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The Spectrum of HNO_3 in the Region 550–800 GHz[1]

In two previous papers on HNO_3 we have reported the measurement of 111 transitions by Cazzoli and De Lucia in the millimeter region (*1*), and 44 transitions by Bowman *et al.* in the submillimeter region (*2*). In this paper we report the measurement of 45 additional submillimeter wave transitions and the extension of the range of the data set by more than 250 GHz to beyond 800 GHz. We have combined the 200 millimeter and submillimeter wave transitions with the 20 centimeter wave transitions reported by Millen and Morton (*3, 4*), and produced a new analysis of the spectrum of HNO_3.

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TABLE I

Observed Transitions of HNO_3 (MHz)

TRANSITION	OBSERVED	CALCULATED	O.-C.
25(22 4)- 24(22 3)	536413.20	536413.16	0.04
25(21 4)- 24(21 3)	543409.04	543409.01	0.03
26(21 6)- 25(21 5)	566581.30	566581.28	0.02
45(0 45)- 44(0 44)	569231.86	569232.16	-0.30
44(1 43)- 43(1 42)	569262.20	569262.24	-0.04
43(2 41)- 42(2 40)	569287.19	569287.21	-0.02
32(14 18)- 31(14 17)	582153.39	582153.36	0.03
31(15 16)- 30(15 15)	582335.56	582335.41	0.15
27(20 8)- 26(20 7)	583781.01	583780.99	0.02
28(18 10)- 27(19 9)	584480.64	584480.62	0.02
28(19 10)- 27(19 9)	584571.76	584571.69	0.07
28(18 10)- 27(18 9)	585018.99	585018.95	0.04
28(19 10)- 27(18 9)	585110.02	585110.02	0.00
26(20 6)- 25(20 5)	589113.15	589113.08	0.07
27(19 8)- 26(19 7)	594642.60	594642.62	-0.02
50(0 50)- 49(0 49)	631654.53	631654.39	0.14
48(2 46)- 47(2 45)	631706.90	631706.94	-0.04
47(3 44)- 46(3 43)	631725.45	631725.40	0.05
46(4 42)- 45(4 41)	631739.79	631739.71	0.08
45(5 40)- 44(5 39)	631750.80	631750.74	0.06
44(6 38)- 43(6 37)	631759.41	631759.41	0.00
43(7 36)- 42(7 35)	631766.69	631766.78	-0.09
42(8 34)- 41(8 33)	631774.09	631774.05	0.04
41(9 32)- 40(9 31)	631782.54	631782.65	-0.11
40(10 30)- 39(10 29)	631794.39	631794.37	0.02
35(15 20)- 34(15 19)	632034.90	632034.78	0.12
33(17 16)- 32(17 15)	632448.11	632448.05	0.06
50(5 45)- 49(5 44)	694121.18	694121.29	-0.11
44(11 33)- 43(11 32)	694135.39	694135.21	0.18
43(12 31)- 42(12 30)	694145.10	694145.03	0.07
43(15 28)- 42(15 27)	731565.47	731565.35	0.12
42(16 26)- 41(16 25)	731612.28	731612.32	-0.04
41(17 24)- 40(17 23)	731686.23	731686.40	-0.17
43(17 26)- 42(17 25)	756534.87	756534.91	-0.04
42(18 24)- 41(18 23)	756621.09	756621.38	-0.29
45(17 28)- 44(17 27)	781384.63	781384.69	-0.06
44(18 26)- 43(18 25)	781449.03	781449.10	-0.07
42(20 22)- 41(20 21)	781705.48	781705.64	-0.16
40(22 18)- 39(22 17)	782343.56	782343.38	0.18
48(16 32)- 47(16 31)	806205.78	806205.63	0.15
46(18 28)- 45(18 27)	806279.72	806279.79	-0.07
45(19 26)- 44(19 25)	806354.89	806354.97	-0.08
43(21 22)- 42(21 21)	806651.75	806651.75	0.00
42(22 20)- 41(22 19)	806933.29	806933.12	0.17
41(23 18)- 40(23 17)	807386.99	807386.82	0.17

0022-2852/84 $3.00

The experimental apparatus has been discussed recently (*5*). A 1-m, 2.5-cm-diameter absorption cell, coated on the inside with clear Krylon, and closed on the ends with Teflon windows, was used.

The techniques used to analyze the data have been discussed in a series of papers on HDS (*6*), HDO (*7*), and D_2S (*8*). A Watson-type Hamiltonian (*9*) is employed to calculate energy levels, and a least-squares procedure (*10*) is used to adjust the rotation and distortion parameters in the Hamiltonian to fit the observed spectrum.

Table I shows the frequencies of the newly observed transitions, together with the frequencies calculated in the least-square analysis. Table II shows the results of the new analysis, which has an overall rms error of 0.122 MHz. The errors indicated in Table II for the spectral constants represent 95% confidence limits.

The data set used in this new analysis is a representative cross-section of the many transitions in HNO_3 through 800 GHz. The spectral constants given in Table II can be used to accurately predict the spectrum of HNO_3 throughout the region covered by the data set.

In the region covered in this study, the spectrum is dominated by strong $\Delta J = 1$ transitions that are quadruply degenerate. These transitions are of the form

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

where J' is the maximum J value for the branch and where $n = 0, 1, 2, \ldots$. These branches have the interesting and useful feature illustrated in Fig. 1 for $J' = 50, 53, 55$, and 58. This near degeneracy of a number of strong lines may be especially important for remote sensing applications. Since there are many

TABLE II

Results of Analysis (MHz)

Constant	Value	2σ
A	13011.0394	0.0036
B	12099.8719	0.0036
C	6260.6468	0.0032
Δ_J $(\times 10^1)$	0.1411597	0.000038
Δ_{JK} $(\times 10^1)$	-0.2016856	0.000074
Δ_K $(\times 10^2)$	0.738618	0.00063
δ_J $(\times 10^2)$	0.118281	0.000074
δ_K $(\times 10^1)$	-0.205481	0.000091
H_J $(\times 10^7)$	0.1893	0.0122
H_{JK} $(\times 10^7)$	-0.90360	0.1012
H_{KJ} $(\times 10^7)$	0.90382	0.2408
H_K $(\times 10^7)$	-0.2289	0.1534
h_J $(\times 10^8)$	-0.9277	0.0240
h_{JK} $(\times 10^6)$	-0.1249	0.0060
h_K $(\times 10^5)$	0.1157	0.0054
L_{JJK} $(\times 10^{11})$	0.5011	0.3180
L_{JK} $(\times 10^{10})$	-0.35170	0.0900
L_{KKJ} $(\times 10^{10})$	0.68194	0.0960
L_K $(\times 10^{10})$	-0.36974	0.0380

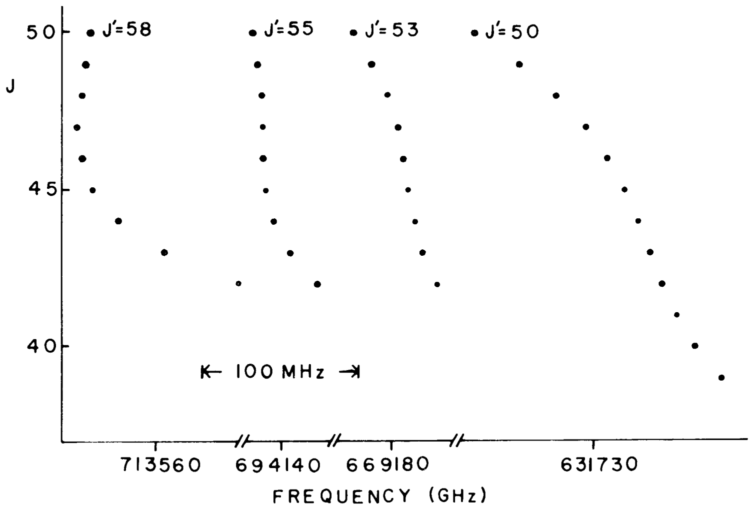

FIG. 1. Examples of regions of concentrated line density.

of these, branches that match the resolution of the instrument and that are compatible with other system parameters can be selected.

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