# Centrifugal Distortion Effect in the Microwave Spectrum of Nitric Acid

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The microwave rotational spectrum of Nitric Acid has been analysed in the frequency region 8000 – 35000 MHz and up to $J=12$. The analysis gives refined rotational constants and all the quartic centrifugal distortion constants.

## *Introduction*

The first microwave study of Nitric Acid was made by Millen and Morten[1] who observed the $HNO_3$ transitions up to $J=3$. Subsequently the same authors extended this study[2] up to $J=12$ in the frequency region 8 – 35 GHz, and also to some of the isotopic species of $HNO_3$. They also calculated the structural parameters of Nitric Acid. Later Cox and Reveros[3] further extended the study of this molecule. Recently the far-infrared spectrum of Nitric Acid vapor has been reported by Fleming[4]. He has found that the transition frequencies calculated using the rigid rotator model differ from the observed frequencies. He attributed this difference to the centrifugal distortion in the molecule.

We have in the present study calculated refined rotational constants and quartic centrifugal distortion constants.

## *Analysis of the Spectrum*

The theory of centrifugal distortion has been given by many authors[5–9] for rotational spectra of asymmetric top molecules. Watson[10] has given the expression for a centrifugal distorted rotator as:

$$W = W_0 - d_J\, J^2 (J+1)^2 - d_{JK}\, J(J+1)\,\langle P_z^2\rangle - d_K\,\langle P_z^4\rangle - d_{WJ}\, W_0\, J(J+1) - d_{WK}\, W_0\,\langle P_z^2\rangle$$

where $W_0$ is the energy of the corresponding rigid rotator, and hence the function of three rotational constants $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ only, and $d_J$, $d_{JK}$, $d_K$, $d_{WJ}$ and $d_{WK}$ are centrifugal distortion constants. The spectrum was fitted to the above formula using techniques described by Marstokk and Mollendal[11]. The constants obtained as a result of the analysis are given in Table 2 along with the distortion-free rotational constants $A$, $B$ and $C$. The agreement between the calculated and observed frequencies can be seen from Table 1. The standard deviation of the fit was 0.025 MHz.

## *General Discussion*

The molecule $HNO_3$ is a near-oblate asymmetric top with $\mu_a = 1.99$ D and $\mu_b = 0.83$ D, hence the spectrum consists of both a- and b-type rotational transitions.

The reported spectrum[1–2] of the molecule mainly consists of two Q-branch and a-type series namely $J_{J-1,1} - J_{J-1,2}$ and $J_{J-2,2} - J_{J-2,3}$. The frequencies of the transitions belonging to these series decrease and the centrifugal distortions increase with increasing rotational quantum number. When the constants obtained as a result of the analysis were used to predict all possible transitions in the frequency region studie and up to $J$ value equal to 12, it was found that even not all the lines of the $J_{J-2,2} - J_{J-2,3}$ series were reported by earlier workers. These lines namely $3_{1,2} - 3_{1,3}$ and $4_{2,2} - 4_{2,3}$ have been predicted at 31046.650 MHz and 30378.453 MHz

Table 1. Microwave spectrum of $HNO_3$.

| Transition | Obs. freq. (MHz) | Cal. freq. (MHz) | $\nu_{obs} - \nu_{cal}$ (MHz) | Cent. dist. (MHz) | Ref. [a] |
|---|---|---|---|---|---|
| a-type | | | | | |
| $2_{1,1} - 2_{1,2}$ | 17517.49 | 17517.518 | −0.028 | −0.194 | 1 |
| $3_{2,1} - 3_{2,2}$ | 16215.64 | 16215.626 | 0.014 | −0.597 | 1 |
| $4_{3,1} - 4_{3,2}$ | 14534.25 | 14534.238 | 0.012 | −1.212 | 2 |
| $5_{4,1} - 5_{4,2}$ | 12540.98 | 12540.991 | −0.011 | −2.083 | 2 |
| $6_{5,1} - 6_{5,2}$ | 10344.23 | 10344.205 | 0.025 | −3.204 | 2 |
| $7_{6,1} - 7_{6,2}$ | 8097.58 | 8097.578 | 0.002 | −4.459 | 2 |
| $5_{3,2} - 5_{3,3}$ | 29175.32 | 29175.283 | 0.037 | −3.173 | 2 |
| $6_{4,2} - 6_{4,3}$ | 27369.67 | 27369.726 | −0.056 | −5.113 | 2 |
| $7_{5,2} - 7_{5,3}$ | 24993.51 | 24993.460 | 0.050 | −7.695 | 2 |
| $8_{6,2} - 8_{6,3}$ | 22147.00 | 22147.049 | −0.049 | −10.904 | 2 |
| $9_{7,2} - 9_{7,3}$ | 18969.56 | 18969.540 | 0.020 | −14.619 | 2 |
| $10_{8,2} - 10_{8,3}$ | 15628.19 | 15628.192 | −0.002 | −18.521 | 2 |
| $11_{9,2} - 11_{9,3}$ | 12317.35 | 12317.341 | 0.009 | −22.061 | 2 |
| $12_{10,2} - 12_{10,3}$ | 9245.56 | 9245.567 | −0.007 | −24.486 | 2 |
| $1_{0,1} - 0_{0,0}$ | 18360.53 | 18360.513 | 0.017 | 0.016 | 1 |
| $3_{3,1} - 3_{1,2}$ | 22161.00 | 22160.984 | 0.016 | −0.883 | 1 |
| b-type | | | | | |
| $1_{1,1} - 0_{0,0}$ | 19271.60 | 19271.617 | −0.017 | −0.063 | 1 |
| $2_{1,2} - 1_{0,1}$ | 31792.80 | 31792.800 | 0.000 | −0.139 | 2 |
| $2_{1,1} - 2_{0,2}$ | 17616.03 | 17616.023 | 0.007 | −0.225 | 1 |
| $3_{3,0} - 3_{2,1}$ | 9447.97 | 9447.969 | 0.001 | −0.377 | 1 |
| $3_{2,1} - 3_{1,2}$ | 16700.74 | 16700.771 | −0.031 | −0.705 | 1 |
| $3_{3,1} - 3_{2,2}$ [b] | 21676.16 | 21675.838 | 0.322 | −0.775 | 1 |

[a] The observed frequency is taken from the reference listed.
[b] Transition not included in the fit, removal of this transition reduces the standard deviation from 0.061 MHz to 0.025 MHz.

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Table 2. Rotational and centrifugal distortion constants of $HNO_3$ (MHz).

Rotational constants

$\tilde{A} = 13011.050$
$\tilde{B} = 12099.867$
$\tilde{C} = 6260.630$

Distortion constants

$d_J = 0.80830 \times 10^{-1}$
$d_{JK} = -0.12705 \times 10^{1}$
$d_K = 0.61503$
$d_{WJ} = -0.52902 \times 10^{-5}$
$d_{WK} = 0.96982 \times 10^{-4}$

Distortion-free rotational constants

$A = 13010.985$
$B = 12099.935$
$C = 6261.233$

respectively with the centrifugal distortion effect as ($-0.817$ MHz) and ($-1.791$ MHz) respectively.

## *Conclusions*

A study of Table 1 shows that the observed frequencies can be explained successfully by considering the non-rigid rotator model of the molecule. A knowledge of these constants will be helpful for further studies of this molecule at higher *J*-values. Since the rotational constants are directly related to the moments of inertia, with the refined rotational constants a better understanding of this molecule is expected.

The distortion constants depend explicitly on the elements of the inverse force field constants matrix [12]. Therefore the present study will also be helpful for the determination of the force field constants, vibrational frequencies and Coriolis coupling constants. The importance of supplementing vibrational frequency data with vibration-rotation data has been pointed out by Duncan and Mills [13, 14].

All the transitions in the frequency region $5-45$ GHz for $J \leqq 12$ have been calculated [15]. Copies of the calculated spectrum may be obtained from the authors on request.

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