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MICROWAVE SPECTRUM OF 2-NITROPHENOL:
STRUCTURE OF THE HYDROGEN BOND

by

Sharron Laas Leavell

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

Doctor of Philosophy

Thesis Director's signature:

A handwritten signature in dark ink, appearing to read "Robert Curl", is written over a horizontal line.

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INTRODUCTION

The determination of the structure of the hydrogen bond in a strongly bonded intramolecular system was the primary purpose for studying the microwave spectrum of 2-nitrophenol. Other systems exhibiting an intramolecular hydrogen bond have been shown to have an O-H bond length longer than that normally found for the free O-H group. The systems studied include allyl alcohol¹, 2-fluoroethanol², 2-chloroethanol³, 2-bromoethanol³, and 2-aminoethanol⁴. These 2-substituted ethanols exhibit significant lengthening of the O-H bond which is linearly related to the shift of the O-H stretching frequency in the infrared spectrum. This relationship is shown graphically in Figure 1.

The shift in O-H stretching frequency is considered a measure of the strength of the hydrogen bond. For allyl alcohol, 2-haloethanols, and 2-aminoethanol the O-H shift is 14, 32, and 115 cm^{-1} respectively. The corresponding bond length determined by microwave spectroscopy using the substitution method are 0.968, 1.008, and 1.14 Å respectively. Several intramolecular systems are known by their IR spectra to have much larger shifts in the O-H stretching frequency than the above mentioned compounds. One such compound is 2-nitrophenol which has a frequency shift⁵ of 345 cm^{-1} . Extrapolating the linear relationship of O-H bond length to infrared shift gives an extraordinarily long bond length for 2-nitrophenol and also for a similar compound, salicyl

Figure 1. Plot of O-H bond length versus frequency shift of the O-H stretching vibration in the infrared spectrum. Points are for methanol (free O-H), allyl alcohol, 2-haloethanols, and 2-aminoethanol.

aldehyde, as shown in Figure 2. Although it was not expected that an O-H bond length as long as that projected from the extrapolation would be found, it did seem likely that some structural effects due to the strong hydrogen bond would be found in 2-nitrophenol and salicyl aldehyde.

A microwave study of salicyl aldehyde has been completed⁶. For this molecule, the non-bonded hydrogen-carbonyl oxygen distance was determined. The data were compatible with a bonded O-H distance not markedly lengthened. The bonded O-H distance, however, was not determined.

The study of 2-nitrophenol can give the bonded O-H distance, and it is of interest to see if there is indeed any effect of hydrogen bonding on the bond length. A second structural effect of the hydrogen bond that may be observed is the constraint of the phenolic proton to the molecular plane despite the repulsive forces arising from large overlap of Van der Waals radii, the extent of which is shown in Figure 3.

Figure 2. Plot of O-H bond length versus frequency shift. Extension of plot in Figure 1 (box in lower left corner) to include those points for 2-nitrophenol and salicyl aldehyde.

Figure 3. Molecular model which fairly closely reproduces the normal species rotational constants and the principal axes coordinates of the phenol oxygen and hydrogen. The "x's" mark the experimentally determined oxygen and hydrogen positions calculated from Kraitchman's equations and second difference equations. The Van der Waals radii of the nitro oxygen, phenol oxygen and hydrogen are indicated.

EXPERIMENTAL

The microwave spectrum of 2-nitrophenol was studied in the 26.5 to 40.0 GHz region using a Hewlett Packard 8460 A MRR spectrometer. The normal species was also examined in the 7 to 26 GHz region using a conventional 100 kHz Stark modulation spectrometer with phase sensitive detection and oscilloscope display.

The sample of normal 2-nitrophenol was obtained from the Aldrich Chemical Company and recrystallized from ethanol before use. At room temperature the equilibrium vapor pressure was about 80-100 μ Hg. Moderately strong lines were observed for the slightly volatile solid.

ISOTOPIC MODIFICATIONS:

2-Nitrophenol-d. The deuterated species was prepared by exchange and recrystallization of the normal species from deuterium oxide. A sample was obtained which was about 96% deuterated as determined by integration of the phenolic and aromatic NMR signals. Prior to introduction of the sample into the waveguide, deuterium oxide was introduced several times and then pumped out for several hours to minimize exchangeable protons in the guide.

2-Nitrophenol- O^{18} . The species with oxygen-18 substituted in the phenol position was prepared by a nucleophilic substitution reaction of 1-fluoro-2-nitrobenzene with oxygen-18 hydroxide. The oxygen-18 enriched hydroxide was prepared by adding a sample of 45% H_2O^{18} to potassium t-butoxide in t-butanol. The potassium t-butoxide was prepared in situ by the procedure in Organic Synthesis⁷.

Between 2.9 - 3.9 g (0.075 - 0.1 mole) potassium and 80-90 ml dry t-butanol were placed in a 250 ml 3-neck flask equipped with condenser, stirrer, and addition funnel which had been previously flame dried and evacuated as directed⁷. The reaction was allowed to proceed to completion, indicated by the cessation of the evolution of hydrogen. When complete, 1 ml of 45% oxygen-18 enriched H₂O was introduced into the addition funnel and added dropwise with stirring. Then 6.77 g (0.048 moles, limiting reagent) of 1-fluoro-2-nitrobenzene that had been dried over CaCl₂ was added dropwise by an addition funnel to the stirred base and the solution heated to 75-80°C. The reaction was run for 2-2½ hours, then the heating mantle was removed, the flask allowed to cool to room temperature, and then surrounded by an ice bath to stop the reaction. The reaction mixture contained a large amount of precipitated potassium 2-nitrophenoxide salt.

A 50 ml portion of diethyl ether was added to the reaction mixture in a separatory funnel to extract any unreacted 1-fluoro-2-nitrobenzene. About 50 ml of H₂O was added to dissolve the precipitated potassium 2-nitrophenoxide salt, then the binary system was shaken, separated, and the ether layer discarded. The aqueous layer was returned to the separatory funnel and the extraction repeated with another 50 ml portion of ether. The aqueous layer (color: deep red) was then separated and placed in a large beaker and acidified with HCl (aq) to about pH = 6. The beaker was placed in some ice to insure complete precipitation of the bright yellow 2-nitrophenol. The crystals were filtered on a

Büchner funnel, washed twice with 25 ml portions of ice water, and then placed in a dessicator to dry overnight.

The oxygen-18 enrichment estimated from the intensity ratio in the microwave spectrum was 40-45%. The enrichment determined from the ratio of the parent peaks at 139 and 141 in the mass spectrum was 45%.

2-Nitrophenol-O¹⁸-d. The deuterated oxygen-18 sample was prepared from the above O¹⁸ sample by exchange with deuterium oxide as described previously for the deuterated normal species. Again about 96% enrichment was achieved as evidenced by the NMR spectrum.

SPECTRA ASSIGNMENT

GROUND STATE:

The approximate structural parameters for a planar hydrogen bonded form were used to predict a spectrum. This model indicated that the compound is a prolate asymmetric rotor with Ray's asymmetry parameter, $\kappa = -0.4$. The model also indicated that the a-component of the dipole was larger than the b-component. The c-direction is perpendicular to the molecular symmetry plane. The model in the principal axis a-b plane is shown in Figure 3.

The initial assignment of the normal species was done on the conventional 100 kHz Stark modulation spectrometer in the region 7-26 GHz. The rotational transitions were found to be about 7 MHz wide. The lines observed were fairly easily assigned to a-type R-branch transitions. Sixteen low J lines were measured and these gave a set of approximate rotational constants which were then used to assign the lines in the higher frequency region of the Hewlett Packard spectrometer. The lowest transitions observed for this molecule were $J = 4 \rightarrow 5$. No resolved Stark effect was found and the dipole moment could not be measured. The observed low J lines for the normal species are given in Table I.

Using the Hewlett Packard spectrometer, each line was resolved into a number of components. These components are undoubtedly vibrational satellites. The most intense was assigned as the vibrational ground state. Thirty rotational transitions for the ground state were measured and assigned. These transition

TABLE I

Observed Low J Transitions for Normal 2-Nitrophenol
in the 7-26 GHz Region

<u>Transition *</u>	<u>ν_{observed}</u>	<u>$\nu_{\text{obs}} - \nu_{\text{calc}}$</u>
$4_{04} \rightarrow 5_{05}$	9196.58	4.27
$4_{14} \rightarrow 5_{15}$	9075.61	1.70
$4_{22} \rightarrow 5_{23}$	11602.60	0.06
$4_{23} \rightarrow 5_{24}$	10285.44	1.57
$4_{31} \rightarrow 5_{32}$	11086.82	- 1.85
$5_{05} \rightarrow 6_{06}$	10822.36	3.78
$5_{15} \rightarrow 6_{16}$	10767.27	2.40
$5_{24} \rightarrow 6_{25}$	12158.62	3.07
$5_{33} \rightarrow 6_{34}$	12884.41	2.08
$5_{42} \rightarrow 6_{43}$	12988.79	- 0.91
$5_{51} \rightarrow 6_{52}$	12921.35	0.84
$6_{06} \rightarrow 7_{07}$	12461.48	0.69
$7_{07} \rightarrow 8_{08}$	14112.87	0.32
$7_{17} \rightarrow 8_{18}$	14106.77	2.90
$10_{0,10} \rightarrow 11_{0,11}$	19085.94	0.03
$11_{0,11} \rightarrow 12_{0,12}$	20744.93	- 0.26

*None of these lines included in least squares fit.

frequencies and the differences from calculated frequencies are given in Table II.

The Hewlett Packard spectrometer only was used for the assignment of the isotopic species. For the deuterated species, 28 lines were assigned and these transition frequencies are given in Table III. In Table IV are listed the 17 transitions observed for the oxygen-18 sample. The doubly substituted species for which 21 lines were measured has its frequencies listed in Table V. In all four species the fit to a rigid rotor model up to $J = 18$ is good, and the effects of centrifugal distortion appear to be insignificant. This is in agreement with the observations on nitrobenzene⁸ and salicyl aldehyde⁶.

Only a-type R-branch transitions were measured for all four forms of 2-nitrophenol. However, the molecule is sufficiently asymmetric to permit determination of accurate values of all three rotational constants. The constant A would be expected to be determined with less certainty than the other two constants, and this is indeed borne out by the calculated error limits. In Table VI the constants are listed for the ground state of all isotopic species with error limits which are the standard error obtained from the least squares fit of the observed transitions. The moments of inertia and the inertia defect are also presented in Table VI.

The rotational spectrum of the normal species in the 27-40 GHz region recorded on the Hewlett Packard spectrometer is shown in Figure 4. The prominent features are the high K a-type R-branch bands.

TABLE II

Observed Transitions of Normal 2-Nitrophenol
in the Ground State in the 26.5-40.0 GHz Region

<u>Transition</u>	<u>ν_{observed}^a</u>	<u>$\nu_{\text{obs}} - \nu_{\text{calc}}$</u>
$11_{56} \rightarrow 12_{57}$	27654.42	0.466
$11_{65} \rightarrow 12_{66}$	26648.38	0.585
$12_{39} \rightarrow 13_{3,10}$	27821.10	0.190
$12_{48} \rightarrow 13_{49}$	29922.98	- 0.247
$12_{49} \rightarrow 13_{4,10}$	27288.09	0.190
$12_{66} \rightarrow 13_{67}$	29246.43	0.152
$13_{2,11} \rightarrow 14_{2,12}$	27427.92	0.228
$13_{3,10} \rightarrow 14_{3,11}$	29326.01	0.118
$13_{49} \rightarrow 14_{4,10}$	31621.91	0.132
$13_{67} \rightarrow 14_{68}$	31982.20	0.343
$14_{77} \rightarrow 15_{78}$	33557.65	0.083
$15_{0,15} \rightarrow 16_{0,16}$	27383.40	0.222
$15_{2,13} \rightarrow 16_{2,14}$	30724.01	- 0.139
$15_{3,13} \rightarrow 16_{3,14}$	30719.90	0.079
$15_{78} \rightarrow 16_{79}$	36258.64	0.202
$15_{88} \rightarrow 16_{89}$	35255.52	0.024
$16_{5,11} \rightarrow 17_{5,12}$	38476.55	0.114
$16_{79} \rightarrow 17_{7,10}$	39083.35	0.043
$16_{88} \rightarrow 17_{89}$	37887.05	- 0.097

TABLE II (Continued)

<u>Transition</u>	<u>ν_{observed}</u>	<u>$\nu_{\text{obs}} - \nu_{\text{calc}}$</u>
$17_{3,14} \rightarrow 18_{3,15}$	35739.75	0.128
$17_{6,12} \rightarrow 18_{6,13}$	38925.31	0.272
$17_{10,7} \rightarrow 18_{10,8}$	39409.17	- 0.606
$17_{10,8} \rightarrow 18_{10,9}$	39403.46	0.066
$17_{12,5} \rightarrow 18_{12,6}$	39033.87	- 0.134
$17_{13,4} \rightarrow 18_{13,5}$	38914.21	- 0.347
$17_{14,3} \rightarrow 18_{14,4}$	38821.01	- 0.155
$17_{15,2} \rightarrow 18_{15,3}$	38746.20	- 0.325
$17_{16,1} \rightarrow 18_{16,2}$	38685.50	- 0.317
$17_{17,0} \rightarrow 18_{17,1}$	38635.36	- 0.355
$18_{5,14} \rightarrow 19_{5,15}$	39090.42	- 0.228

^a Frequencies are in MHz.

TABLE III

Observed Transitions of Deuterated 2-Nitrophenol
in the Ground State

Transition	ν_{observed}^a	$\nu_{\text{obs}} - \nu_{\text{calc}}$
$11_{65} \rightarrow 12_{66}$	26601.93	0.409
$12_{48} \rightarrow 13_{49}$	29695.53	0.167
$12_{49} \rightarrow 13_{4,10}$	27081.00	0.057
$12_{66} \rightarrow 13_{67}$	29225.81	0.143
$13_{2,11} \rightarrow 14_{2,12}$	27191.87	0.297
$13_{3,11} \rightarrow 14_{3,12}$	27170.75	- 0.644
$13_{49} \rightarrow 14_{4,10}$	31324.46	0.256
$13_{76} \rightarrow 14_{77}$	30943.45	0.182
$14_{1,13} \rightarrow 15_{1,14}$	27155.50	0.152
$14_{2,12} \rightarrow 15_{2,13}$	28824.92	0.182
$14_{3,12} \rightarrow 15_{3,13}$	28815.80	- 0.692
$14_{77} \rightarrow 15_{78}$	33524.47	0.206
$14_{78} \rightarrow 15_{79}$	33020.43	- 0.208
$15_{0,15} \rightarrow 16_{0,16}$	27152.65	0.343
$15_{1,14} \rightarrow 16_{1,15}$	28800.26	0.192
$15_{5,11} \rightarrow 16_{5,12}$	33730.45	0.138
$15_{88} \rightarrow 16_{89}$	35145.62	0.099
$16_{3,13} \rightarrow 17_{3,14}$	33805.50	0.249
$16_{4,13} \rightarrow 17_{4,14}$	33781.31	0.164
$16_{5,11} \rightarrow 17_{5,12}$	38089.34	- 0.081
$16_{88} \rightarrow 17_{89}$	37835.65	- 0.051
$17_{2,15} \rightarrow 18_{2,16}$	33746.32	- 0.343

TABLE III (Continued)

<u>Transition</u>	<u>ν_{observed}</u>	<u>$\nu_{\text{obs}} - \nu_{\text{calc}}$</u>
$17_{10,7} \rightarrow 18_{10,8}$	39284.43	- 0.347
$17_{10,8} \rightarrow 18_{10,9}$	39276.16	0.118
$17_{12,5} \rightarrow 18_{12,6}$	38888.66	- 0.098
$17_{13,4} \rightarrow 18_{13,5}$	38763.62	- 0.054
$17_{14,3} \rightarrow 18_{14,4}$	38665.80	- 0.178
$17_{15,2} \rightarrow 18_{15,3}$	38587.59	- 0.359

^a Frequencies are in MHz.

TABLE IV

Observed Transitions of 2-Nitrophenol-Oxygen 18
in the Ground State

<u>Transition</u>	<u>ν_{observed}</u> ^a	<u>$\nu_{\text{obs}} - \nu_{\text{calc}}$</u>
$11_{65} \rightarrow 12_{66}$	26761.82	- 0.005
$12_{48} \rightarrow 13_{49}$	29506.52	- 0.042
$12_{49} \rightarrow 13_{4,10}$	26934.64	0.250
$12_{66} \rightarrow 13_{67}$	29454.88	0.252
$13_{3,10} \rightarrow 14_{3,11}$	28802.32	0.263
$13_{3,11} \rightarrow 14_{3,12}$	26989.51	- 0.123
$13_{49} \rightarrow 14_{4,10}$	31036.05	- 0.059
$13_{76} \rightarrow 14_{77}$	31115.80	0.084
$14_{1,13} \rightarrow 15_{1,14}$	26973.67	0.026
$14_{5,10} \rightarrow 15_{5,11}$	31813.50	0.168
$14_{77} \rightarrow 15_{78}$	33777.08	0.039
$15_{0,15} \rightarrow 16_{0,16}$	26971.37	0.161
$15_{3,12} \rightarrow 16_{3,13}$	31956.03	- 0.002
$15_{5,10} \rightarrow 16_{5,11}$	36269.41	0.039
$15_{87} \rightarrow 16_{88}$	35479.76	- 0.046
$16_{3,13} \rightarrow 17_{3,14}$	33566.85	- 0.546
$16_{88} \rightarrow 17_{89}$	38098.70	- 0.285

^a Frequencies are in MHz.

TABLE V

Observed Transitions of Deuterated 2-Nitrophenol-Oxygen 18
in the Ground State

Transition	^a <u>ν_{observed}</u>	<u>$\nu_{\text{obs}} - \nu_{\text{calc}}$</u>
$11_{47} \rightarrow 12_{48}$	27545.31	0.054
$11_{65} \rightarrow 12_{66}$	26730.65	0.157
$12_{66} \rightarrow 13_{67}$	29445.38	0.380
$13_{2,11} \rightarrow 14_{2,12}$	26780.89	0.000
$13_{3,11} \rightarrow 14_{3,12}$	26770.00	- 0.363
$13_{76} \rightarrow 14_{77}$	31072.97	- 0.066
$13_{12,2} \rightarrow 14_{12,3}$	29909.23	0.013
$14_{1,13} \rightarrow 15_{1,14}$	26754.81	0.046
$14_{5,10} \rightarrow 15_{5,11}$	31582.12	0.160
$15_{0,15} \rightarrow 16_{0,16}$	26752.81	0.178
$15_{3,12} \rightarrow 16_{3,13}$	31688.69	- 0.005
$15_{4,12} \rightarrow 16_{4,13}$	31660.89	0.145
$15_{5,10} \rightarrow 16_{5,11}$	35928.83	- 0.034
$16_{2,14} \rightarrow 17_{2,15}$	31627.93	- 0.344
$16_{3,13} \rightarrow 17_{3,14}$	33290.49	0.489
$16_{4,13} \rightarrow 17_{4,14}$	33278.66	- 0.019
$16_{88} \rightarrow 17_{89}$	38078.23	- 0.052
$16_{11,6} \rightarrow 17_{11,7}$	36729.68	0.051
$16_{12,5} \rightarrow 17_{12,6}$	36573.19	- 0.162
$16_{14,3} \rightarrow 17_{14,4}$	36361.34	- 0.168
$16_{15,2} \rightarrow 17_{15,3}$	36286.85	- 0.342

^aFrequencies are in MHz.

TABLE VI

Ground State Rotational Constants and Moments of Inertia
for the Isotopic Species of 2-Nitrophenol

<u>Species</u>	<u>Rotational Constants</u> ^a	<u>Moments of Inertia</u> ^b
$O^{16}\text{-H}$	$A = 2368.738 \pm .050$ $B = 1276.110 \pm .006$ $C = 829.812 \pm .012$	$I_a = 213.353 \pm .005$ $I_b = 396.029 \pm .002$ $I_c = 609.026 \pm .005$ $\Delta = - 0.356 \pm .008^c$
$O^{16}\text{-D}$	$A = 2325.514 \pm .049$ $B = 1272.217 \pm .006$ $C = 822.816 \pm .005$	$I_a = 217.318 \pm .005$ $I_b = 397.241 \pm .002$ $I_c = 614.204 \pm .004$ $\Delta = - 0.355 \pm .007$
$O^{18}\text{-H}$	$A = 2269.967 \pm .036$ $B = 1276.040 \pm .005$ $C = 817.329 \pm .005$	$I_a = 222.636 \pm .004$ $I_b = 396.051 \pm .002$ $I_c = 618.328 \pm .004$ $\Delta = - 0.359 \pm .006$
$O^{18}\text{-D}$	$A = 2231.529 \pm .042$ $B = 1272.113 \pm .005$ $C = 810.706 \pm .005$	$I_a = 226.471 \pm .004$ $I_b = 397.274 \pm .002$ $I_c = 623.379 \pm .004$ $\Delta = - 0.366 \pm .006$

^a Error limits given are the standard error calculated from least squares fit. Constants are in MHz.

^b Conversion of rotational constant to moment of inertia:
 $I_b = 505377/B$ where B is in MHz and I_b is in Amu-Å^2 .

^c The inertia defect, $\Delta = I_c - I_a - I_b$.

Figure 4. Spectrum of 2-nitrophenol at 700 volts and 5 MHz/sec.

SATELLITE SPECTRA

In addition to the ground state, satellite spectra for the $v = 1$ through $v = 4$ vibrationally excited states were assigned for the normal species. Two examples of the vibrational pattern are given in Figures 5a and 5b which are for the transitions $13_{67} \rightarrow 14_{68}$ and $15_{78} \rightarrow 16_{79}$ respectively. Twenty three lines were assigned for the first excited state, 22 lines for the $v = 2$ state, 10 lines for the $v = 3$ state and 6 lines for the $v = 4$ state. The observed frequencies and differences from the calculated values are given in Table VII for the 4 vibrational states. The observed constants for the excited states and also the ground state are given in Table VIII. The error limits given are the standard errors computed from the least squares fit.

The variation in rotational constants, especially B and C, with vibrational quantum number is fairly linear as shown in Figure 6. The uncertainties in the excited state A constants are rather large, but the deviation from linearity is slightly greater than one standard error. The B and C constants are better determined and fit the linear plot fairly well.

Using the ground and first excited state, the observed constants are fit to the following equations:

$$\begin{aligned} A_v &= A^\circ - \alpha^A(v + \tfrac{1}{2}) \\ B_v &= B^\circ - \alpha^B(v + \tfrac{1}{2}) \\ C_v &= C^\circ - \alpha^C(v + \tfrac{1}{2}) \end{aligned} \quad [1]$$

Figure 5a. Transition $13_{67} \rightarrow 14_{68}$ showing the ground state line and the vibrational satellites for states $v = 1$ through $v = 4$.

Figure 5b. Transition 15₇₈ → 16₇₉ showing the ground state line and the vibrational satellites for states v = 1 through v = 3.

where A_v , B_v , C_v are the observed constants, and A° , B° , C° and α^A , α^B , α^C are the parameters fitted. Values for these parameters are given in Table IX. In the graphs in Figure 6, the observed constants with error bars of one standard error are the points plotted.

Comparison of these satellites with those observed in the spectrum of nitrobenzene leads one to believe that this vibration is due to torsion of the nitro group. The frequency of the torsional vibration can be determined for both 2-nitrophenol and nitrobenzene utilizing the variation of the inertia defect with vibrational state.

Given in reference 8 on nitrobenzene, the difference of the inertia defect in the ground state and first torsionally excited state is related to the torsional frequency by the following equation:

$$(\Delta^{v=1} - \Delta^{v=0}) = -4h/8\pi^2 c \tilde{\nu} \quad [2]$$

assuming harmonicity.

Rearranging and solving for $\tilde{\nu}$, one obtains

$$\tilde{\nu} = -4h/8\pi^2 c (\Delta^{v=1} - \Delta^{v=0}) \quad [3]$$

Substitution of the appropriate constants, $h/8\pi^2 c = 16.8627 \text{ amu-Å}^2$, one obtains

$$\tilde{\nu} = -67.451/(\Delta^{v=1} - \Delta^{v=0}) \quad [4]$$

For nitrobenzene $\Delta^{v=0}$ is -0.4811 and $\Delta^{v=1}$ is -1.8626, and the calculated frequency turns out to be $\tilde{\nu} = 49 \text{ cm}^{-1}$. Similarly for 2-nitrophenol $\Delta^{v=0}$ is -0.356 and $\Delta^{v=1}$ is -1.364. The resulting

calculated frequency is 67 cm^{-1} . This is in fairly good agreement with the result for nitrobenzene and also for other planar molecules with low frequency out of plane vibrations. Such calculations for nitrosobenzene⁹ give 82 cm^{-1} and for nitroethylene¹⁰ give 92 cm^{-1} in good agreement with the values found from other measurements (100 cm^{-1} and 103 cm^{-1} respectively).

Another method for estimating the frequency of the torsion is from the relative intensity of the first excited state compared to the ground state. Accurate intensity measurements can not be made because of the proximity and overlap of other lines; however, estimations from the recorded intensities such as in Figure 5 for 9 different lines give an average torsional frequency of $94 \pm 25 \text{ cm}^{-1}$.

The contribution to the inertia defect of 2-nitrophenol appears to come from the nitro group with no significant contribution from the phenol group. This is borne out by the fact that isotopic substitution at the phenol group has no effect on the inertia defect. The values of the inertia defect for the four isotopic species (given in Table VI) are the same within the error limits.

One other feature of the vibrational satellite pattern should be noted. In addition to the series of lines generally progressing to low frequency relative to the ground state line, there is a single line found to the high frequency side of the ground state line. Although this line is fairly intense, no higher satellites of a series can be observed for it. The origin of this line has not been determined. However, it was noted that the position of this satellite relative to the ground state line did not change

from the normal to the deuterated and oxygen-18 samples. In addition, there is a strong satellite at a slightly lower frequency than the ground state. This also has not been vibrationally assigned.

A similar satellite pattern is observed for the isotopically substituted species. However, the satellite series lines were not measured and assigned.

TABLE VII

Observed Transitions for Excited Vibrational States
of the Normal Species

<u>Vibrational State</u>	<u>Rotational Transition</u>	ν_{observed}^a	$\nu_{\text{obs}} - \nu_{\text{calc}}$
v = 1	$11_{56} \rightarrow 12_{57}$	27629.33	0.169
	$11_{65} \rightarrow 12_{66}$	26630.87	0.344
	$12_{39} \rightarrow 13_{3,10}$	27835.59	0.012
	$12_{49} \rightarrow 13_{4,10}$	27295.42	0.444
	$12_{66} \rightarrow 13_{67}$	29222.30	- 0.027
	$13_{3,10} \rightarrow 14_{3,11}$	29342.39	0.609
	$13_{49} \rightarrow 14_{4,10}$	31630.52	- 0.123
	$13_{67} \rightarrow 14_{68}$	31951.73	0.280
	$14_{77} \rightarrow 15_{78}$	33532.32	0.291
	$15_{78} \rightarrow 16_{79}$	36224.71	0.044
	$15_{88} \rightarrow 16_{89}$	35239.41	0.083
	$16_{5,11} \rightarrow 17_{5,12}$	38490.14	- 0.153
	$16_{79} \rightarrow 17_{7,10}$	39043.09	0.086
	$16_{88} \rightarrow 17_{89}$	37860.44	- 0.123
	$17_{6,12} \rightarrow 17_{6,13}$	38929.97	0.020
	$17_{10,7} \rightarrow 18_{10,8}$	39392.39	- 0.455
	$17_{10,8} \rightarrow 18_{10,9}$	39386.62	- 0.077
	$17_{12,5} \rightarrow 18_{12,6}$	39020.79	- 0.214
	$17_{13,4} \rightarrow 18_{13,5}$	38902.78	0.065
	$17_{14,3} \rightarrow 18_{14,4}$	38810.15	- 0.065
	$17_{15,2} \rightarrow 18_{15,3}$	38736.05	- 0.233
	$17_{16,1} \rightarrow 18_{16,2}$	38675.88	- 0.268
	$17_{17,0} \rightarrow 18_{17,1}$	38626.32	- 0.197
v = 2	$11_{56} \rightarrow 12_{57}$	27603.52	0.348
	$11_{65} \rightarrow 12_{66}$	26612.47	0.054
	$12_{49} \rightarrow 13_{4,10}$	27301.58	0.329

TABLE VII (Continued)

<u>Vibrational State</u>	<u>Rotational Transition</u>	<u>ν_{observed}</u>	<u>$\nu_{\text{obs}} - \nu_{\text{calc}}$</u>
v = 2	$12_{66} \rightarrow 13_{67}$	29197.87	0.460
	$13_{3,10} \rightarrow 14_{3,11}$	29357.08	0.169
	$13_{49} \rightarrow 14_{4,10}$	31637.75	- 0.214
	$13_{67} \rightarrow 14_{68}$	31920.23	0.404
	$14_{77} \rightarrow 15_{78}$	33505.67	0.226
	$15_{78} \rightarrow 16_{79}$	36189.71	0.029
	$15_{88} \rightarrow 16_{89}$	35222.03	0.072
	$16_{5,11} \rightarrow 17_{5,12}$	38502.18	- 0.049
	$16_{79} \rightarrow 17_{7,10}$	39000.28	- 0.846
	$16_{88} \rightarrow 17_{89}$	37832.97	0.153
	$17_{6,12} \rightarrow 18_{6,13}$	38933.66	0.220
	$17_{10,7} \rightarrow 18_{10,8}$	39374.64	- 0.014
	$17_{10,8} \rightarrow 18_{10,9}$	39369.19	0.360
	$17_{12,5} \rightarrow 18_{12,6}$	39006.96	0.167
	$17_{13,4} \rightarrow 18_{13,5}$	38889.22	- 0.461
	$17_{14,3} \rightarrow 18_{14,4}$	38797.94	- 0.150
	$17_{15,2} \rightarrow 18_{15,3}$	38724.77	- 0.108
	$17_{16,1} \rightarrow 18_{16,2}$	38664.82	- 0.505
	$17_{17,0} \rightarrow 18_{17,1}$	38615.97	- 0.204
v = 3	$11_{56} \rightarrow 12_{57}$	27576.54	- 0.126
	$12_{39} \rightarrow 13_{3,10}$	27862.93	0.300
	$13_{3,10} \rightarrow 14_{3,11}$	29371.46	- 0.013
	$13_{49} \rightarrow 14_{4,10}$	31644.74	0.103
	$13_{67} \rightarrow 14_{68}$	31887.81	0.170
	$14_{77} \rightarrow 15_{78}$	33778.41 ^b	0.067
	$15_{78} \rightarrow 16_{79}$	36154.28	0.179
	$15_{88} \rightarrow 16_{89}$	35204.17	0.254
	$16_{5,11} \rightarrow 17_{5,12}$	38513.17	- 0.202

TABLE VII (Continued)

<u>Vibrational State</u>	<u>Rotational Transition</u>	<u>ν_{observed}</u>	<u>$\nu_{\text{obs}} - \nu_{\text{calc}}$</u>
$v = 3$	$16_{88} \rightarrow 17_{89}$	37804.21	- 0.230
	$17_{13,4} \rightarrow 18_{13,5}$	38875.57	- 0.312
$v = 4$	$11_{56} \rightarrow 12_{57}$	27548.57	- 0.258
	$12_{39} \rightarrow 13_{3,10}$	27875.71	0.014
	$13_{3,10} \rightarrow 14_{3,11}$	29385.65	0.115
	$14_{77} \rightarrow 15_{78}$	33449.89	0.554
	$16_{88} \rightarrow 17_{89}$	37773.99	- 0.063
	$17_{13,4} \rightarrow 18_{13,5}$	38859.93	- 0.329

^a Frequencies are in MHz.

^b This line not included in least squares fit.

TABLE VIII

Observed Rotational Constants for the Ground State
and Four Excited Vibrational States
of the Normal Species

$v =$	A	B	C (MHz)
0	$2368.74 \pm .05$	$1276.110 \pm .006$	$829.812 \pm .007$
1	$2368.98 \pm .10$	$1275.031 \pm .012$	$830.760 \pm .018$
2	$2368.90 \pm .13$	$1273.873 \pm .016$	$831.730 \pm .023$
3	$2368.93 \pm .12$	$1272.705 \pm .015$	$832.660 \pm .025$
4	$2369.6 \pm .4$	$1271.535 \pm .046$	$833.485 \pm .065$

Inertia Defect from the above Constants^a

$v =$	$\Delta =$
0	- 0.356
1	- 1.364
2	- 2.442
3	- 3.482
4	- 4.389

^a Rotational constants are related to the moments of inertia by the following relation:

$A = 505377/I_a$ where A is in MHz and I_a is in $\text{amu}\cdot\text{\AA}^2$.
The inertia defect, Δ , is given by $\Delta = I_c - I_a - I_b$.

TABLE IX

Parameters from Linear Expansion
of Observed Rotational Constants

$A^\circ = 2368.62$	$\alpha^A = - 0.245$
$B^\circ = 1276.65$	$\alpha^B = 1.079$
$C^\circ = 829.34$	$\alpha^C = - 0.948$

Figure 6a. Plot of observed A rotational constants versus vibrational quantum number for the normal species.

Figure 6b. Plot of observed B and C rotational constants versus vibrational quantum number.

MOLECULAR STRUCTURE

The spectroscopically determined moments of inertia can be used to calculate the coordinates of the atoms in the principal axis system, and hence, the molecular structure. However, for larger molecules it is generally experimentally impossible to observe the spectra for so many different isotopic species ($N - 2$ isotopically substituted species are required for a planar asymmetric rotor) to obtain a complete structure. Instead isotopic substitutions of specific atoms are effected, and the coordinates of the atoms of interest are determined. Hence with this method in microwave spectroscopy, one can selectively determine those bond lengths and angles that are of particular interest, provided that a synthetic route to the appropriately substituted isotopic species can be found.

This method depends on the fact that isotopically modified species exhibit different spectra, i.e., have different moments of inertia from the parent species, but assumes that this difference is due only to the mass change and not to any change in molecular geometry.

Kraitchman¹¹ derived a set of equations whereby the coordinates of an isotopically substituted atom could be calculated from differences in the moments of inertia. The equations for substitution in a planar asymmetric rotor are

$$\begin{aligned} |x| &= [\mu^{-1}(I_y' - I_y)(I_x' - I_y)/(I_x - I_y)]^{\frac{1}{2}} \\ |y| &= [\mu^{-1}(I_x' - I_x)(I_y' - I_x)/(I_y - I_x)]^{\frac{1}{2}} \end{aligned} \quad [5]$$

where $|x|$ and $|y|$ are the absolute values of the coordinates of the substituted atom in the principal axis system of the unsubstituted molecule; μ is the reduced mass for the substitution, $M\Delta m/(M + \Delta m)$ where M is the molecular weight of the parent molecule and Δm is the mass change upon substitution; I_x and I_x' are the moments of inertia about the x axis of the unsubstituted and substituted molecules respectively, and similarly for I_y and I_y' . The z axis is perpendicular to the molecular plane.

Kraitchman's equations are exact solutions for the molecular coordinates in terms of the equilibrium moments of inertia. However, what is actually determined by microwave spectroscopy is the effective moments of inertia averaged over the ground vibrational state. Costain¹² has shown, however, that if one only uses Kraitchman's equations and determines the atoms independently without recourse to the moment equations, a good structure can be obtained. He has found a structure derived only from substitution coordinates to be virtually independent of the isotopic species used. More importantly, the substitution structure provides a good approximation to the equilibrium structure of the molecule as evinced by comparison with the limited equilibrium data available.

One important assumption of Kraitchman's substitution method is that isotopic substitution is accompanied by no change in the bond length. For some diatomic molecules, however, variations in bond distances with substitution have been found¹³. This effect is most prominent when deuterium is substituted for hydrogen. A

bond length decrease of 0.003 to 0.005 Å occurs when H is replaced by D. For heavier atoms the changes in bond length are about 0.0001 Å. For 2-nitrophenol the uncertainty in the O-H bond length from this isotope effect is much less than uncertainties arising from other origins.

Another assumption of Kraitchman's method is that the moments of inertia are much more sensitive to the isotope effect than are the zero point terms. This assumption is valid for large coordinates, but breaks down when a substituted atom is near a principal axis or the center of mass. Costain¹² has observed that Kraitchman's equations give reliable results for distances greater than 0.15 Å from a principal axis.

A method for locating near axis atoms in planar asymmetric tops has been developed by Krisher and Pierce¹⁴. This is an extension of the treatment given by Pierce¹⁵ for linear molecules. This method utilizes second differences of moments of inertia and requires determination of moments of inertia of doubly isotopically substituted molecules.

In 2-nitrophenol the phenol oxygen lies close to the b-axis. The second difference calculation is outlined below for the calculation of the oxygen a coordinate in this molecule. The moments of inertia of four species, designated O¹⁶-H, O¹⁶-D, O¹⁸-H, and O¹⁸-D, are required. The coordinate, a_0 , is calculated from the second difference, $\Delta\Delta I_b = \Delta I_b(D) - \Delta I_b(H)$ where

$$\begin{aligned}\Delta I_b(D) &= I_b(O^{18}-D) - I_b(O^{16}-D) \\ \Delta I_b(H) &= I_b(O^{18}-H) - I_b(O^{16}-H)\end{aligned}\tag{6}$$

The coordinate, a_O , is the oxygen coordinate in the O^{16} -H axis system. The coordinate, b_O , can be calculated from Kraitchman's equations as can the coordinates of the hydrogen, a_H and b_H --all in the O^{16} -H framework.

Rearrangement of Kraitchman's equation gives

$$\Delta I_b(H) = \mu a^2 \{1 + [\Delta I_a(H)/(I_a - I_b)]\}^{-1} = k a^2 \quad [7]$$

Here I_a and I_b are the principal moments of the O^{16} -H molecule; $\mu = M\Delta m/(M + \Delta m)$ where M = mass of 2-nitrophenol- O^{16} -H and $\Delta m = m(O^{18}) - m(O^{16})$; and the oxygen coordinate in the O^{16} -H system, a_O , is designated simply as a . Hence k is calculable from known quantities.

An analogous expression for $\Delta I_b(D)$ is

$$\Delta I_b(D) = \mu' (a')^2 \{1 + [\Delta I_a(D)/(I_a' - I_b')]\}^{-1} = k' (a')^2 \quad [8]$$

where I_a' , I_b' are the moments of the O^{16} -D molecule; $\mu' = M'\Delta m/(M' + \Delta m)$ where M' is the mass of 2-nitrophenol- O^{16} -D and $\Delta m = m(O^{18}) - m(O^{16})$; and a' is the oxygen coordinate in the O^{16} -D system. Thus k' is also directly calculable.

The coordinates a' and a are related by a known transformation between the O^{16} -H and the O^{16} -D axis systems:

$$\begin{aligned} a' &= (a - A)\cos\theta - (b - B)\sin\theta \\ a' &= a\cos\theta - [(b - B)\sin\theta + A\cos\theta] \end{aligned} \quad [9]$$

where A, B are the coordinates of the center of mass of 2-nitrophenol- O^{16} -D in the O^{16} -H framework and θ is the angle of rotation from the O^{16} -H to the O^{16} -D system.

The coordinates, A and B , are given by the following:

$$A = \Delta m a_H / (M + \Delta m) \quad B = \Delta m b_H / (M + \Delta m) \quad [10]$$

where $\Delta m = m(D) - m(H)$, $M = \text{mass of } O^{16}\text{-H molecule}$, and a_H, b_H are the hydrogen coordinates from Kraitchman's equations in the $O^{16}\text{-H}$ axis system.

The angle of rotation of the axes upon deuteration is

$$\theta = \mu a_H b_H / (I_a - I_b) \quad [11]$$

where μ, a_H , and b_H are the same as defined for Eq. [10], and I_a, I_b are the moments of inertia of $O^{16}\text{-H}$.

The a' oxygen coordinate in the $O^{16}\text{-D}$ system is thus related to the a coordinate in the $O^{16}\text{-H}$ system in the following way:

$$a' = a \cos \theta + C$$

where C is a calculable constant.

The second difference of the moments can now be related to the oxygen a coordinate:

$$\begin{aligned} \Delta \Delta I_b &= \Delta I_b(D) - \Delta I_b(H) = k'(a')^2 - k a^2 \\ &= (k' \cos^2 \theta - k) a^2 + (2k' C \cos \theta) a + k' C^2 \end{aligned} \quad [13]$$

Just as the Kraitchman method is only valid at some distance from the principal axes, there is an analogous limitation in this second difference method: the second axis system, in this case $O^{16}\text{-D}$, should be shifted as far as possible with respect to the first axis system ($O^{16}\text{-H}$) along the direction in question. Thus for 2-nitrophenol where the small oxygen a coordinate is to be determined, it is desired that the second isotopic species ($O^{16}\text{-D}$) cause a large shift in the a direction. Krisher and Pierce¹⁴ feel a shift of 0.03 Å or more is desirable.

The Kraitchman and second difference calculations for 2-nitrophenol are presented below with a discussion of errors and method limitations peculiar to this molecule.

Utilizing Kraitchman's method given in Equation [5], the coordinates of the hydrogen and oxygen can be calculated using the moments of inertia in Table VI. For the hydrogen calculation $\mu^{-1} = 1.00095 \text{ Amu}^{-1}$ and for the oxygen calculation $\mu^{-1} = 0.50613 \text{ Amu}^{-1}$. The absolute values of the coordinates are calculated, and the signs of the coordinates are deduced from the molecular model, Figure 3. The results are given in Table X.

TABLE X

Calculated Coordinates from Kraitchman's Equations

	a	b (Å)
Hydrogen	+ 1.089 ± .002	- 1.999 ± .002
Oxygen	+ or - 0.103 ± .008 *	- 2.168 ± .001

* Sign is indeterminate.

Since the oxygen coordinate is small, its reliability is questionable; moreover, its sign cannot be deduced. The double substitution method is used to better determine the coordinate. The values of various quantities and constants used in the calculation are presented in Table XI. The calculated a oxygen coordinate is presented in Table XII. The error limits given are from the error limits of the moments of inertia propagated through

the calculation. Also in Table XII are the Kraitchman a_H , b_H , b_O coordinates and the oxygen and hydrogen coordinates calculated from the model in Figure 3.

TABLE XI

Calculated Quantities Used for Double Substitution Method

$$\begin{aligned}\Delta I_b(D) &= 0.033 \pm .003 \\ \Delta I_b(H) &= 0.022 \pm .003 \\ \Delta \Delta I_b &= 0.011 \pm .004 \\ k &= 2.0815 \pm .0002 \\ k' &= 2.0819 \pm .0002 \\ A &= 0.0078 \\ B &= - 0.0144 \\ \theta &= 41'15'' \\ C &= 0.018\end{aligned}$$

TABLE XII

Coordinates

<u>Experimental</u>	a	b	in Å
Hydrogen	+ 1.089 ± .002	- 1.999 ± .002	
Oxygen	+ 0.137 ± .053	- 2.168 ± .001	
<u>Model</u>			
Hydrogen	+ 1.121	- 1.993	
Oxygen	+ 0.138	- 2.179	

As can be seen in Table XII, the calculated value of a_0 is positive; however, the error limits are quite large. This is because the criterion of a framework shift of at least $.03 \text{ \AA}$ in the a direction is not satisfied. The shift of the deuterated framework with respect to the unsubstituted framework is $C = 0.018$. This shift is about half the desired minimum. The shift upon deuteration is very small for 2-nitrophenol because of its large molecular weight.

The O-H bond length can be calculated from the determined oxygen and hydrogen coordinates. The bond length computed is $0.967 \pm .055 \text{ \AA}$.

The coordinates calculated agree quite well with those determined from the model as can be seen in Table XII. The model is based on the bond lengths and angles shown in Figure 3. The tilt of the phenol group of 6° from the ring diagonal is in keeping with the x-ray study of potassium 2-nitrophenoxide¹⁶ in which this angle of tilt was observed.

These results would seem to indicate an O-H bond length not markedly lengthened by the hydrogen bond effect in keeping with the result for the similar hydrogen bonded salicyl aldehyde. The poor determination of the oxygen coordinate could not be improved unless a double substitution was effected in a system where a large shift in the a direction upon substitution occurred. Such a system might have O¹⁸ substitution in the nitro group. This substitution would give a framework shift in the a direction relative to

the nitro- O^{16} compound of about 0.1 Å which is greater than the minimum suggested for good results. However, feasible synthetic routes to both nitro- O^{18} -phenol- O^{16} and nitro- O^{18} -phenol- O^{18} compounds have not been found.

The moments of inertia determined for 2-nitrophenol are given in Table VI. For rigid planar molecules, the inertia defect $\Delta = I_c - I_a - I_b$ is zero, but vibrational averaging effects cause the inertia defect of most molecules to become non-zero. A negative inertia defect indicates that out of plane vibrations predominate. As discussed in the previous section, the inertia defect of 2-nitrophenol, $\Delta = -0.35$, can be predominantly attributed to the torsion of the nitro group. Comparison of 2-nitrophenol with nitrobenzene⁸, $\Delta = -0.48$ and salicyl aldehyde⁶, $\Delta = -0.085$, lead one to conclude that 2-nitrophenol like the above molecules is indeed planar. As indicated in Figure 3, this geometry results in large overlap of Van der Waals radii. This high energy configuration, however, is evidently more than compensated by the hydrogen bond stabilization energy.

DISCUSSION

Although the O-H bond length of 2-nitrophenol is not well determined, it can be inferred from the value obtained that the bond distance is not markedly lengthened by the intramolecular hydrogen bond, in contrast to the effect observed in the weaker H-bonded system, 2-aminoethanol. This observation, moreover, is in keeping with the O-H bond distance inferred from the study of salicyl aldehyde. For salicyl aldehyde, an O-H bond length of 1.04 Å was found to be consistent with the Kraitchman coordinates determined. This is about 0.1 Å less than the O-H distance found in 2-aminoethanol⁴. For 2-nitrophenol, the distance is found to be $0.967 \pm .055$ Å, comparable to salicyl aldehyde and also to a free phenolic O-H bond, determined by Forest and Dailey¹⁷ to be 0.944 Å.

Hence, 2-nitrophenol exhibits no marked structural effect of the hydrogen bond. The similar absence of effect found in salicyl aldehyde has been rationalized⁶ in terms of the hydrogen bonding forces affecting the hydrogen. For a hydrogen bonding hydrogen, in these cases a hydroxyl group, brought from infinity toward a donor atom, the energy will decrease to a minimum and then increase as repulsive terms begin to dominate. Systems that are not constrained by structure, i.e., intermolecular hydrogen bonded systems, will approach until the minimum energy is attained. The observed structure of strongly hydrogen bonding intermolecular systems of the O-H...O type is an O...O distance of 2.5-2.6 Å. The H...O distance is generally about 1.6 Å.

The observed O...O distance in propionic acid dimer¹⁸, for example, is 2.64 Å.

The O...O distance of 2-nitrophenol from an x-ray study¹⁶ is 2.64 Å. In some intramolecular systems, such as 2-aminoethanol, the molecular framework prevents the hydrogen and the base from approaching to a minimum energy configuration. The N...O distance in 2-aminoethanol is 2.8 Å. The H...O distance in 2-nitrophenol is about 1.6 - 1.7 Å whereas the H...N distance in 2-aminoethanol is 2.14 Å.

The forces thus acting on the proton in the 2-aminoethanol system are primarily attractive and could thus account for the bond lengthening. The hydrogen is not at an equilibrium distance from the base, but instead at a point on the energy curve as indicated in Figure 7 where there is a rapid change of energy with distance. This indicates that the force attracting the hydrogen to the base is strong.

In a system such as 2-nitrophenol or salicyl aldehyde, the hydrogen is near the equilibrium distance from the base and hence no strong force is operative to elongate the O-H bond by attraction toward the base. The point corresponding to nitrophenol is shown in Figure 7. The force or the derivative of the curve at this point is small or zero. The energy of the hydrogen bond, however, is greater for 2-nitrophenol than for 2-aminoethanol, as is indicated in Figure 7.

Figure 7. Plot of hydrogen bonding energy versus hydrogen-base distance.

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