theoretical predictions, in combination with the results in this paper, provide the parameters necessary to calculate the atmospheric spectral properties of nitric acid for most applications involving these vibrational states.

Table 3. Assignments of observed transitions for ground state (MHz).

J"K"-K"+ J"K"-K"+	Observation	Observed - Calculated	J"K"-K"+ J"K"-K"+	Observation	Observed - Calculated
9 2 7 - 8 0 8	319698.861	-0.065	32 <sub>26</sub> 7 - 31 <sub>26</sub> 6	697731.753	-0.027
9 9 0 - 8 7 1	262111.726	-0.062	33 <sub>9</sub> 25 - 33 <sub>7</sub> 26	319081.784	-0.045
9 9 1 - 8 8 0	231328.815	0.020	34 <sub>14</sub> 20 - 33 <sub>14</sub> 19	607041.079	-0.058
11 9 3 - 10 9 2	235167.573	-0.093	34 <sub>17</sub> 17 - 33 <sub>17</sub> 16	644820.104	-0.081
12 6 6 - 11 6 5	232178.597	-0.118	34 <sub>26</sub> 9 - 33 <sub>26</sub> 8	744035.380	0.155
13 3 10 - 12 11 1	457515.938	0.044	34 <sub>27</sub> 7 - 33 <sub>27</sub> 6	755750.279	-0.188
13 6 7 - 12 6 6	244528.077	-0.026	35 <sub>0</sub> 35 - 34 <sub>1</sub> 34	444283.608	-0.110
13 11 2 - 12 11 1	284871.069	-0.109	35 <sub>24</sub> 11 - 34 <sub>24</sub> 10	751809.933	0.013
14 4 10 - 13 4 9	231777.605	-0.143	35 <sub>25</sub> 11 - 34 <sub>25</sub> 10	749187.616	0.061
14 8 6 - 13 8 5	283003.024	-0.139	35 <sub>30</sub> 5 - 34 <sub>30</sub> 4	753963.992	0.165
15 4 11 - 14 4 10	244286.975	-0.161	36 <sub>0</sub> 36 - 35 <sub>0</sub> 35	456784.097	-0.102
15 10 6 - 14 7 7	454869.796	0.079	36 <sub>18</sub> 18 - 35 <sub>18</sub> 17	682227.925	0.060
15 10 6 - 14 8 7	454865.045	-0.011	36 <sub>24</sub> 13 - 35 <sub>24</sub> 12	747097.412	-0.103
16 8 8 - 15 6 9	506141.746	0.004	37 <sub>18</sub> 19 - 36 <sub>18</sub> 18	694608.396	0.004
16 9 8 - 15 7 9	506143.100	0.065	38 <sub>11</sub> 27 - 37 <sub>11</sub> 26	619342.933	0.085
16 11 6 - 15 9 7	479188.769	0.055	38 <sub>21</sub> 17 - 37 <sub>21</sub> 16	745021.509	-0.034
17 13 5 - 16 10 6	491280.049	0.048	39 <sub>1</sub> 38 - 38 <sub>1</sub> 37	506804.754	-0.156
18 0 18 - 17 0 17	231627.279	-0.114	39 <sub>7</sub> 32 - 38 <sub>7</sub> 31	581849.575	-0.034
18 11 7 - 17 11 6	371392.224	-0.038	39 <sub>9</sub> 30 - 38 <sub>9</sub> 29	606833.467	0.019
18 12 7 - 17 12 6	370541.181	-0.141	39 <sub>10</sub> 29 - 38 <sub>10</sub> 28	619322.672	-0.049
18 14 5 - 17 12 6	515772.928	-0.096	40 <sub>8</sub> 32 - 39 <sub>8</sub> 31	606821.346	0.001
18 16 2 - 17 15 3	456347.584	0.038	40 <sub>12</sub> 28 - 39 <sub>12</sub> 27	656764.256	0.006
18 16 3 - 17 15 2	454557.490	-0.049	41 <sub>5</sub> 36 - 40 <sub>5</sub> 35	581825.226	0.014
18 18 0 - 17 17 1	465630.266	-0.018	41 <sub>7</sub> 34 - 40 <sub>7</sub> 33	606811.282	-0.001
18 18 1 - 17 17 0	465628.278	0.002	41 <sub>11</sub> 30 - 40 <sub>11</sub> 29	656745.307	-0.050
19 3 16 - 18 3 15	281782.006	-0.106	42 <sub>6</sub> 36 - 41 <sub>6</sub> 35	606801.677	0.027
19 7 13 - 18 5 14	168985.797	-0.062	42 <sub>10</sub> 32 - 41 <sub>10</sub> 31	656733.531	0.054
19 7 13 - 18 7 12	319432.672	-0.016	42 <sub>14</sub> 28 - 41 <sub>14</sub> 27	706641.215	0.027
19 14 6 - 18 11 7	552005.830	0.151	42 <sub>18</sub> 24 - 41 <sub>18</sub> 23	756621.405	0.053
19 14 6 - 18 12 7	551842.758	-0.012	43 <sub>5</sub> 38 - 42 <sub>5</sub> 37	606791.141	0.012
20 7 13 - 19 7 12	344496.104	-0.052	43 <sub>10</sub> 34 - 42 <sub>10</sub> 33	656725.943	0.031
20 15 5 - 19 13 6	546033.763	0.120	43 <sub>13</sub> 30 - 42 <sub>13</sub> 29	706616.667	0.070
20 15 5 - 19 15 4	453822.024	-0.164	43 <sub>16</sub> 27 - 42 <sub>16</sub> 26	744046.298	0.054
20 18 3 - 19 17 2	507143.929	0.047	43 <sub>20</sub> 23 - 42 <sub>20</sub> 22	794085.971	-0.144
21 16 6 - 20 14 7	600598.700	0.076	44 <sub>2</sub> 42 - 43 <sub>2</sub> 41	581774.235	0.044
21 17 4 - 20 16 5	536810.322	0.058	44 <sub>4</sub> 40 - 43 <sub>4</sub> 39	606778.578	-0.018
21 17 5 - 20 16 4	508458.978	-0.287	44 <sub>8</sub> 36 - 43 <sub>8</sub> 35	656720.743	0.095
21 19 2 - 20 17 3	606534.497	-0.042	44 <sub>12</sub> 32 - 43 <sub>12</sub> 31	706602.522	0.023
22 0 22 - 21 0 21	281685.373	-0.068	44 <sub>14</sub> 30 - 43 <sub>14</sub> 29	731536.408	-0.195
22 7 15 - 21 7 14	369487.272	-0.172	44 <sub>16</sub> 28 - 43 <sub>16</sub> 27	756479.879	0.074
22 17 6 - 21 14 7	626621.982	0.028	44 <sub>20</sub> 24 - 43 <sub>20</sub> 23	806471.651	0.076
23 16 7 - 22 17 6	491178.870	0.032	45 <sub>1</sub> 44 - 44 <sub>1</sub> 43	581749.428	0.064
23 18 5 - 22 18 4	517883.893	0.091	45 <sub>3</sub> 42 - 44 <sub>3</sub> 41	606762.991	-0.053
23 19 5 - 22 19 4	499212.170	0.020	46 <sub>3</sub> 43 - 45 <sub>3</sub> 42	619245.039	0.047
23 20 3 - 22 20 2	495303.929	0.110	46 <sub>6</sub> 40 - 45 <sub>6</sub> 39	656711.004	0.046
24 9 15 - 23 7 16	794479.102	-0.020	46 <sub>14</sub> 32 - 45 <sub>14</sub> 31	756427.074	0.139
24 15 9 - 23 15 8	496741.849	-0.008	46 <sub>16</sub> 30 - 45 <sub>16</sub> 29	781344.745	-0.004
24 22 3 - 23 22 2	511210.940	0.054	46 <sub>19</sub> 28 - 45 <sub>19</sub> 27	806279.639	0.017
25 15 10 - 24 16 9	508461.962	0.217	47 <sub>2</sub> 45 - 46 <sub>2</sub> 44	619225.822	-0.078
25 16 10 - 24 16 9	508471.401	-0.002	47 <sub>5</sub> 42 - 46 <sub>5</sub> 41	656703.976	-0.109
25 16 9 - 24 14 10	738366.836	0.111	47 <sub>6</sub> 41 - 46 <sub>6</sub> 40	669184.388	0.213
27 9 19 - 27 7 20	243964.774	0.011	47 <sub>8</sub> 40 - 46 <sub>8</sub> 39	506641.259	0.014
27 9 18 - 26 9 17	457042.054	-0.189	47 <sub>9</sub> 39 - 46 <sub>9</sub> 38	493923.543	0.108
27 16 11 - 26 16 10	545907.157	0.020	47 <sub>11</sub> 36 - 46 <sub>11</sub> 35	731510.657	-0.056
27 23 4 - 26 21 5	755465.728	0.101	47 <sub>15</sub> 32 - 46 <sub>15</sub> 31	781322.205	0.198
28 9 19 - 28 9 20	243809.970	-0.034	48 <sub>0</sub> 48 - 47 <sub>0</sub> 47	606689.260	0.022
28 20 8 - 27 20 7	622601.317	-0.072	48 <sub>4</sub> 44 - 47 <sub>4</sub> 43	656694.546	0.081
29 0 29 - 28 0 28	369257.890	-0.125	48 <sub>6</sub> 43 - 47 <sub>6</sub> 42	669178.253	0.057
29 25 4 - 28 25 3	624775.530	0.010	48 <sub>12</sub> 36 - 47 <sub>12</sub> 35	756415.986	-0.205
30 20 11 - 29 20 10	621886.823	-0.006	48 <sub>39</sub> 10 - 48 <sub>39</sub> 11	231235.699	0.030
30 21 9 - 29 21 8	656060.041	0.142	49 <sub>3</sub> 47 - 48 <sub>3</sub> 46	595347.120	-0.249
30 26 4 - 29 25 5	756713.391	-0.143	49 <sub>3</sub> 46 - 48 <sub>3</sub> 45	656681.163	0.006
31 10 22 - 31 8 23	281380.457	-0.058	49 <sub>5</sub> 45 - 48 <sub>5</sub> 44	669169.325	0.031
31 20 11 - 30 20 10	647591.809	0.040	49 <sub>11</sub> 39 - 48 <sub>11</sub> 38	493413.354	-0.001
32 10 22 - 31 10 21	531988.102	-0.025	50 <sub>2</sub> 48 - 49 <sub>2</sub> 47	656663.285	0.013
32 16 16 - 31 16 15	607388.926	-0.001	50 <sub>4</sub> 47 - 49 <sub>4</sub> 46	595068.762	-0.120

Table 3—continued

J'K'-K'+	J''K''-K''+	Observation	Observed - Calculated	J'K'-K'+	J''K''-K''+	Observation	Observed - Calculated
50 3 47 - 49 3 46		669156.576	0.033	57 10 48 - 57 8 49		605675.142	0.029
50 14 36 - 49 14 35		806188.657	-0.303	57 9 48 - 56 9 47		831130.632	-0.111
51 1 50 - 50 1 49		656640.006	0.054	57 15 43 - 57 13 44		541939.071	0.023
51 5 47 - 51 3 48		594783.135	-0.107	58 0 58 - 57 0 57		731440.736	0.194
51 3 49 - 50 3 48		669139.069	0.011	58 1 57 - 57 1 56		743934.850	0.064
51 9 42 - 50 9 41		756431.152	-0.118	58 3 56 - 58 1 57		707784.455	0.139
52 0 52 - 51 0 51		656610.428	0.072	58 4 54 - 57 4 53		781361.368	0.017
52 2 51 - 51 2 50		669115.955	-0.029	58 16 43 - 58 14 44		541604.648	0.010
52 4 48 - 51 4 47		706583.259	-0.066	58 22 37 - 58 20 38		465230.769	0.021
52 6 47 - 52 4 48		594490.337	-0.009	59 1 58 - 58 1 57		756398.030	-0.016
52 8 44 - 51 8 43		756437.867	-0.131	59 4 56 - 59 2 57		707409.179	0.174
52 10 42 - 51 10 41		781329.098	-0.022	59 4 56 - 58 4 55		781353.353	-0.180
53 1 53 - 52 1 52		669086.478	-0.004	59 12 48 - 59 10 49		604985.260	-0.057
53 3 50 - 52 3 49		706572.175	-0.056	59 32 26 - 59 32 27		323167.487	-0.035
54 0 54 - 53 0 53		681560.943	0.062	60 0 60 - 59 0 59		756369.150	0.004
54 2 52 - 53 2 51		706555.832	-0.105	60 5 56 - 60 3 57		707026.291	0.154
54 4 46 - 53 4 45		781348.653	-0.045	60 24 37 - 60 22 38		464504.224	-0.006
54 9 46 - 54 7 47		581122.605	-0.015	60 35 26 - 60 33 27		322575.366	0.019
54 12 42 - 53 12 41		831082.382	0.257	61 25 37 - 61 23 38		464123.828	-0.024
55 1 54 - 54 1 53		706533.566	-0.029	62 0 62 - 61 0 61		781289.975	0.066
55 3 52 - 54 3 51		731506.928	-0.042	62 15 48 - 62 13 49		603889.642	-0.107
55 7 48 - 54 7 47		781356.497	-0.155	62 26 37 - 62 24 38		463731.655	0.004
55 20 36 - 55 18 37		453513.656	0.060	63 16 48 - 63 14 49		603507.920	0.104
56 0 56 - 55 0 55		706504.437	0.072	63 27 37 - 63 25 38		463327.274	-0.032
56 2 54 - 55 2 53		731491.550	0.086	64 28 37 - 64 26 38		462910.543	0.055
56 9 48 - 56 7 49		606008.131	-0.069	65 29 37 - 65 27 38		462480.858	0.002
56 14 43 - 56 12 44		542264.840	-0.004	66 30 37 - 66 28 38		462038.013	-0.044
57 0 57 - 56 0 56		718973.467	0.083	67 31 37 - 67 29 38		461581.756	0.025
57 1 56 - 56 1 55		731469.683	0.081	68 32 37 - 68 30 38		461111.508	0.007
57 2 55 - 56 2 54		743956.380	-0.031	69 33 37 - 69 31 38		460626.956	-0.026
57 3 54 - 56 3 53		756433.958	-0.201	70 34 37 - 70 32 38		460127.787	0.014

Table 4. Transitions not included in the ground state fit.

J' K'-K'+	J'' K''-K''+	Observation	Reference
14 0 14 - 13 1 13		181560.28	3
58 45 13 - 58 45 14		30957.151	5
50 0 50 - 49 0 49		631654.53	6

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