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Millimeter and Submillimeter Wave Spectra of HNO_2 (*cis*), HNO_2 (*trans*), and HNO_3[1]

In gas phase equilibrium, HNO_2 (nitrous acid) exists only as a component of a mixture which also contains NO, NO_2, H_2O, N_2O_3, N_2O_4, and HNO_3. The resulting spectral overlap and reduced concentration have made studies of the rotational structure of HNO_2 difficult, especially in the infrared. However, Allegrini *et al.* (*1*) have recently reported results from a CO laser intracavity Stark experiment, and high-resolution diode laser measurements are currently underway (*2*). The pure rotational structure of HNO_2 has also been studied in the centimeter spectral region by Cox *et al.* (*3*) and Finnigan *et al.* (*4*).

In this paper we report measurements of 133 new millimeter and submillimeter wave transitions of HNO_2 and HNO_3. The reported measurements and new analysis of HNO_3 are an extension of work previously reported by us (*5*). HNO_2 and HNO_3 are small asymmetric rotors with rotational constants of 10–100 GHz and large dipole moments. As such they exhibit an intense, dense spectrum throughout the millimeter and submillimeter wave spectral region. From the several thousand observable transitions, those reported have been selected so that they form the basis of analyses capable of producing accurate spectral maps for each species in this region of the spectrum.

TABLE I

Observed Transitions (MHz)

Transition	Observed Frequency	Calc.-Obs.
	HNO_3	
$18_{7\,11} - 17_{8\,10}$	319514.60	-0.02
$20_{5\,15} - 19_{6\,14}$	319382.89	0.01
$21_{4\,17} - 20_{5\,16}$	319346.13	0.05
$21_{9\,12} - 20_{10\,11}$	382109.52	-0.08
$22_{3\,19} - 21_{4\,18}$	319314.69	0.03
$23_{2\,21} - 22_{3\,20}$	319284.71	0.06
$24_{1\,23} - 23_{2\,22}$	319254.14	0.06
$24_{11\,13} - 23_{12\,12}$	444783.24	-0.12
$25_{0\,25} - 24_{1\,24}$	319221.53	0.09
$25_{5\,20} - 24_{6\,19}$	381908.39	0.02
$25_{10\,15} - 24_{11\,14}$	444638.93	-0.10
$26_{9\,17} - 25_{10\,16}$	444556.47	-0.09
$27_{8\,19} - 26_{9\,18}$	444504.01	-0.02
$27_{2\,26} - 27_{3\,25}$	-319897.18	0.13
$27_{0\,27} - 26_{0\,26}$	344241.56	0.08
$27_{1\,27} - 27_{1\,26}$	-332546.76	0.26
$28_{7\,21} - 27_{8\,20}$	444467.19	0.00
$29_{6\,23} - 28_{7\,22}$	444438.62	0.01
$29_{14\,15} - 28_{14\,14}$	544866.66	-0.14
$30_{5\,25} - 29_{6\,24}$	444414.11	0.02
$30_{13\,17} - 29_{13\,16}$	544685.06	0.00
$31_{4\,27} - 30_{5\,26}$	444391.12	-0.02
$32_{3\,29} - 31_{4\,28}$	444367.83	-0.06
$33_{2\,31} - 32_{3\,30}$	444342.84	-0.04
$33_{10\,23} - 32_{10\,22}$	544467.21	0.30
$34_{1\,33} - 33_{2\,32}$	444315.15	-0.01
$34_{7\,28} - 34_{7\,27}$	-344260.78	-0.13
$35_{0\,35} - 34_{1\,34}$	444283.75	0.13
$36_{4\,32} - 35_{5\,31}$	506874.30	-0.03
$37_{4\,33} - 36_{5\,32}$	519367.21	-0.05
$38_{5\,33} - 37_{5\,32}$	544365.32	0.06
$39_{3\,37} - 39_{4\,36}$	-457533.02	0.13
$40_{0\,40} - 39_{1\,39}$	506774.11	0.18
$40_{4\,37} - 40_{5\,36}$	-457342.27	-0.48
$40_{3\,37} - 39_{3\,36}$	544330.58	[illegible]
$41_{0\,41} - 40_{1\,40}$	519268.35	0.25
$41_{2\,39} - 40_{2\,38}$	544309.07	-0.37
$42_{1\,41} - 41_{1\,40}$	544283.39	-0.17
$43_{0\,43} - 42_{0\,42}$	544252.97	0.22
$43_{17\,27} - 43_{17\,26}$	-329666.23	-0.03
$45_{19\,27} - 45_{19\,26}$	-329102.09	0.00
$48_{22\,27} - 48_{22\,26}$	-328142.95	0.11
$50_{23\,28} - 50_{23\,27}$	-340279.33	0.06
$50_{24\,27} - 50_{24\,26}$	-327420.52	0.19
	Cis HNO_2[a]	
$9_{2\,8} - 9_{1\,9}$	256952.24	0.05
$9_{1\,9} - 8_{0\,8}$	256549.85	0.04
$10_{2\,9} - 10_{1\,10}$	266316.39	0.03
$10_{1\,10} - 9_{0\,9}$	274708.15	0.01
$11_{2\,10} - 11_{1\,11}$	276649.37	-0.01
$12_{0\,12} - 11_{1\,11}$	256148.69	0.01
$12_{2\,11} - 12_{1\,12}$	287945.39	0.02
$12_{3\,9} - 12_{2\,10}$	338872.68	0.06
$13_{0\,13} - 12_{1\,12}$	283335.43	-0.04
$13_{3\,10} - 13_{2\,11}$	332960.86	0.03
$13_{4\,9} - 12_{5\,8}$	-325162.96	0.04
$14_{3\,12} - 14_{2\,13}$	374551.54	-0.10
$14_{3\,11} - 14_{2\,12}$	326345.89	0.00
$14_{2\,13} - 14_{1\,14}$	313374.36	0.03
$14_{0\,14} - 13_{1\,13}$	310011.10	-0.10
$15_{0\,15} - 14_{1\,14}$	336167.60	-0.06
$15_{1\,14} - 15_{0\,15}$	223686.00	0.03
$15_{2\,14} - 15_{1\,15}$	327464.94	0.00
$15_{4\,11} - 14_{5\,10}$	-274913.52	-0.03
$15_{3\,12} - 15_{2\,13}$	319193.49	0.01
$16_{1\,15} - 15_{2\,14}$	281025.03	-0.01
$16_{2\,15} - 16_{1\,16}$	342433.56	0.07
$16_{3\,13} - 16_{2\,14}$	311719.54	0.00
$17_{1\,16} - 17_{0\,17}$	270858.23	-0.02
$17_{1\,16} - 16_{2\,15}$	315434.00	0.09
$17_{3\,15} - 17_{2\,16}$	390007.14	-0.16
$18_{2\,16} - 18_{1\,17}$	206036.03	-0.01
$19_{1\,18} - 19_{0\,19}$	321900.09	0.03
$19_{2\,17} - 19_{1\,18}$	217139.48	-0.01
$19_{5\,14} - 18_{6\,13}$	-319236.79	-0.08
$20_{2\,18} - 20_{1\,19}$	230415.58	-0.04
$21_{3\,18} - 21_{2\,19}$	279196.57	0.07
$21_{5\,16} - 20_{6\,15}$	-268582.68	0.04
$22_{2\,20} - 22_{1\,21}$	263500.93	0.07
$22_{3\,19} - 22_{2\,20}$	275705.43	0.06
$23_{3\,20} - 23_{2\,21}$	273842.76	0.08
$23_{5\,18} - 22_{6\,17}$	-217376.27	0.02
$23_{1\,22} - 23_{0\,23}$	428201.88	-0.05
$24_{3\,21} - 24_{2\,22}$	273824.31	0.02
$25_{2\,23} - 25_{1\,24}$	328250.73	0.06
$25_{3\,22} - 25_{2\,23}$	275834.71	-0.05
$25_{3\,22} - 24_{4\,21}$	203964.40	-0.02
$26_{3\,23} - 26_{2\,24}$	280028.24	-0.02
$27_{3\,24} - 27_{2\,25}$	286529.79	-0.05
$27_{3\,24} - 26_{4\,23}$	285170.03	0.02
$27_{6\,21} - 26_{7\,20}$	-261791.16	0.06
$29_{6\,23} - 28_{7\,22}$	-210345.14	-0.05
$30_{3\,27} - 30_{2\,28}$	320659.26	-0.01
$33_{4\,29} - 32_{5\,28}$	271920.51	0.00
	Trans HNO_2[a]	
$9_{5\,5} - 8_{5\,4}$	211944.29	0.04
$9_{6\,4} - 8_{6\,3}$	211899.86	0.03
$9_{7\,3} - 8_{7\,2}$	211866.97	0.02
$9_{8\,2} - 8_{8\,1}$	211838.93	0.04
$11_{6\,6} - 10_{6\,5}$	259006.25	0.01
$11_{5\,7} - 10_{5\,6}$	259080.74	0.00
$11_{4\,8} - 10_{4\,7}$	259206.31	0.20
$11_{4\,7} - 10_{4\,6}$	259210.56	0.05
$11_{3\,8} - 10_{3\,7}$	259607.46	0.02
$11_{0\,11} - 10_{0\,10}$	254550.85	0.04
$11_{7\,5} - 10_{7\,4}$	258954.10	0.01
$11_{8\,4} - 10_{8\,3}$	258912.20	0.00
$11_{9\,3} - 10_{9\,2}$	258874.87	0.01
$11_{10\,2} - 10_{10\,1}$	258839.26	-0.06
$12_{2\,10} - 12_{1\,11}$	206817.18	-0.05
$14_{7\,8} - 13_{7\,7}$	329591.10	0.00
$14_{10\,5} - 13_{10\,4}$	329405.20	0.03
$14_{1\,14} - 13_{1\,13}$	316907.59	0.01
$14_{1\,13} - 13_{1\,12}$	337198.86	0.02
$14_{0\,14} - 13_{0\,13}$	321236.27	0.02
$14_{11\,4} - 13_{11\,3}$	329353.07	0.03
$14_{12\,3} - 13_{12\,2}$	329301.07	-0.02
$16_{0\,16} - 15_{0\,15}$	365184.15	-0.01
$16_{1\,15} - 15_{1\,14}$	384150.20	-0.01
$16_{2\,14} - 16_{1\,15}$	204696.36	-0.03
$17_{0\,17} - 16_{0\,16}$	387069.00	0.03
$18_{2\,16} - 18_{1\,17}$	211160.91	-0.12
$19_{0\,19} - 18_{0\,18}$	430751.32	0.01
$19_{1\,19} - 18_{1\,18}$	428289.02	0.01
$19_{4\,15} - 18_{5\,14}$	-277372.95	0.00
$20_{2\,18} - 20_{1\,19}$	223818.67	0.05
$20_{4\,16} - 19_{5\,15}$	-252837.45	0.01
$21_{1\,20} - 21_{0\,21}$	333925.02	-0.03
$22_{2\,20} - 21_{3\,19}$	218966.68	0.01
$25_{2\,23} - 25_{2\,24}$	224897.25	-0.01
$26_{5\,21} - 25_{6\,20}$	-271218.02	0.00
$28_{5\,23} - 27_{6\,22}$	-221734.75	0.00
$29_{3\,26} - 28_{4\,25}$	217898.84	0.01
$31_{3\,28} - 31_{2\,29}$	320214.10	0.00
$36_{4\,32} - 35_{5\,31}$	205320.96	0.00

a. Transitions have been corrected for the electric quadrapole interaction.

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TABLE II

Rotational Constants (MHz)

	Cis HNO_2 value	Cis HNO_2 σ	Trans HNO_2 value	Trans HNO_2 σ	HNO_3 value	HNO_3 σ
A	84 101.8381	0.011	92 892.0204	0.011	13 011.0485	0.0023
B	13 169.0755	0.0019	12 524.9742	0.0017	12 099.8803	0.0023
C	11 364.1644	0.0019	11 016.6671	0.0017	6 260.6488	0.0029
$\Delta_J(x10^1)$	0.170502	0.000065	0.153081	0.000047	0.141390	0.000031
$\Delta_{JK}(x10^2)$	-0.86971	0.0076	5.17709	0.0046	-2.018697	0.00033
$\Delta_K(x10^{-1})$	0.195859	0.000028	0.299596	0.000053	.000738540	0.00000025
$\delta_J(x10^2)$	0.280810	0.000023	0.206190	0.000046	0.118256	0.000045
$\delta_K(x10^1)$	0.84811	0.00058	0.93120	0.0018	-0.205601	0.000048
$H_J(x10^7)$	-0.3248	0.067	-0.2469	0.049	0.3145	0.012
$H_{JK}(x10^5)$	----	----	-0.1735	0.024	-0.010756	0.00036
$H_{KJ}(x10^4)$	-0.2027	0.011	-0.2297	0.0091	.0011465	0.00011
$H_K(x10^3)$	0.1496	0.0086	0.2909	0.011	-.00003809	0.000008
$h_J(x10^8)$	----	----	----	----	-0.9344	0.014
$h_{JK}(x10^6)$	-0.202	0.067	-0.439	0.19	-0.1369	0.0031
$h_K(x10^4)$	0.4024	0.061	-0.2688	0.20	0.01089	0.00030
rms	0.049		0.048		0.143	
Number of independent data points	73		66		175	

Our basic millimeter and submillimeter wave experimental technique has been discussed previously (*6*). The cell used for most of the work was 1 m long, 2.5 cm diameter, and had Teflon windows at the ends. The inside of the cell was coated with clear Krylon to inhibit chemical decomposition. For *cis*- and *trans*-HNO_2, we also utilized a 3-m cell.

HNO_3 is a stable molecule and a standard laboratory preparation was used to generate the sample. Various methods of preparing our HNO_2 sample were tried, but it was found that the highest yield was achieved by following the procedures of Varma and Curl (*7*). The final method adopted was to mix a few Torr each of NO_2, NO, and H_2O in the ratio of 2:1:1 in a mixing bulb. The sample was isolated and allowed to equilibrate for a few minutes. The mixing bulb was insulated and the temperature of the sample could be varied to maximize the concentration of HNO_2. Measurements were made with a continuous flow of gas from the mixing bulb through the cell. Pressure in the cell was typically 0.05 Torr.

HNO_3 and HNO_2 are asymmetric rotors with electric dipole moments that give rise to both *a*- and *b*-type transitions. We have used Watson's reduced centrifugal distortion Hamiltonian (*8*) and the computational and statistical techniques that we have discussed previously (*9*, *10*) for the analysis of the rotational spectrum of these molecules.

The high barriers to internal rotation divide the spectrum of HNO_2 into that of two distinct asymmetric rotors which are labeled *cis* and *trans*. Previous lower-frequency measurements ($<$40 GHz) (*3*, *4*) were included in our analysis of both of these species. We measured 49 *cis* transitions and 40 *trans* transitions, extending the data set into the submillimeter region. The measurements were corrected for shifts due to an electric quadrupole interaction. Our data are presented in Table I along with the differences between these measured values and the frequencies calculated from the spectral constants shown in Table II. The analyses that lead to these spectral constants also include the earlier data discussed above. As can be seen from the rms deviations of the analyses, the fit to the earlier data is comparable to that shown in Table I.

For HNO_3 the data base consists in part the 111 transitions measured by Cazzoli and De Lucia in the millimeter range (*5*) and the 20 centimeter wave lines of Millen and Morton (*11*, *12*). We have extended this data set by measuring 44 transitions in the submillimeter wave region of the spectrum. The results of our measurements are presented in Table I, and the new spectral constants are listed in Table II.

These new measurements and analyses provide accurate spectral maps throughout this spectral region. Because of their length they are on deposit at the Editorial Office of this journal. Anyone interested should first consult the second author and if unsuccessful should write to the Editor, Journal of Molecular Spectroscopy.

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