

Millimeter- and Submillimeter-Wave Spectra of the ONO' Bending Mode (ν_7) in Nitric Acid¹

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Over 140 rotational transitions have been assigned and measured for the ONO' bending mode (ν_7) of gaseous nitric acid. These observations, over a wide range of J and K values in the region 100–600 GHz, have been used as the basis for an analysis of the rotational structure of this vibrational state. The resulting rotation–distortion parameters make possible the calculation, with good accuracy, of all the transition frequencies arising from thermally populated levels of the ν_7 vibrational state. Also, a novel spectrometer capable of broad spectral scans in the millimeter and submillimeter region is described. © 1988 Academic Press, Inc.

I. INTRODUCTION

Nitric acid has been studied extensively due to its presence in the atmosphere and its chemical significance. This species is a near-oblate asymmetric rotor with strong a -type and weaker b -type transitions. The large dipole moment and rotational constants on the order of 10 GHz contribute to a dense spectrum which is further complicated by the presence of several thermally populated vibrational states. The ground state rotational spectrum has been extensively investigated in the past (1–5).

Two decades ago, Cohn *et al.* (6) recorded the infrared spectrum and provided tentative assignments of the vibrational bands. McGraw *et al.* (7) later utilized observations of isotopic nitric acids along with Raman spectra to assign the vibrational bands with more certainty. Recently, Brockman *et al.* (8) and Maki and Wells (9–11) have conducted high-resolution infrared studies of several vibrational levels.

In this work we have observed the ν_7 band which is centered 579.0 cm^{-1} above the ground state and derives from the ONO' bend (7). Our measurements comprise a data set of 148 diverse transitions spanning the region from 100 to 600 GHz. Analysis of these lines makes very accurate predictions possible for all rotational transitions between thermally populated states within the millimeter and submillimeter spectral regions.

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II. EXPERIMENTAL DETAILS

Initial work on the excited vibrational states was facilitated by use of a broadband millimeter-submillimeter-wave spectrometer developed recently. The spectrometer is shown schematically in Fig. 1. A Digital Equipment Corp. (DEC) PDP11 computer is used to translate operator-entered start frequency, stop frequency, and sweep duration into instructions for a programmable 0- to 21-MHz frequency synthesizer. A 10- to 15-GHz YIG oscillator is phase locked, under computer control, to a frequency derived from the synthesizer. The output of the YIG oscillator is in turn multiplied in a passive tripler and amplified to approximately 1 W in a 26- to 40-GHz TWT amplifier.

The microwave power is matched onto a King and Gordy (12) crystal harmonic generator where this nonlinear device produces harmonics of the driving signal. The millimeter-wave output from the harmonic generator is then propagated quasi-optically through a 1-m-long, krylon coated, copper absorption cell. An absorption spectrum is then detected by a InSb hot electron bolometer operating at 1.5 K.

For signal recovery, a small FM modulation at frequency f is applied via the synthesizer. The second-derivative lineshapes which result from lock-in detection at $2f$ are digitized, signal averaged, and displayed by the DEC computer. The collected spectra are then passed to a Harris 800 computer for automated measurement of the absorption line frequencies and for graphical display of the resulting spectra.

Transitions above 440 GHz were measured using the experimental techniques which this laboratory developed for use in the millimeter- and submillimeter-wave spectral region; these techniques have been described previously in detail (13, 14). Briefly, submillimeter power was derived from a King and Gordy (12) crystal harmonic generator driven by a klystron oscillating in the 55-GHz range. Harmonics having a

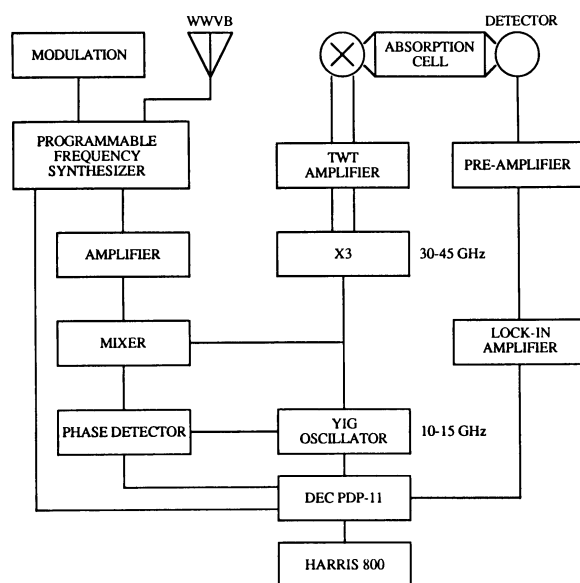


FIG. 1. Block diagram of the broadband millimeter-submillimeter spectrometer capable of long continuous sweeps under microcomputer control.

frequency greater than 440 GHz were selected by a 'beyond cutoff' waveguide filter, propagated through a 0.8-m-long absorption cell made of 3-mm-diameter copper tubing with Teflon windows, and detected by an Infrared Laboratories Ge bolometer operating at 0.3 K.

The vapor-phase nitric acid was taken from a sample containing sulfuric acid to limit the partial pressure of water. All measurements were made at pressures below 0.05 Torr and samples were changed frequently to avoid significant contamination by decomposition products which might arise from reaction with the walls.

The spectrum of ν_7 was assigned initially by using the broadband spectrometer to make continuous scans of about 1 GHz centered on the frequencies of the strong ground state *R*-branch series. Near the bandheads, the quadruply degenerate transitions are separated by approximately $(A + B - 4C)$ in frequency; this number is small, but varies widely for the several vibrational states of HNO_3 . As a result, the rotational spectra of several vibrational states were identified and assigned in a reasonably straightforward manner. The relative strengths of the absorption lines were used to correlate the different vibrational states with the several assigned spectra. Since ν_7 is the second lowest lying excited vibrational state, the spectrum represented in this paper corresponds to the second most intense observed spectrum. In addition, its intensity relative to the ground state is consistent with the known vibrational energy of ν_7 .

III. THEORY

We have used Watson's *A*-reduced centrifugal distortion Hamiltonian (15) which is in the form of a power series that is easily extended to arbitrarily high order. The Hamiltonian, through terms in eighth power, is given by

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

$$\mathbf{H}_r = 1/2(B + C)P^2 + [A - 1/2(B + C)](P_z^2 - b_p P_-^2), \quad (2)$$

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

$$\begin{aligned} \mathbf{H}_d^{(6)} = & H_J P^6 + H_{JK} P^4 P_z^2 + H_{KJ} P^2 P_z^4 + H_K P_z^6 + 2h_J P^4 P_-^2 \\ & + h_{JK} P^2 (P_z^2 P_-^2 + P_-^2 P_z^2) + h_K (P_z^4 P_-^2 + P_-^2 P_z^4), \quad (4) \end{aligned}$$

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

where Δ_J , etc., are the quartic distortion coefficients; H_J , etc., are the sextic distortion coefficients; L_J , etc., are the eighth-order distortion coefficients; and $b_p = (C - B)/(2A - B - C)$ is Wang's asymmetry parameter, $P^2 = P_x^2 + P_y^2 + P_z^2$, where we have defined

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

Our computational and statistical techniques have been thoroughly discussed in previous publications (16-18).

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	130959.130	0.106	16	2 15 ⁻ 15	217466.671	0.018
8	3 6 ⁻ 7	130957.665	-0.111	16	9 7 ⁻ 15	319691.633	-0.005
8	3 5 ⁻ 7	143728.955	0.052	16	10 6 ⁻ 15	334428.798	0.033
9	2 7 ⁻ 8	143354.443	-0.057	16	10 7 ⁻ 15	319468.730	-0.002
9	3 6 ⁻ 8	156073.583	0.026	16	11 6 ⁻ 15	334972.546	-0.140
9	4 6 ⁻ 8	156068.212	-0.039	16	11 6 ⁻ 15	332050.687	-0.002
10	1 9 ⁻ 9	143061.578	-0.004	16	12 5 ⁻ 15	341730.456	0.025
10	2 8 ⁻ 9	155752.490	-0.025	17	1 16 ⁻ 16	229866.611	-0.087
10	4 6 ⁻ 9	181212.939	0.029	17	9 8 ⁻ 16	331748.254	0.014
10	4 6 ⁻ 9	193893.017	0.068	17	9 8 ⁻ 16	331717.980	-0.018
11	3 8 ⁻ 10	180848.486	-0.038	17	10 8 ⁻ 16	461087.111	0.074
11	3 8 ⁻ 10	168151.455	0.033	18	13 4 ⁻ 17	254944.511	0.012
11	3 9 ⁻ 10	193571.826	0.178	18	3 16 ⁻ 17	461171.458	0.069
11	4 7 ⁻ 10	206393.935	0.016	18	17 1 ⁻ 17	461081.013	-0.009
11	5 6 ⁻ 10	247597.744	0.045	18	18 0 ⁻ 17	466227.012	-0.100
11	8 3 ⁻ 10	244305.611	0.031	18	18 1 ⁻ 17	466225.257	0.045
12	2 10 ⁻ 11	180550.703	0.020	19	1 18 ⁻ 18	254665.940	0.027
12	3 9 ⁻ 11	193242.919	-0.068	19	2 17 ⁻ 18	267342.563	-0.017
12	4 8 ⁻ 11	205951.455	-0.072	19	7 12 ⁻ 18	330765.720	0.000
12	6 6 ⁻ 11	231642.842	-0.013	20	2 18 ⁻ 19	279740.309	-0.010
12	7 5 ⁻ 11	245745.120	-0.038	20	6 14 ⁻ 19	330447.295	-0.016
12	7 6 ⁻ 11	231507.226	0.105	21	0 21 ⁻ 20	266787.453	-0.012
12	9 3 ⁻ 11	270925.443	-0.054	21	1 20 ⁻ 20	279463.840	-0.003
12	10 2 ⁻ 11	264418.941	-0.113	21	5 16 ⁻ 20	330155.096	-0.038
12	10 3 ⁻ 11	256962.852	-0.063	21	5 16 ⁻ 20	464495.316	0.059
12	10 3 ⁻ 11	338621.038	-0.043	22	17 4 ⁻ 21	329874.836	0.052
13	11 1 ⁻ 12	180264.990	-0.004	22	4 18 ⁻ 21	445043.710	-0.065
13	11 2 ⁻ 12	205638.818	0.012	22	13 9 ⁻ 21	459297.773	-0.025
13	3 10 ⁻ 12	243867.304	-0.122	22	14 8 ⁻ 21	444942.779	0.065
13	6 7 ⁻ 12	231064.910	-0.070	22	14 9 ⁻ 21	458165.446	0.002
13	6 8 ⁻ 12	243851.679	0.027	22	15 8 ⁻ 21	496920.157	0.033
13	7 7 ⁻ 12	336139.911	0.069	22	17 5 ⁻ 21	483583.180	-0.135
13	13 0 ⁻ 12	336085.154	0.075	22	18 4 ⁻ 21	473787.461	-0.144
14	0 14 ⁻ 13	179981.982	0.014	22	19 3 ⁻ 21	472899.657	-0.104
14	1 13 ⁻ 13	192665.771	-0.009	22	19 4 ⁻ 21	464707.777	-0.027
14	2 12 ⁻ 13	205349.365	0.037	22	21 2 ⁻ 21	464705.541	0.093
14	4 10 ⁻ 13	230728.779	-0.020	23	2 21 ⁻ 21	329599.925	-0.025
15	0 15 ⁻ 14	192383.495	0.009	23	3 20 ⁻ 22	342267.455	0.044
15	0 15 ⁻ 14	205066.357	0.017	23	4 19 ⁻ 22	457055.110	0.037
15	1 14 ⁻ 14	230432.099	0.065	23	13 10 ⁻ 22	470481.471	0.084
15	3 12 ⁻ 14	243120.957	0.062	23	14 9 ⁻ 22	470275.420	0.022
15	5 11 ⁻ 14	325584.880	0.020	23	15 9 ⁻ 22	520813.234	0.113
15	10 5 ⁻ 14	338643.066	0.010	23	17 6 ⁻ 22	489302.548	0.022
15	11 4 ⁻ 14	334950.815	0.063	23	21 2 ⁻ 22	489268.148	0.062
15	12 3 ⁻ 14	322817.708	0.036	24	2 21 ⁻ 23	329327.451	0.032
15	12 4 ⁻ 14	230147.216	-0.199	24	2 22 ⁻ 23	341994.326	0.011
16	2 14 ⁻ 15			24	3 21 ⁻ 23		

$J'_{K'} K'_+$	$J'_{K'} K'_+$	Observation	Obs-Calc	$J''_{K''} K''_+$	$J''_{K''} K''_+$	Observation	Obs-Calc
24	13 12 ⁻ 23	456296.738	-0.063	33	5 28 ⁻ 32	478807.270	-0.105
24	14 10 ⁻ 23	482339.686	0.033	33	9 25 ⁻ 33	322387.955	0.038
24	16 8 ⁻ 23	512009.385	-0.207	33	8 25 ⁻ 32	516720.849	-0.064
24	21 3 ⁻ 23	514836.438	0.045	34	3 31 ⁻ 33	465908.481	-0.070
24	21 4 ⁻ 23	514520.614	-0.027	34	4 30 ⁻ 33	478551.641	-0.043
25	12 14 ⁻ 24	455819.348	-0.017	34	7 27 ⁻ 33	516461.972	0.083
26	1 25 ⁻ 25	341452.079	-0.044	35	2 33 ⁻ 34	465651.310	0.007
26	10 17 ⁻ 25	442763.699	0.012	35	3 32 ⁻ 34	478296.575	0.025
26	11 16 ⁻ 25	455450.901	-0.010	35	6 29 ⁻ 34	516207.921	0.163
27	1 26 ⁻ 27	323245.109	0.057	36	1 35 ⁻ 35	465392.450	-0.055
27	3 25 ⁻ 27	442466.433	0.178	36	1 35 ⁻ 35	478040.741	-0.024
27	9 19 ⁻ 26	455133.635	0.100	37	2 34 ⁻ 36	465131.214	0.037
27	10 18 ⁻ 26	480506.387	0.026	37	0 37 ⁻ 36	477783.334	0.060
27	12 16 ⁻ 26	323123.077	-0.067	38	1 36 ⁻ 37	477523.050	-0.051
28	4 25 ⁻ 28	442186.164	-0.107	40	0 38 ⁻ 39	514951.319	-0.048
28	8 21 ⁻ 27	454842.810	0.025	40	1 39 ⁻ 39	578096.110	0.038
28	9 20 ⁻ 27	480173.981	0.097	41	6 34 ⁻ 39	514694.779	0.056
28	11 18 ⁻ 27	454566.935	-0.015	41	0 41 ⁻ 40	577855.272	0.028
29	8 22 ⁻ 28	467219.220	0.034	42	5 36 ⁻ 42	461612.829	-0.056
29	9 21 ⁻ 28	479875.134	0.043	43	2 41 ⁻ 42	564746.161	0.075
30	6 25 ⁻ 30	322855.376	-0.013	43	3 40 ⁻ 42	577372.836	-0.083
30	9 22 ⁻ 29	479595.306	-0.002	43	8 36 ⁻ 43	461387.711	0.005
31	7 25 ⁻ 31	322708.689	-0.070	44	9 36 ⁻ 44	461154.521	-0.010
31	8 24 ⁻ 30	479326.758	-0.041	45	0 45 ⁻ 44	564246.220	-0.040
32	5 27 ⁻ 31	466422.817	-0.065	45	10 36 ⁻ 45	460913.198	0.045
32	6 26 ⁻ 31	479065.073	-0.023	46	0 46 ⁻ 45	576632.087	0.013
32	8 25 ⁻ 32	322553.087	0.007	47	12 36 ⁻ 47	460404.869	-0.051
33	4 29 ⁻ 32	466165.238	-0.089	48	13 36 ⁻ 48	460137.636	0.023

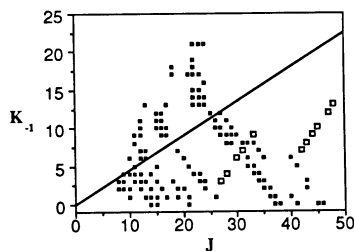


FIG. 2. Scatter plot of the ν_7 data set where K_{-1} and J are taken from the upper rotational level for each transition. Solid boxes represent P - or R -type transitions while open boxes denote Q -type transitions. Transitions above the diagonal solid line demonstrate asymmetric splitting.

IV. RESULTS AND DISCUSSION

The work described here is part of a larger project to study the rotational structure of the excited states of nitric acid. Because of the large dipole moment, relatively small rotational constants, and many thermally populated vibrational state of this species, its millimeter and submillimeter spectra are very dense. In this environment it is necessary to assign lines with caution and to have a significantly redundant data set.

Table I displays 148 transitions observed for the ν_7 vibrational state. The data set includes P -, Q -, and R -type transitions with $J = 8$ – 48 and $K = 0$ – 21 ; both a -type and b -type transitions are included. Figure 2 is a scatter plot of the data set where the K -prolate value is plotted as a function of the principal quantum number J ; both values are taken from the upper state. The preponderance of low K transitions at higher J reflects the drop in intensity which accompanies lifting of the K degeneracy approximately two-thirds of the way up each K stack; the area of splitting is shown by a solid line in Fig. 2.

TABLE II
Results of Analysis (MHz)

Constants	Value	σ
A	13028.9751	0.0020
B	12098.5694	0.0018
C	6201.61605	0.0011
Δ_J ($\times 10^1$)	0.1455271	0.000023
Δ_{JK}^a ($\times 10^1$)	-0.2009457	0.000086
Δ_{JK}^b ($\times 10^2$)	0.604707	0.00078
δ_J^a ($\times 10^2$)	0.12785	0.00046
δ_K^a ($\times 10^1$)	-0.27632	0.00055
H_J ($\times 10^7$)	0.41398	0.031
H_{JK}^a ($\times 10^6$)	-0.532575	0.023
H_{JK}^b ($\times 10^5$)	0.113406	0.0040
H_K ($\times 10^6$)	-0.680644	0.020
h_J ($\times 10^7$)	-0.194	0.073
h_{JK}^a ($\times 10^6$)	0.6103	0.10
h_K ($\times 10^6$)	-0.2870	0.099
L_{JK} ($\times 10^{11}$)	0.1937	0.034
rms	0.068	

In order to test the assignment of the lines, each transition was individually removed from the analysis and an analysis of the remaining data was used to predict the frequency of the removed line. In addition, the calculated spectra of the five lowest vibrational states were combined together and frequency sorted, and each line was checked against these global predictions for possible alternative assignments.

Table II shows the constants derived from our analysis along with the rms deviation of the fit, 0.068 MHz: a sufficient number of digits have been provided to reproduce the observed spectrum. All calculations were performed on a Harris H800 computer in quadruple precision (96 bit) arithmetic.

These constants and predicted spectra, as well as those for a variety of other molecules, may be obtained via telephone modem from the Harris H800. Interested parties should contact one of us (F.C.D.) for telephone numbers and passwords. One copy of the predicted frequencies is on deposit in the Editorial Office of the *Journal of Molecular Spectroscopy* for reference in case F.C.D. could not be reached.

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