JOURNAL OF MOLECULAR SPECTROSCOPY **128**, 306–308 (1988)

Millimeter- and Submillimeter-Wave Spectra of the NO′ Stretching Mode (ν_6) in Nitric Acid[1]

Nitric acid has been the subject of a number of spectroscopic investigations because of its chemical significance and its presence in numerous physical systems of practical importance. In a recent paper (*1*) on the pure rotational spectrum of the ν_7 vibrational state, we have reviewed our earlier millimeter and submillimeter investigations of this species as well as previous infrared work (*2–7*). In that article the theoretical and experimental methods used for the analysis of the rotational spectrum of ν_6 in this work were discussed.

The spectrum observed in this work was assigned to the band that has been designated as ν_6 in the infrared on the basis of its intensity. This band, derived from the NO′ stretching mode (*3*), is the third lowest lying, being centered 647 cm^{-1} above the ground state. We have previously analyzed the lowest lying ν_9 state (*8*), which is identified by a distinctive triplet structure arising from its twofold internal rotation, and ν_7, the

TABLE I

Assignments of Observed Transitions (MHz)

$J'_{K'_- K'_+}$ - $J''_{K''_- K''_+}$	Observation	Obs-Calc	$J'_{K'_- K'_+}$ - $J''_{K''_- K''_+}$	Observation	Obs-Calc
$8_{2\,6} - 7_{2\,5}$	131682.587	0.161	$17_{12\,5} - 16_{10\,6}$	480520.193	0.083
$8_{3\,6} - 7_{3\,5}$	131680.830	-0.119	$17_{13\,4} - 16_{11\,5}$	458422.301	0.057
$8_{3\,5} - 7_{3\,4}$	144232.919	-0.013	$17_{14\,3} - 16_{12\,4}$	456925.378	-0.141
$8_{4\,5} - 7_{4\,4}$	144166.757	0.037	$18_{1\,17} - 17_{1\,16}$	244800.878	-0.088
$9_{1\,8} - 8_{1\,7}$	131769.755	0.092	$18_{5\,13} - 17_{5\,12}$	294630.351	-0.063
$9_{2\,7} - 8_{2\,6}$	144238.193	-0.010	$18_{3\,15} - 18_{3\,16}$	192942.480	-0.036
$9_{9\,1} - 8_{8\,0}$	231239.841	0.181	$18_{4\,14} - 18_{4\,15}$	180390.234	-0.111
$10_{0\,10} - 9_{0\,9}$	131869.072	0.008	$18_{15\,3} - 17_{14\,4}$	456147.433	0.107
$10_{1\,9} - 9_{1\,8}$	144331.122	0.040	$18_{16\,3} - 17_{15\,2}$	454362.220	-0.037
$10_{2\,8} - 9_{2\,7}$	156796.728	0.250	$18_{18\,0} - 17_{17\,1}$	465416.776	-0.214
$10_{4\,6} - 9_{4\,5}$	181811.158	-0.037	$18_{18\,1} - 17_{17\,0}$	465415.529	0.013
$11_{0\,11} - 10_{0\,10}$	144430.732	0.039	$19_{0\,19} - 18_{0\,18}$	244898.046	-0.107
$11_{3\,8} - 10_{3\,7}$	181827.509	-0.041	$19_{4\,15} - 18_{4\,14}$	294720.156	0.113
$11_{4\,7} - 10_{4\,6}$	194327.197	-0.051	$19_{4\,15} - 19_{4\,16}$	192844.873	-0.068
$11_{4\,8} - 10_{4\,7}$	181827.535	0.022	$19_{16\,3} - 18_{15\,4}$	479932.499	0.022
$11_{5\,7} - 10_{5\,6}$	194325.244	-0.012	$19_{17\,3} - 18_{16\,2}$	480656.689	-0.025
$11_{6\,6} - 10_{6\,5}$	206872.802	-0.034	$20_{2\,18} - 19_{2\,17}$	282364.617	-0.029
$11_{8\,4} - 10_{8\,3}$	229542.324	0.048	$20_{3\,17} - 19_{3\,16}$	294817.812	0.218
$12_{0\,12} - 11_{0\,11}$	156991.728	-0.009	$20_{1\,19} - 20_{1\,20}$	242935.273	-0.258
$12_{2\,10} - 11_{2\,9}$	181914.355	-0.019	$20_{6\,14} - 20_{6\,15}$	180153.027	0.002
$12_{3\,9} - 11_{3\,8}$	194381.884	0.028	$20_{14\,6} - 19_{14\,5}$	442954.400	0.067
$12_{4\,8} - 11_{4\,7}$	206866.210	-0.148	$20_{15\,5} - 19_{15\,4}$	451980.100	0.001
$12_{1\,11} - 12_{1\,12}$	143264.257	-0.001	$21_{6\,15} - 21_{6\,16}$	192609.521	-0.031
$12_{6\,6} - 11_{6\,5}$	232134.472	0.006	$21_{7\,14} - 21_{7\,15}$	180009.716	0.162
$12_{7\,6} - 11_{7\,5}$	231974.882	-0.047	$21_{14\,7} - 20_{14\,6}$	450745.773	0.005
$12_{8\,5} - 11_{8\,4}$	244127.016	0.047	$21_{16\,6} - 20_{16\,5}$	453048.382	0.039
$13_{1\,12} - 12_{1\,11}$	182012.548	-0.019	$21_{17\,4} - 20_{17\,3}$	461891.293	-0.024
$13_{2\,11} - 12_{2\,10}$	194473.095	0.035	$21_{18\,4} - 20_{18\,3}$	450473.441	-0.055
$13_{3\,10} - 12_{3\,9}$	206937.255	-0.013	$22_{7\,15} - 22_{7\,16}$	192469.091	-0.054
$13_{6\,7} - 12_{6\,6}$	244502.157	-0.132	$22_{13\,9} - 21_{13\,8}$	445630.805	-0.104
$13_{6\,8} - 12_{6\,7}$	231916.526	-0.012	$22_{13\,9} - 21_{14\,8}$	445475.719	-0.065
$13_{1\,12} - 13_{1\,13}$	155724.706	0.022	$22_{14\,8} - 21_{14\,7}$	459871.706	0.015
$14_{0\,14} - 13_{0\,13}$	182111.816	-0.034	$22_{14\,9} - 21_{14\,8}$	445498.185	0.010
$14_{1\,14} - 13_{1\,13}$	182111.860	0.010	$22_{15\,8} - 21_{15\,7}$	458466.675	-0.005
$14_{1\,13} - 13_{1\,12}$	194571.826	-0.003	$22_{16\,6} - 21_{17\,5}$	459189.224	-0.053
$14_{5\,10} - 13_{5\,9}$	231962.539	0.039	$22_{20\,2} - 21_{20\,1}$	467035.967	-0.045
$14_{8\,6} - 13_{8\,5}$	282965.011	-0.013	$22_{20\,3} - 21_{20\,2}$	466988.464	-0.038
$15_{1\,14} - 14_{1\,13}$	207130.419	0.060	$22_{21\,1} - 21_{21\,0}$	463441.320	-0.023
$15_{6\,10} - 14_{6\,9}$	256992.109	0.029	$22_{21\,2} - 21_{21\,1}$	463439.696	0.099
$15_{9\,6} - 14_{7\,7}$	452955.244	0.104	$23_{1\,23} - 22_{1\,22}$	295109.315	-0.127
$16_{1\,15} - 16_{1\,16}$	193103.417	0.084	$23_{2\,22} - 22_{2\,21}$	307565.457	0.004
$16_{3\,13} - 15_{3\,12}$	244603.759	-0.075	$23_{4\,19} - 23_{4\,20}$	242646.630	0.119
$16_{3\,14} - 15_{3\,13}$	232145.751	-0.008	$23_{13\,10} - 22_{13\,9}$	457765.690	-0.061
$16_{14\,2} - 15_{12\,3}$	445620.663	0.047	$23_{13\,10} - 22_{14\,9}$	457743.259	-0.101
$17_{2\,15} - 16_{2\,14}$	244701.806	-0.045	$23_{14\,9} - 22_{14\,8}$	471048.913	0.160
$17_{3\,14} - 17_{3\,15}$	180487.157	-0.057	$23_{14\,10} - 22_{13\,9}$	457768.701	0.089

[1] Support provided by NASA Grant NSG-7540. Construction of the broadband spectrometer was supported by ARO Instrumentation Grant DAAG29-83-G-0047.

0022-2852/88 $3.00

TABLE I—*Continued*

$J'_{K'_-\,K'_+}\ J''_{K''_-\,K''_+}$	Observation	Obs-Calc	$J'_{K'_-\,K'_+}\ J''_{K''_-\,K''_+}$	Observation	Obs-Calc
$23_{14\,10} - 22_{14\,9}$	457746.169	-0.051	$35_{8\,28} - 34_{8\,27}$	532650.239	-0.006
$23_{15\,9} - 22_{15\,8}$	470779.322	-0.063	$35_{18\,18} - 35_{16\,19}$	227514.394	-0.042
$23_{21\,3} - 22_{21\,2}$	487785.918	-0.069	$35_{18\,18} - 34_{18\,17}$	657096.366	-0.162
$24_{11\,13} - 23_{11\,12}$	444759.791	0.012	$36_{0\,36} - 35_{0\,35}$	458147.992	0.117
$24_{14\,10} - 23_{14\,9}$	483008.387	0.016	$36_{7\,29} - 35_{7\,28}$	545172.576	0.060
$24_{15\,9} - 23_{15\,8}$	496612.678	-0.018	$36_{10\,27} - 36_{8\,28}$	341356.906	0.060
$24_{15\,10} - 23_{15\,9}$	482965.261	-0.200	$36_{19\,18} - 36_{17\,19}$	227163.145	0.038
$24_{16\,9} - 23_{16\,8}$	496090.342	-0.012	$37_{1\,36} - 36_{1\,35}$	483125.608	-0.007
$25_{6\,19} - 25_{6\,20}$	242403.418	0.004	$37_{4\,34} - 36_{4\,33}$	508001.911	-0.114
$25_{10\,15} - 24_{10\,14}$	444737.532	0.029	$37_{11\,27} - 37_{9\,28}$	341162.714	-0.086
$25_{11\,14} - 24_{11\,13}$	457246.663	-0.010	$37_{20\,18} - 37_{18\,19}$	226783.821	0.077
$26_{10\,16} - 25_{10\,15}$	457251.022	0.051	$38_{3\,35} - 37_{3\,34}$	520527.486	0.027
$27_{8\,19} - 26_{8\,18}$	444857.388	0.092	$38_{12\,27} - 38_{10\,28}$	340958.075	-0.071
$27_{8\,19} - 27_{8\,20}$	242112.773	-0.060	$38_{21\,18} - 38_{19\,19}$	226374.492	-0.020
$27_{10\,18} - 26_{10\,17}$	457306.726	-0.035	$39_{3\,37} - 39_{1\,38}$	466887.393	-0.023
$27_{17\,11} - 26_{17\,10}$	545635.273	0.226	$39_{2\,37} - 38_{2\,36}$	520618.122	0.065
$28_{8\,20} - 27_{8\,19}$	457387.885	0.055	$39_{4\,36} - 39_{2\,37}$	454258.617	0.096
$28_{7\,21} - 27_{7\,20}$	444948.383	0.023	$39_{4\,35} - 38_{4\,34}$	545477.908	0.023
$28_{14\,15} - 27_{14\,14}$	519764.447	-0.081	$39_{13\,27} - 39_{11\,28}$	340742.603	0.181
$29_{6\,23} - 28_{6\,22}$	445046.730	-0.009	$40_{3\,37} - 39_{3\,36}$	545572.514	0.054
$29_{8\,22} - 28_{8\,21}$	457481.540	-0.020	$40_{5\,36} - 40_{3\,37}$	454061.581	0.016
$29_{10\,19} - 29_{10\,20}$	241768.046	0.186	$40_{5\,35} - 39_{5\,34}$	570417.867	0.027
$29_{13\,17} - 28_{13\,16}$	519735.026	0.047	$40_{14\,27} - 40_{12\,28}$	340514.930	-0.218
$29_{14\,15} - 28_{14\,14}$	544783.723	0.072	$41_{2\,39} - 40_{2\,38}$	545661.356	-0.086
$30_{1\,29} - 29_{1\,28}$	395383.419	0.008	$41_{15\,27} - 41_{13\,28}$	340275.900	0.075
$30_{6\,24} - 29_{6\,23}$	457581.173	-0.012	$42_{1\,41} - 41_{1\,40}$	545743.851	0.005
$30_{11\,20} - 29_{11\,19}$	507321.424	0.082	$42_{7\,36} - 42_{5\,37}$	453644.788	0.014
$30_{11\,19} - 30_{11\,20}$	241572.578	-0.054	$43_{1\,43} - 42_{1\,42}$	545818.819	0.052
$30_{12\,19} - 29_{12\,18}$	519770.431	0.071	$43_{2\,41} - 42_{2\,40}$	570696.821	0.176
$31_{4\,27} - 30_{4\,26}$	445248.670	0.019	$43_{5\,39} - 43_{3\,40}$	491329.593	-0.040
$31_{5\,26} - 30_{5\,25}$	457682.771	0.068	$43_{8\,36} - 43_{6\,37}$	453424.546	0.032
$31_{11\,21} - 31_{9\,22}$	266642.856	-0.065	$43_{7\,36} - 42_{7\,35}$	632773.438	-0.066
$31_{12\,20} - 30_{12\,19}$	532281.476	0.008	$44_{1\,43} - 43_{1\,42}$	570776.877	-0.129
$32_{8\,24} - 31_{8\,23}$	507499.548	-0.092	$44_{9\,36} - 44_{7\,37}$	453195.992	-0.060
$32_{11\,21} - 31_{11\,20}$	544792.806	0.036	$45_{0\,45} - 44_{0\,44}$	570849.429	-0.133
$32_{17\,15} - 31_{17\,14}$	619893.053	-0.056	$45_{9\,37} - 45_{7\,38}$	465590.059	-0.085
$33_{2\,31} - 32_{2\,30}$	445442.119	-0.045	$45_{10\,36} - 45_{8\,37}$	452959.161	0.004
$33_{3\,30} - 32_{3\,29}$	457881.830	0.079	$46_{11\,36} - 46_{9\,37}$	452713.542	-0.051
$33_{7\,27} - 33_{5\,28}$	341879.854	0.143	$47_{2\,46} - 46_{2\,45}$	608310.693	0.067
$33_{11\,23} - 32_{11\,22}$	544873.953	0.036	$47_{12\,36} - 47_{10\,37}$	452459.106	-0.008
$33_{16\,18} - 32_{16\,17}$	607149.494	0.020	$48_{1\,48} - 47_{1\,47}$	608379.614	0.019
$33_{17\,16} - 32_{17\,15}$	632272.855	0.082	$48_{10\,39} - 48_{8\,40}$	490111.378	0.094
$34_{6\,28} - 33_{6\,27}$	507703.203	-0.033	$48_{13\,36} - 48_{11\,37}$	452195.464	-0.006
$34_{12\,23} - 33_{12\,22}$	569814.092	-0.180	$49_{14\,36} - 49_{12\,37}$	451922.467	0.068
$34_{17\,18} - 34_{15\,19}$	227839.422	-0.031	$51_{16\,36} - 51_{14\,37}$	451346.928	0.030
$35_{0\,35} - 34_{0\,34}$	445615.989	0.013	$52_{17\,36} - 52_{15\,37}$	451043.960	0.055
$35_{5\,30} - 34_{5\,29}$	507805.591	-0.022	$53_{17\,37} - 53_{15\,38}$	463381.780	-0.033
$35_{5\,31} - 34_{5\,30}$	495377.781	-0.051	$54_{18\,37} - 54_{16\,38}$	463061.846	-0.040

state immediately below ν_6; this allowed us to compare ν_6 intensities with transitions in the ground vibrational state, ν_9 and ν_7. We find the intensity for well-resolved lines of reasonable signal to noise to be consistently within about 10% of the expected value.

TABLE II

Results of Analysis (MHz)

Constants		Value	σ
A		13006.2313	0.0019
B		12057.4635	0.0014
C		6282.34695	0.0010
Δ_J	$(\times 10^1)$	0.1450237	0.000023
Δ_{JK}	$(\times 10^1)$	-0.2195221	0.000062
Δ_K	$(\times 10^2)$	0.969217	0.00059
δ_J	$(\times 10^2)$	0.14689	0.00014
δ_K	$(\times 10^1)$	-0.13082	0.00035
H_{JK}	$(\times 10^6)$	-0.13798	0.042
H_{KJ}	$(\times 10^6)$	0.41976	0.13
H_K	$(\times 10^6)$	-0.25066	0.088
h_{JK}	$(\times 10^6)$	-0.125	0.089
h_K	$(\times 10^6)$	-0.6546	0.36
L_{JJK}	$(\times 10^{10})$	0.34299	0.23
L_{JK}	$(\times 10^{10})$	-0.94605	0.69
L_{KKJ}	$(\times 10^{10})$	0.59592	0.47
l_{JK}	$(\times 10^{10})$	-0.621	0.41
l_{KJ}	$(\times 10^9)$	0.2290	0.20
rms		0.086	

Our measurements comprise a data set of 188 diverse transitions spanning the region from 100 to 700 GHz. They include both $\Delta J = 0$ and $\Delta J = \pm 1$ transitions and span the range to $J = 54$ and $K = 21$; both *a*-type and *b*-type transitions are included: these are shown in Table I. Table II shows the constants derived from our analysis along with the rms deviation of the fit, 0.086 MHz. A sufficient number of digits have been provided to reproduce the observed spectrum.

We find no evidence of a perturbation in the observed spectrum. The fit is well behaved and stable, all lines that we predicted to have sufficient intensity for observation and which were searched for were found at the expected frequency, and the distortion constants show reasonable variation from the ground state values. Thus, it would appear that the analysis of these lines make possible accurate predictions for all rotational transitions between thermally populated levels within the millimeter and submillimeter spectral regions.

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