JOURNAL OF MOLECULAR SPECTROSCOPY **139,** 241–243 (1990)

The Millimeter and Submillimeter Wave Spectrum of the $\nu_8 + \nu_9$ State of HNO_3

Because of the chemical significance of nitric acid and especially because of its presence in the upper atmosphere, its spectrum has been extensively studied in the infrared and millimeter and submillimeter (mm/submm) wave regions. In a recent paper we have reviewed our earlier mm/submm work as well as previous infrared work (*1*). More recently, we have reported the rotational spectrum of the ν_6 state (*2*) and Maki has reported the infrared spectrum of the $\nu_8 + \nu_9$ band (*3*). In this note we report the mm/submm rotational spectrum of the $\nu_8 + \nu_9$ vibrational state.

We have previously discussed the experimental techniques used for our studies of the various vibrational states of HNO_3 (*1, 4, 5*). The single experimental modification of significance was the use of a cell which was typically heated to ~200°C. Although this was effective in increasing the absolute strength of the lines in $\nu_8 + \nu_9$, its primary purpose was to increase the strength of the lines in its spectrum *relative* to lines arising from states of lower energy.

In the mm/submm regions the rotational spectra of all of the vibrational states are overlapped. Ordinarily, because the mm/submm lines are two to three orders of magnitude narrower than lines in the infrared, spectral overlap is uncommon. However, because $\nu_8 + \nu_9$ lies at ~1200 cm^{-1}, its lines are ~400 times weaker at 300 K than ground state lines. They are also substantially weaker than many of the lines arising from other, lower vibrational states. In addition, because of the similarity of the rotational constants of the vibrational states and the concentration of the spectra of HNO_3 into fairly dense bands, many of the $\nu_8 + \nu_9$ lines are observed as blends or are obscured by stronger lines.

In this environment the assignment of lines must be done with care. Several things aided us. First, the predictions provided to us by Maki, especially of the bandheads, were very good. In addition, our earlier work on many of the other vibrational states ordinarily made it possible to find several assignable lines of known strength nearby, thus allowing an evaluation of the absolute strength of each candidate $\nu_8 + \nu_9$ line. Linestrength was thus one of the assignment criteria, and several lines which were close to predicted frequencies were not included in the fit because they were too strong.

We have previously identified the rotational spectra of excited states of HNO_3 with particular vibrational states from the relative intensities of the observed lines. These assignments have been proven to be correct by subsequent analyses of infrared spectra which have been able to use the constants derived from the mm/submm studies to largely define the rotational structure of the infrared bands. Our assignment of the observed rotational spectrum to $\nu_8 + \nu_9$ was initially based on the excellent agreement with predictions based on Maki's analysis as well as on relative intensity measurements. In addition, for lines with adequate signal-to-noise ratio in relatively uncrowded spectral regions, the unique triplet structure associated with the ν_9 tunneling was observed. This adds additional weight to Maki's selection of the $\nu_8 + \nu_9$ assignment for his spectra rather than the $\nu_6 + \nu_7$.

Table I shows the 107 measured mm/submm lines and Table II the constants derived from an analysis which used Watson's *A*-reduced centrifugal distortion Hamiltonian for oblate rotors (*6*). Because of the crowded spectrum, we have run analyses in which each of the lines in Table I was removed and predicted on the basis of the remaining 106 lines. As a result of the substantial redundancy in the data set and the well-behaved Hamiltonian, the differences between the observed and *predicted* frequencies are almost identical to the residuals of the *fit* itself.

Maki has remarked on the difficulty of separating the *A* and *B* rotational constants solely from the information contained in the dominant *P*- and *R*-branch transitions of the infrared spectrum. In the infrared the separation was accomplished by the assignment of a few of the crowded *Q*-branch lines. The mm/submm spectrum is also dominated by *P*- and *R*-branch *a*-type transitions. However, it was possible for the mm/submm spectrum to break this correlation both by measuring *Q*-branch lines and by extending the *P* and *R* branches well beyond the point of asymmetry splitting. A manifestation of this is that the infrared predictions

0022-2852/90 $3.00

TABLE I

Assignments of Observed Transitions for $\nu_8 + \nu_9$ (MHz)

$J'_{K'_-K'_+}$	$J''_{K''_-K''_+}$	Observation	Obs-Calc	$J'_{K'_-K'_+}$	$J''_{K''_-K''_+}$	Observation	Obs-Calc
$9_{6\ 4}$	$8_{6\ 3}$	179801.976	-0.156	$19_{10\ 10}$	$18_{10\ 9}$	355482.035	-0.278
$10_{4\ 6}$	$9_{4\ 5}$	180942.000	-0.213	$20_{5\ 16}$	$19_{5\ 15}$	305829.950	-0.123
$10_{6\ 5}$	$9_{6\ 4}$	193239.610	0.028	$20_{6\ 15}$	$19_{6\ 14}$	318205.814	-0.052
$11_{3\ 8}$	$10_{3\ 7}$	180956.796	0.017	$20_{7\ 14}$	$19_{7\ 13}$	330589.732	-0.020
$11_{7\ 4}$	$10_{7\ 3}$	235634.840	0.117	$21_{1\ 21}$	$20_{1\ 20}$	268844.080	-0.020
$11_{8\ 3}$	$10_{8\ 2}$	244535.015	-0.162	$21_{2\ 20}$	$20_{2\ 19}$	281216.793	0.063
$11_{9\ 3}$	$10_{9\ 2}$	231532.380	0.054	$21_{8\ 14}$	$20_{8\ 13}$	355467.390	0.068
$12_{3\ 10}$	$11_{3\ 9}$	181064.666	0.117	$22_{3\ 20}$	$21_{3\ 19}$	306086.470	0.120
$12_{4\ 9}$	$11_{4\ 8}$	193455.584	0.220	$22_{8\ 14}$	$22_{8\ 15}$	178558.635	-0.010
$12_{6\ 6}$	$11_{6\ 5}$	231103.601	0.095	$22_{9\ 14}$	$21_{9\ 13}$	380347.190	-0.077
$12_{7\ 5}$	$11_{7\ 4}$	245531.918	-0.224	$23_{2\ 22}$	$22_{2\ 21}$	306216.950	-0.173
$12_{8\ 4}$	$11_{8\ 3}$	261658.176	0.096	$23_{3\ 21}$	$22_{3\ 20}$	318584.760	-0.033
$12_{8\ 5}$	$11_{8\ 4}$	242682.118	-0.108	$23_{7\ 17}$	$22_{7\ 16}$	368052.320	-0.163
$12_{11\ 1}$	$11_{9\ 2}$	341676.140	0.000	$23_{9\ 14}$	$23_{9\ 15}$	178339.880	0.098
$13_{3\ 11}$	$12_{3\ 10}$	193568.828	-0.099	$23_{14\ 9}$	$22_{14\ 8}$	469292.396	-0.068
$13_{4\ 10}$	$12_{4\ 9}$	205955.788	0.196	$23_{15\ 9}$	$22_{15\ 8}$	468633.240	0.078
$13_{5\ 8}$	$12_{5\ 7}$	230795.060	-0.002	$24_{1\ 24}$	$23_{1\ 23}$	306346.590	-0.066
$13_{6\ 8}$	$12_{6\ 7}$	230793.776	0.097	$24_{2\ 23}$	$23_{2\ 22}$	318716.120	0.006
$13_{7\ 6}$	$12_{7\ 5}$	256413.308	-0.116	$24_{6\ 18}$	$24_{6\ 19}$	228409.690	0.090
$13_{7\ 7}$	$12_{7\ 6}$	243303.132	0.049	$24_{7\ 18}$	$23_{7\ 17}$	380540.250	0.111
$13_{9\ 5}$	$12_{9\ 4}$	267100.036	-0.010	$24_{9\ 16}$	$23_{9\ 15}$	405294.296	0.083
$13_{10\ 3}$	$12_{8\ 4}$	349378.558	0.048	$24_{10\ 15}$	$23_{10\ 14}$	417693.420	0.068
$14_{2\ 13}$	$13_{2\ 12}$	193693.348	-0.120	$24_{12\ 13}$	$23_{12\ 12}$	442596.136	-0.062
$14_{3\ 12}$	$13_{3\ 11}$	206073.208	0.159	$25_{1\ 25}$	$24_{1\ 24}$	318846.018	0.080
$14_{6\ 8}$	$13_{6\ 7}$	255744.816	-0.003	$25_{2\ 24}$	$24_{2\ 23}$	331214.240	-0.013
$14_{6\ 9}$	$13_{6\ 8}$	243268.492	-0.020	$25_{3\ 23}$	$24_{3\ 22}$	343578.940	-0.140
$14_{8\ 7}$	$13_{8\ 6}$	268305.220	-0.087	$25_{7\ 18}$	$25_{7\ 19}$	228251.420	0.049
$15_{2\ 14}$	$14_{2\ 13}$	206198.432	-0.178	$25_{8\ 18}$	$24_{8\ 17}$	405395.120	0.070
$15_{5\ 11}$	$14_{5\ 10}$	243346.088	0.158	$26_{2\ 25}$	$25_{2\ 24}$	343711.460	-0.046
$15_{7\ 8}$	$14_{7\ 7}$	280726.400	-0.022	$26_{3\ 24}$	$25_{3\ 23}$	356074.880	0.039
$16_{3\ 14}$	$15_{3\ 13}$	231079.928	-0.107	$27_{1\ 27}$	$26_{1\ 26}$	343842.180	0.223
$16_{6\ 11}$	$15_{6\ 10}$	268239.030	0.038	$27_{2\ 26}$	$26_{2\ 25}$	356207.628	-0.207
$16_{7\ 10}$	$15_{7\ 9}$	280661.472	-0.049	$27_{9\ 18}$	$27_{9\ 19}$	227883.160	-0.164
$16_{8\ 8}$	$15_{8\ 7}$	305752.710	-0.033	$28_{2\ 27}$	$27_{2\ 26}$	368703.160	-0.040
$16_{9\ 7}$	$15_{9\ 6}$	318885.006	0.049	$28_{3\ 26}$	$27_{3\ 25}$	381063.530	0.168
$16_{14\ 3}$	$15_{14\ 2}$	337216.070	0.001	$28_{10\ 18}$	$28_{10\ 19}$	227671.430	0.084
$17_{2\ 16}$	$16_{2\ 15}$	231207.120	-0.092	$29_{1\ 29}$	$28_{1\ 28}$	368834.340	-0.034
$17_{3\ 15}$	$16_{3\ 14}$	243582.980	0.236	$29_{3\ 27}$	$28_{3\ 26}$	393556.110	0.088
$17_{5\ 13}$	$16_{5\ 12}$	268339.530	-0.057	$30_{2\ 29}$	$29_{2\ 28}$	393690.920	0.053
$17_{6\ 12}$	$16_{6\ 11}$	280729.245	0.043	$30_{7\ 24}$	$29_{7\ 23}$	455453.868	-0.057
$17_{9\ 9}$	$16_{9\ 8}$	318105.490	0.103	$31_{1\ 31}$	$30_{1\ 30}$	393822.812	-0.109
$17_{11\ 6}$	$16_{11\ 5}$	361299.450	-0.008	$31_{5\ 27}$	$30_{5\ 26}$	443238.544	-0.073
$18_{3\ 16}$	$17_{3\ 15}$	256085.040	0.191	$31_{6\ 26}$	$30_{6\ 25}$	455587.372	0.038
$18_{4\ 14}$	$18_{4\ 15}$	179195.970	-0.007	$32_{1\ 32}$	$31_{1\ 31}$	406315.560	-0.092
$18_{7\ 12}$	$17_{7\ 11}$	305619.051	-0.068	$32_{2\ 31}$	$31_{2\ 30}$	418674.090	-0.047
$18_{8\ 11}$	$17_{8\ 10}$	318044.657	0.000	$33_{1\ 33}$	$32_{1\ 32}$	418807.400	0.097
$18_{9\ 9}$	$17_{9\ 8}$	343114.401	0.069	$34_{1\ 34}$	$33_{1\ 33}$	431298.000	0.168
$19_{1\ 19}$	$18_{1\ 18}$	243838.796	0.031	$34_{2\ 33}$	$33_{2\ 32}$	443652.598	0.005
$19_{3\ 17}$	$18_{3\ 16}$	268586.380	0.076	$34_{4\ 31}$	$33_{4\ 30}$	468345.648	0.018
$19_{5\ 15}$	$18_{5\ 14}$	293333.645	0.068	$35_{1\ 35}$	$34_{1\ 34}$	443787.216	0.022
$19_{6\ 14}$	$18_{6\ 13}$	305713.304	0.064	$36_{1\ 36}$	$35_{1\ 35}$	456275.144	-0.198
$19_{7\ 13}$	$18_{7\ 12}$	318103.474	-0.060	$37_{1\ 37}$	$36_{1\ 36}$	468762.264	0.036
$19_{8\ 12}$	$18_{8\ 11}$	330514.258	0.166	$38_{1\ 38}$	$37_{1\ 37}$	481247.820	0.025
$19_{9\ 10}$	$18_{9\ 9}$	355483.703	-0.173				

of the mm/submm P- and R-branch lines near the bandheads were remarkably good, often better than 1 MHz, but this accuracy decreased to 10–20 MHz for transitions more dependent on this separation.

The distortion parameters of $\nu_8 + \nu_9$ differ more from their ground state counterparts than do the constants of the other excited vibrational states we have studied. Such a change is often an indication that a small perturbation is correlated with the distortion parameters. Since $\nu_6 + \nu_7$ is located only about 20 cm^{-1} higher

TABLE II

Results of Analysis (MHz)

Constants		Value	σ
A		12992.0744	0.0079
B		11946.4481	0.0081
C		6254.9817	0.0040
Δ_J	($\times 10^1$)	0.24543	0.00043
Δ_{JK}	($\times 10^1$)	-0.90377	0.00092
Δ_K	($\times 10^1$)	0.67443	0.00053
δ_K	($\times 10^0$)	0.28582	0.00014
H_J	($\times 10^5$)	-0.7762	0.0085
H_{JK}	($\times 10^5$)	0.250	0.021
H_{KJ}	($\times 10^4$)	0.4592	0.0018
H_K	($\times 10^4$)	-0.40577	0.00068
L_J	($\times 10^8$)	0.4247	0.0055
L_{JJK}	($\times 10^8$)	-0.882	0.011
L_{KKJ}	($\times 10^8$)	0.870	0.012
L_K	($\times 10^8$)	-0.4143	0.0068
rms		0.115	

in energy (*3*), much closer than any neighbor of the other excited states for which a rotational analysis has been reported, this is the most probably explanation.

ACKNOWLEDGMENTS

We thank Arthur Maki for providing preliminary results and the NASA Upper Atmosphere Research Program for support.

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Received August 31, 1989