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Note

The millimeter and submillimeter spectra of the ground state and excited ν_9, ν_8, ν_7, and ν_6 vibrational states of HNO_3

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The purpose of this note is to report in the literature the latest millimeter and submillimeter spectroscopic measurements and analyses for the rotational structure of a number of vibrational states of HNO_3. Subsets of these data (and more commonly spectroscopic constants, energy levels, etc. derived from them) are widely used, often in multi-step, weighted analyses with infrared data [1–14]. However, these multi-step processes do not make optimal use of the data and have the potential to significantly affect the calculation of spectroscopic constants and especially the uncertainties in these constants and synthetic spectra calculated from them [15,16]. For example, in the specific case of ThO, Albritton et al. [15] show examples of *both* overestimates and under estimates by factors of 5–10 in the uncertainties of derived parameters that result from such a multi-step process. In this paper we report new analyses of these states and deposit in electronic form all of the original spectral data upon which they are based. This will make possible the direct inclusion of the data in mixed analyses, thereby maximizing the usefulness of their information content.

We have published analyses of the rotational structures of the ground state, ν_9, ν_8, ν_7, and ν_6 [17–22]. During the course of subsequent work, we have accumulated significant additional data and have continually updated these analyses. In various forms these data have been incorporated in many analyses. For example, in most infrared analyses of rovibrational spectra, microwave data have been used to largely determine the ground state, often in conjunction with infrared combination differences in a weighted fit [3,4,6–8,13].

The inclusion of the very accurate microwave data in this reduction has been especially valuable because, without it, the many sums and differences (which are imposed by the $\Delta J = 0, \pm 1$ selection rule) necessary to calculate the energy of a high J line would result in significant accumulated error and a need to carefully consider the impact of this error in subsequent processing steps. Not only would this accumulated error make comparisons among different sets of energy levels difficult, it also would require rather detailed statistical procedures to make, for example, the uncertainties in calculated spectroscopic constants meaningful. However, with the microwave data largely defining the ground state and the error in the absolute energy of upper state levels coming mostly from individual infrared line measurements, the statistical problems associated with the inability to access the original data are largely transcended.

However, in many states there have been enough microwave data available to make significant contributions to the definitions the rotational structure of the upper state as well. These include analyses of ν_6, ν_7, ν_8, and ν_9 [1,11,23,24] the $\nu_5/2\nu_9$ dyad [5,9], and $\nu_8 + \nu_9$ [12,14]. Since these data are comparable in accuracy to the ground state data, it is statistically important that all of the data be available for direct inclusion in the analysis.

Additionally, the processed data (e.g., energy levels) often reflects the interests of the authors. For example, the torsional motion associated with the ν_9 mode

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produces about a 2 MHz splitting in ν_9, about 50 MHz in $2\nu_9$, and by mixing about 35 MHz in ν_5. Because the 2 MHz splitting is much smaller than the Doppler width in the infrared and the ~50 MHz splitting in $2\nu_9$ is only marginally resolvable [25], in analyses this effect is often eliminated by averaging. However, even in the case where the Doppler/instrument broadening obscures the splitting, it has been shown that a direct accounting of this effect in a weighted fit with the experimental microwave line frequencies improves the fit to the infrared lines because of systematic shifts [9].

Most of the new data reported here were obtained with either a phase-locked backward wave oscillator system with lock-in detection or the FASSST system. Details of the experimental methods can be found in earlier papers [20,26]. All our previously published millimeter and submillimeter-wave data, as well as earlier centimeter-wave results [27,28], have been included in the analysis and weighted equally with an uncertainty of 0.100 MHz. With the lower frequency phased-locked BWO systems, the quadrupole splitting is resolvable (up to ~150 GHz) in all vibrational states for many transitions where $K_a \sim J$. We assigned at least 15 quadrupole split transitions for each state and determined the corresponding quadrupole constants, which are all very similar to the ground state constants of [28].

Table 1 shows the rotational and quadrupole constants and statistics of the fits for the ground, ν_9, ν_8, ν_7, and ν_6 states that were determined using Pickett's SPFIT program [29] that is available on the JPL web site (http://spec.jpl.nasa.gov/). The output of each fit is deposited electronically with the journal and includes the experimental data, predictions, determined constants with uncertainties, and the co-variance matrix. The standard deviation of each analysis is near or below the estimated experimental uncertainty of 0.100 MHz, which indicates the high quality of the analyses. Each state was fit with the standard Watson A-reduced Hamiltonian in the I^r representation [30] with the quadrupole terms fitted simultaneously.

Table 1
Results of analyses (MHz)[a]

Parameter	Ground state	ν_9[b]	ν_9[c]	ν_7	ν_6	ν_8
ν_o[d]	–	458.228664	458.228664	580.303505	647.826262	763.154270
E_ρ	–	1.170(4)	–	–	–	–
A	13010.98738(53)	12961.8487(1907)	12998.94120(100)	13028.91227(48)	13006.20089(61)	12998.02165(77)
B	12099.92317(51)	12052.2569(1907)	12015.16454(85)	12098.64240(41)	12057.50335(59)	12005.52809(75)
C	6260.63733(49)	6255.23036(29)	6255.23197(62)	6201.60841(44)	6282.33923(51)	6260.81246(55)
D_{ab}	–	−187.3874(4628)	–	–	–	–
$\Delta_J \times 10^3$	8.906290(265)	8.67215(83)	8.77006(65)	8.81562(49)	9.83341(54)	8.89983(71)
$\Delta_{JK} \times 10^3$	−4.547276(536)	−2.50332(1053)	−3.98741(225)	−2.84274(90)	−7.92931(72)	−3.74552(122)
$\Delta_K \times 10^3$	7.38981(70)	4.55778(1346)	6.5461(40)	6.00382(119)	9.68565(80)	6.35593(111)
$\delta_J \times 10^3$	3.785507(107)	3.66130(40)	3.709899(280)	4.151786(178)	3.797805(154)	3.77758(26)
$\delta_K \times 10^3$	7.47837(65)	7.7598(36)	7.25864(120)	7.89166(64)	7.80192(35)	6.80815(49)
$H_J \times 10^8$	−0.0580(48)	−0.1805(110)	−0.5232(193)	−1.0687(175)	0.4133(163)	1.269(27)
$H_{JK} \times 10^7$	0.27277(145)	−0.63307(1292)	0.1375(94)	1.0017(56)	−0.0312(44)	−0.55084(710)
$H_{KJ} \times 10^6$	−0.11050(63)	0.24130(390)	–	−0.31196(131)	0.008693(786)	0.07959(106)
$H_K \times 10^6$	0.12337(91)	−0.16307(301)	0.01813(246)	0.25916(75)	0.02421(66)	−0.00627(91)
$h_J \times 10^9$	0.0345(221)	−0.561(60)	−2.386(87)	9.855(66)	−11.945(52)	6.433(94)
$h_{JK} \times 10^8$	0.2058(420)	−3.490(74)	−0.786(60)	−4.288(64)	4.8121(228)	0.136(35)
$h_K \times 10^7$	0.5205(43)	0.9710(120)	0.4275(115)	1.46177(273)	−0.01911(243)	0.2104(28)
$L_{JK} \times 10^{12}$	–	–	–	2.258(233)	–	–
$L_{KKJ} \times 10^{12}$	3.5557(2636)	–	–	–	–	–
$L_K \times 10^{12}$	−4.426(399)	–	–	–	–	–
$l_{JK} \times 10^{12}$	−0.5731(724)	−1.598(180)	–	–	–	–
$l_{KJ} \times 10^{12}$	0.635(134)	3.551(342)	–	−1.743(142)	–	–
χ_{aa}	1.046(48)	1.165(95)	–	1.046(64)	1.062(95)	0.993(223)
$\chi_{bb} - \chi_{cc}$	−0.832(132)	−0.904(164)	–	−0.832[e]	−1.056(326)	−1.116(809)
No. of transitions	634	795	327	862	858	617
$J_{\max}$	74	61	61	60	58	56
$K_{a\ \max}$	57	47	41	43	44	41
Frequency range (GHz)	8–831	78–655	84–655	78–578	78–657	78–519
Std. Dev. (kHz)	105	68	115	90	94	82

[a] Numbers in parentheses are standard errors (1σ) and enough digits are supplied to reproduce the observed spectra.

[b] To model the torsional splitting, the internal axis method was used with $\rho = 1.468285$. See [31].

[c] Only includes a-type transitions that will fit a normal Watson-type Hamiltonian in a principal axis system and does not include quadrupole data.

[d] Band origins are from [1,11,23].

[e] Parameter not determinable and was constrained to the value determined for the ground state.

Two separate analyses were performed for the ν_9 vibrational state. This state exhibits a large amplitude torsional motion, which produces an $\sim$2 MHz splitting. In the first analysis, an internal axis system that included torsional parameters was used to account for this splitting. However, for analyses of infrared bands (which do not resolve this splitting) a different analysis is more appropriate, especially for the calculation of intensities. For this purpose we include a second analysis in which 327 *a*-type transitions that are unaffected by the torsional splitting are fit in the principal axis system, with 25 *a*-type transitions and 394 *b*-type transitions either rejected or weighted out of the fit. As pointed out in [1], the *a*-type microwave transitions alone are sufficient to determine the rotational structure of ν_9.

We have also recently published an extensive analysis of the $\nu_5/2\nu_9$ interacting dyad and deposited in the JMS electronic archive the complete set of millimeter and submillimeter spectral measurements on which it was based [31]. In that paper it was shown that the *predictions* of the 'infrared' energy levels by microwave analysis had a distribution of difference essentially the same as the *fit* to these same energy levels. Similarly, the spectroscopic constants and data presented here for ν_9 and in [31] for ν_5 and $2\nu_9$ can be used to accurately synthesize the line positions of the pure rotational spectra as well as the rotational structure of the infrared bands. This has been demonstrated by the detailed synthesis of high-resolution FTIR data of the ν_9, $2\nu_9 - \nu_9$, and $\nu_5 - \nu_9$ bands in the 22 μm region [32].

As noted in previous infrared studies of these states [1], the pure rotational transitions of our early publications [17–22] determined the rotational constants in combined analyses while the infrared data mainly determined the vibrational band origins. In more recent infrared studies [11,23], high-resolution infrared data over a larger range of quantum numbers was combined with the aforementioned rotational measurements without any significant changes in the rotational constants from the earlier values. This is not surprising since the pure rotational data extended as far as or farther in rotational quantum numbers than the infrared data and had a much higher experimental accuracy.

For all of the vibrational states presented in this note, the measurements of rotational transitions have been extended to higher quantum numbers than previously published for either microwave or infrared work. Due to this extension, additional higher order distortion constants have been included in the fits. When comparing the new constants to the earlier constants, statistically significant differences exist, but these are presumably due to the differences in the Hamiltonian terms selected.

In summary, the spectral data and constants presented here should make possible the calculation of the thermally populated rotational structure of all vibrational states below $1000\,\text{cm}^{-1}$. Since the spectral data are included in the electronic archive, future workers on these problems will be able to include it directly in their analyses, thereby obtaining maximal use of the information they contain in the context of analyses with meaningful statistics.

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Appendix A

Supplementary data for this article is available online.

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