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 Morten¹ who observed the HNO₃ transitions up to J=3. Subsequently the same authors extended this study² up to J=12 in the frequency region 8-35 GHz, and also to some of the isotopic species of HNO₃. They also calculated the structural parameters of Nitric Acid. Later Cox and Reveros³ further extended the study of this molecule. Recently the far-infrared spectrum of Nitric Acid vapor has been reported by Fleming⁴. 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 Mollendal¹¹. 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 HNO₃ is a near-oblate asymmetric top with $\mu_a = 1.99 \text{ D}$ and $\mu_b = 0.83 \text{ D}$, 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 HNO3 .

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Transition	Obs. freq. (MHz)	Cal. freq. (MHz)	$\nu_{\rm obs} - \nu_{\rm cal}$ (MHz)	Cent. dist. (MHz)	Ref. a
a-type					
$2_{1,1} - 2_{1,2}$	17517.49	17517.518	-0.028	-0.194	1
3.1-3.2	16215.64	16215.626	0.014	-0.597	1
$4_{3,1} - 4_{3,2}$	14534.25	14534.238	0.012	-1.212	2
54.1-54.9	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
$5_{3,9} - 5_{3,3}$	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
86.2-86.3	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
$12_{10,2} - 12_{10,2}$	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					
$1, -0_{0,0}$	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
33.	9447.97	9447.969	0.001	-0.377	1
3.1-3.3	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 HNO₃ (MHz).

\widetilde{A} = 13011.050 \widetilde{C} =	tional constants $\tilde{B} = 12099.867$ = 6260.630				
Distortion constants					
$d_J = 0.80830 imes 10^{-1}$	$d_{JK} = -0.12705 imes 10^{1}$				
$d_K = 0.61503$	$d_{WJ} = -0.52902 \times 10^{-5}$				
$d_{W\mathrm{K}} = 0.96982\! imes\!10^{-4}$					
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 consider-

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ing 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 $J \leq 12$ have been calculated ¹⁵. Copies of the calculated spectrum may be obtained from the authors on request.

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