Analysis of v_9, v_7, v_6, and v_8 Rotational Spectrum of $H^{15}NO_3$

Ashley M. Jones, University of California at Santa Cruz
Douglas T. Petkie, Wright State University
Brian J. Drouin, Jet Propulsion Laboratory

Purpose:

Depletion of the ozone layer has lead to studies of the composition of the upper stratosphere. Nitric acid is one of the components found in the stratosphere that contributes to ozone depletion. The purpose of studying the isotope $H^{15}NO_3$ is so the spectral analysis of nitric acid is more complete and will allow for more accurate determination of the states.

Properties of Nitric Acid:

$H^{15}N^{16}O_3$ is a *asymmetric rotor* or *asymmetric top* meaning all principal moments of inertia, and therefore the rotational constants, are unequal.

$I_A \neq I_B \neq I_C$ $\quad I_A < I_B < I_C$ $\longrightarrow$ $A \geq B > C$

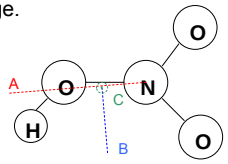
$A = h/(8\pi I_a)$ $\quad I_a = \Sigma m_i r_{ia}^2$

Nitric Acid is a *planar* molecule, with the hydrogen, nitrogen and oxygen atoms all lying in the same plane.

In order for there to be a rotational absorption spectrum, nitric acid must have a permanent electric *dipole moment*. This occurs when the separate parts of the molecule have a difference in charge.

The spectral lines are transitions between rotational states described by the quantum numbers below:

$J'\ K_a'\ K_c' \longleftarrow J\ K_a\ K_c$ Ex: $30_{2\,28} \longleftarrow 29_{2\,27}$



J is the total rotational angular momentum, while K is the projection of J onto the A or C axis.

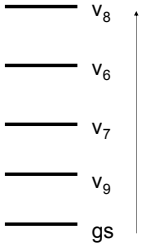
Each vibrational mode has a different average structure and results in a change of the rotational constants described by the following equation below. The table below illustrates these effects.

$\beta = \beta_{gs} + \alpha_i$ $\quad \beta = A, B, C$ $\quad i = 1, 2, 3, \ldots$

Data:

The lines were fit to a Watson Hamiltonian in the A-reduced I^R representation. The statistics of the fitted lines are shown below:

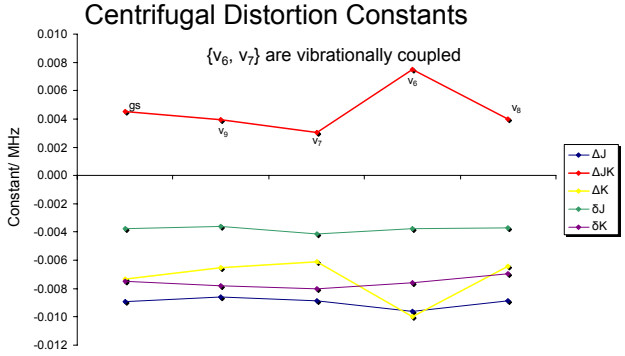
Energy bands of $N^{15}H^{16}O_3$.



v (cm^{-1})	J_{max}	$K_{a\,max}$	$K_{c\,max}$	Reduced rms	No. of Lines
646.96	56	40	51	5.26	304
743.61	57	22	52	1.24	233
578.47	51	29	47	0.98	416
458.29	67	44	52	1.25	396
~~	57	32	41	1.20	642

Rotational motion results in *centrifugal distortion*, which causes the bonds to stretch, changing the moments of inertia. The centrifugal constants for each vibrational state are shown below.

Centrifugal Distortion Constants

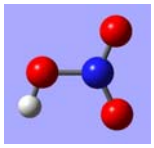


Comparison of Vibration-Rotation Constants of $H^{14}NO_3$ and $H^{15}NO_3$

Parameter	Ground State (β_{gs})		v_9=1 (α_9)		v_7=1(α_7)		v_6=1(α_6)		v_8=1(α_8)	
	$H^{14}N$	$H^{15}N$	$H^{14}N$	$H^{15}N$	$H^{14}N$	$H^{15}N$	$H^{14}N$	$H^{15}N$	$H^{14}N$	$H^{15}N$
A_v-A_{gs}	13010.99	13012.31	-49.14	-49.45	17.92	16.04	-4.79	-4.95	-12.97	-11.38
B_v-B_{gs}	12099.92	12096.87	-47.67	-47.58	-1.28	-1.04	-42.42	-42.81	-94.40	-93.08
C_v-C_{gs}	6260.64	6260.15	-5.41	-5.43	-59.03	-57.23	21.70	19.76	0.18	0.16

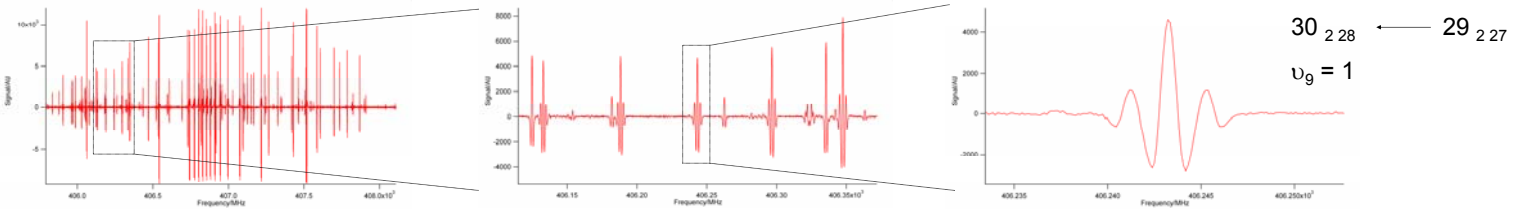
Vibrational Modes:

v_6	$O\text{-}NO_2$	stretch
v_7	$O\text{-}NO_2$	bend
v_8	NO_2	bend (out of plane)
v_9	O-H	torsion (out of plane)



Nitric Acid
$H^{15}N^{16}O_3$

Sample Spectra: This sample was taken of $H^{15}N^{16}O_3$. The spectra data ranged from 75-110 GHz, 320-330 GHz, 402-410GHz, and 638-656 GHz.



Acknowledgments for support and funding:

National Science Foundation
Physics REU Program
Jet Propulsion Laboratory
Department of Defense