Study of an Intramolecular, Bifurcated Hydrogen Bond in 1,3-Dioxan-5-ol by Microwave Spectroscopy

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Abstract: The microwave spectrum of 1,3-dioxan-5-ol and the deuterium-substituted isotopic species has been investigated in the 18.0–40.0-GHz frequency region. The molecule has been found to exist in a chair conformation. Only one axial conformer was detected with an intramolecular hydrogen bond of the O–H···O type. The evidence suggests that the O–H group lies in the plane of symmetry and that therefore it is part of a bifurcated hydrogen bond to the two ring oxygens. Assuming this "normal" position of the hydrogen atom in the symmetry plane, the hydroxy-d_1 data suggests a "decrease" in the O···O ring distance of ~0.002 Å upon deuteration. The rotational spectra of two excited vibrational states have been observed. The average intensity ratio for the rotational transitions between the ground and excited vibrational states indicates that the first excited state is about 160 cm^{-1} and the next higher is roughly 225 cm^{-1} above the ground state. The dipole moment was determined from Stark effect measurements to be 2.64 (0.03) D with its principal axis components $|\mu_a| = 1.61$ (0.01), $|\mu_b| \simeq 0.0$, and $|\mu_c| = 2.09$ (0.02) D.

Hydrogen-bonding studies involving hydroxyl groups as proton donors and oxygen atoms as proton acceptors have been carried out by microwave spectroscopy for 2-methoxyethanol,[1] salicylaldehyde,[2] glycolaldehyde,[3] 6-hydroxy-2-formylfulvene,[4] malonaldehyde,[5] glyoxylic acid,[6] and 2-tetrahydropyranylcarbinol,[7] among others. Investigation of 1,3-dioxan-5-ol was undertaken in order to determine the influence of the intramolecular hydrogen bonding on this molecule's conformations. In particular, the molecule possibly shows a bifurcated hydrogen bond with the O–H hydrogen simultaneously bonded to both ring oxygens.

A common index of the intramolecular hydrogen bonding for hydrogen bonds having a hydroxyl group donor is the difference, $\Delta\nu_{OH}$, between the stretching frequencies of the hydrogen-bonded and non-hydrogen-bonded hydroxyl groups. A preliminary investigation[8] of the infrared spectrum of 1,3-dioxan-5-ol in dilute CCl_4 solution (under which only "free" and intramolecular hydrogen-bonded molecules are possible) gave a $\Delta\nu_{OH}$ value of 42 cm^{-1} for that compound. The experimental data, based on extinction coefficients and intensity ratios, indicates that most of the hydroxyl groups are hydrogen bonded. It was expected that, to facilitate hydrogen bonding, the preferred conformation would be the axial (see Figure 1).

Microwave studies of intramolecular hydrogen-bonded alcohols have in many cases resulted in anomalous r_s structures for the hydrogen involved in the hydrogen bond. Various values for the O–H length and C–O–H angle have been published.[9-12] These anomalies may be due to small changes in the molecular structure ("shrinkage" of the O···O distances) accompanying deuteration of the hydrogen bond. The microwave study of 1,3-dioxan-5-ol was undertaken in order to clarify this situation.

Microwave Spectra

Preliminary rotational constants of the axial and equatorial conformers of 1,3-dioxan-5-ol were calculated from an assumed structure in which the structural parameters of 1,3-dioxane[13] and the normal parameters of the hydroxyl group were combined. Experimentally, only the axial conformer could be detected. It was expected that to facilitate hydrogen bonding the preferred conformation would be the axial. The dominant feature of the spectrum is a strong set of double Q-branch series of μ_c type. These were assigned by their characteristic Stark effect. The branch heads, which are transitions of the type $J_{J,0} \leftarrow J_{J-1,2}$ and $J_{J,1} \leftarrow J_{J-1,1}$, occur at intervals of 2.56 GHz. The subbranches with $K_{-1} + K_{+1} = J \leftrightarrow K_{-1} + K_{+1} = J + 1$ proceed to lower frequency with increasing J. From these frequencies approximate values of $(A - C)/2$ and κ were obtained. The low J, a- and c-type, R-branch transitions were then predicted. The $5_{5,0}$–$4_{4,0}$ and $5_{5,1}$–$4_{4,1}$ transitions, split by only 12 MHz, were easily seen close to prediction by scanning at low Stark voltage. This assignment was confirmed also by radio-frequency–microwave double resonance. Further a- and c-type R-branch transitions were then assigned. The b-type spectrum has not been observed. This indicates a small or zero μ_b dipole component.

To assign the spectrum of the deuterium isotopic species, the rotational constants were predicted from the assumed structure and then corrected slightly by the observed rotational constants of the normal species. The rotational constants were calculated by applying a least-squares fit neglecting the effects of the centrifugal distortion. Transitions lower than $J = 12$ were used. Some transitions used in the fitting are shown in Table I. The rotational constants obtained for the normal and deuterated species are given in Table II.

Dipole-Moment Determination

Stark effect measurements were made for a number of transitions, using the Stark effect of OCS and its reported dipole moment of 0.715 21 D[14] to calibrate the electric field strength in the absorption cell. Several transitions were carefully chosen so that their lobes were largely free of interferences from other transitions. The average value of the frequency shifts divided by the square of the electric field strengths for the selected 12 Stark components was used in a least-squares fit in which the value of the b component was assumed to be zero because no μ_b-type transitions were observed in the spectra. Also, Stark shifts of transitions that depend on μ_b were measured. It was found that these shifts, when μ_b was assumed to be zero, fit very well with those shifts of only μ_a and μ_c type. The Stark measurement data and the dipole-moment components are given in Table III.

Vibrational Satellite Spectra

The ground-state vibrational lines were accompanied by intense satellites. Each ground vibrational state Q-branch series was seen to have two vibrational satellite series toward higher frequencies. No intense satellites of the type characteristic of pseudorotation were present. This phenomenon would not be expected to occur for a molecule that has the relatively rigid chair form structure. Some transitions of the two assigned modes in the first excited state are given in Table IV.

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Table I. Observed Rotational Transitions for the Normal and Deuterated Species of 1,3-Dioxan-5-ol (MHz)

transition[a] $J'_{K'_{-1}K'_{+1}}$–$J''_{K''_{-1}K''_{+1}}$	OH species		OD species	
	ν_{obsd}[b]	$\Delta\nu$[c]	ν_{obsd}[b]	$\Delta\nu$[c]
$3_{2,1} \leftarrow 2_{1,1}$	19 525.11	0.15		
$3_{1,2} \leftarrow 2_{0,2}$	18 947.37	0.14		
$3_{3,0} \leftarrow 2_{2,0}$	22 070.58	0.31	21 729.30	0.09
$3_{3,1} \leftarrow 2_{2,1}$	22 277.15	0.30	21 919.57	0.14
$4_{4,0} \leftarrow 3_{3,0}$	29 969.78	0.36	29 499.90	0.13
$4_{4,1} \leftarrow 3_{3,1}$	30 027.28	0.29	29 550.52	0.35
$4_{3,1} \leftarrow 3_{2,1}$	27 057.48	0.32	26 646.05	−0.03
$5_{5,0} \leftarrow 4_{4,0}$	37 821.17	0.33	37 224.40	0.50
$5_{5,1} \leftarrow 4_{4,1}$	37 833.79	0.24	37 235.12	0.58
$5_{2,3} \leftarrow 4_{1,3}$	31 465.48	−0.09	30 858.75	0.07
$7_{0,7} \leftarrow 6_{0,6}$	31 831.88	−0.14	31 637.68	0.08
$7_{1,7} \leftarrow 6_{1,6}$	31 827.47	0.00	31 632.21	−0.10
$8_{8,0} \leftarrow 8_{7,2}$	19 446.53	−0.11	19 091.11	0.71
$8_{8,1} \leftarrow 8_{7,1}$	19 445.33	0.08	19 090.13	0.76
$9_{8,1} \leftarrow 9_{7,3}$	19 264.85	0.16		
$9_{8,2} \leftarrow 9_{7,2}$	19 254.08	0.11		
$10_{8,2} \leftarrow 10_{7,4}$	19 022.77	0.53	18 705.93	−0.22
$10_{8,3} \leftarrow 10_{7,3}$	18 965.75	0.54	18 663.17	−0.87
$11_{8,3} \leftarrow 11_{7,5}$	18 736.28	0.90	18 438.13	−0.62
$11_{8,4} \leftarrow 11_{7,4}$	18 502.99	1.10		
$9_{9} \leftarrow 9_{8}$	22 061.56	−0.64	21 656.82	0.59
$10_{9,1} \leftarrow 10_{8,3}$	21 890.37	−0.09		
$10_{9,2} \leftarrow 10_{8,2}$	21 888.10	−0.05		
$11_{9,2} \leftarrow 11_{8,4}$	21 660.51	0.40	21 294.54	0.00
$11_{9,3} \leftarrow 11_{8,3}$	21 646.55	0.32	21 284.36	−0.38
$10_{10} \leftarrow 10_{9}$	24 675.87	−0.97	24 221.70	0.51
$11_{10} \leftarrow 11_{9}$	24 513.59	−0.69	20 075.32	0.15
$11_{11} \leftarrow 11_{10}$	27 289.17	−1.50		

[a] Unresolved asymmetry doublets labeled by limiting prolate quantum number only. [b] Accurate to ±0.05 MHz. [c] Observed minus calculated frequency from rotational constants of Table II.

Table II. Rotational Constants (MHz)[a]

species	*A*	*B*	*C*
normal	3913.488 (0.007)	2922.762 (0.009)	2193.407 (0.010)
hydroxy-d_1	3851.201 (0.016)	2867.789 (0.023)	2183.161 (0.027)
$v_a = 1$	3916.418 (0.020)	2919.870 (0.037)	2195.367 (0.096)
$v_b = 1$	3918.143 (0.017)	2914.477 (0.035)	2185.191 (0.085)

[a] Standard deviations are given in parentheses.

Relative intensity measurements[15] were made of a number of transitions belonging to the ground vibrational state and the excited vibrational states. The average relative intensities obtained at room temperature (~25 °C) are shown in Table V. It appears that the first excited state is about 160 cm^{-1} above the ground vibrational state, and the second state is about 225 cm^{-1} above the ground vibrational state. Because of their low values, these frequencies may be attributed to ring deformation vibrations, such as those found for 1,3-dioxane.[13]

Molecular Structure

Most known heterocyclic six-membered rings are most stable in the chair form.[16] The expected structure of 1,3-dioxan-5-ol is, of course, the chair form.

The observation of only μ_a and μ_c dipole components does not rule out either the axial or equatorial conformer. In many cases, the rotational constants along with reasonable structural parameters can be used to establish the conformation. Using values listed in Table VIII, calculations for the inertial moments of axial and equatorial conformations were made. Comparisons can be made between calculated and observed planar and principal inertial moments given in Table VI. The observed values are consistent with the axial conformer.

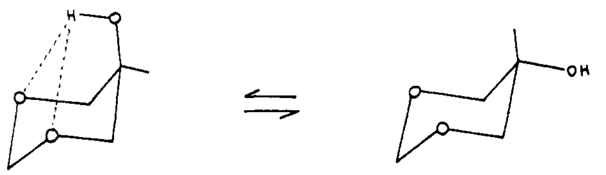

Figure 1. Axial and equatorial conformers of 1,3-dioxan-5-ol.

Table III. Dipole Moment of 1,3-Dioxan-5-ol

transition	*M*	$\Delta\nu/E^2$, (MHz cm^2 V^{-2}) × 10^4 obsd[a]	calcd
$4_{1,3} \rightarrow 5_{2,3}$	2	0.581 (0.014)	0.578
	4	2.288 (0.002)	2.307
$4_{3,1} \rightarrow 5_{4,1}$	1	0.543 (0.022)	0.539
	2	2.185 (0.051)	2.168
	3	4.884 (0.151)	4.885
$4_{3,2} \rightarrow 5_{4,2}$	1	−0.555 (0.010)	−0.552
	2	−2.253 (0.039)	−2.207
	3	−4.948 (0.072)	−4.977
$5_{1,4} \rightarrow 6_{2,4}$	2	1.084 (0.022)	1.076
	4	4 328 (0.030)	4.297
$5_{2,4} \rightarrow 6_{3,4}$	2	−1.058 (0.008)	−1.072
	4	−4.270 (0.057)	−4.296

$\mu_a = 1.61\ (0.01)^a$ D
$\mu_b \simeq 0.00^b$ D
$\mu_c = 2.09\ (0.02)^a$ D
$\mu_{total} = 2.64\ (0.03)^a$ D

[a] The uncertainties are standard deviations. [b] Assumed value; see text.

Table IV. Transitions of 1,3-Dioxan-5-ol in Excited States (MHz)

transition[c] $J'_{K'_{-1}K'_{+1}}$–$J''_{K''_{-1}K''_{+1}}$	$v_a = 1$		$v_b = 1$	
	ν_{obsd}[a]	$\Delta\nu$[b]	ν_{obsd}[a]	$\Delta\nu$[b]
$4_{4,0} \leftarrow 3_{3,0}$	29 989.59	0.22	29 993.94	0.18
$4_{4,1} \leftarrow 3_{3,1}$	30 045.96	0.29	30 050.69	0.30
$5_{5,0} \leftarrow 4_{4,0}$	37 846.37	0.17	37 854.33	0.15
$5_{5,1} \leftarrow 4_{4,1}$	37 858.77	0.27	37 866.67	0.12
$5_{3,3} \leftarrow 4_{2,3}$	33 582.82	0.12	33 560.43	0.33
$6_{3,3} \leftarrow 5_{2,3}$	37 756.16	−0.23	37 711.24	−0.06
$10_{8,2} \leftarrow 10_{7,4}$	19 093.58	0.04	19 228.43	0.24
$10_{8,3} \leftarrow 10_{7,3}$	19 039.32	−0.58	19 173.99	−0.26
$11_{9,2} \leftarrow 11_{8,4}$	21 740.09	0.04	21 893.57	0.28
$11_{9,3} \leftarrow 11_{8,3}$	21 726.88	−0.26	21 880.30	0.00
$10_{10} \leftarrow 10_{9}$	24 758.75	0.10	24 933.04	0.24
$11_{10} \leftarrow 11_{9}$	24 598.58	−0.19	24 771.95	0.03
$11_{11} \leftarrow 11_{10}$	27 380.46	−0.37	27 573.25	−0.16

[a] Accurate to ±0.05 MHz. [b] Observed minus calculated frequency from rotational constants of Table II. [c] Unresolved asymmetry doublets labeled by limiting prolate quantum number only.

One further argument for this conformation can be made through the expected magnitudes of the dipole-moment components along the principal axes. These were computed for the two possible conformations using the bond moments C-O = 0.86, H-O = 1.53, and H-C = 0.3 D[17] and the simple assumption that the total dipole moment is given by their vector sum. The results are shown in Table VII. The observed dipole moments are also consistent with the axial conformer.

Since only two isotopic forms have been investigated in the present work, detailed structural information cannot be obtained. A pseudostructure can be obtained by choosing reasonable structural parameters and adjusting them to fit the experimental rotational constants. In this way, the ring-bending angles α and β, defined in Figure 2, are determined once the bond distances and interior ring angles are specified. In Figure 3 are plotted the calculated rotational constants for a fixed α angle and a range of β values in the axial form. The assumed value α = 57° was taken from 1,3-dioxane and the β angle obtained with a remarkably good agreement was 47°.

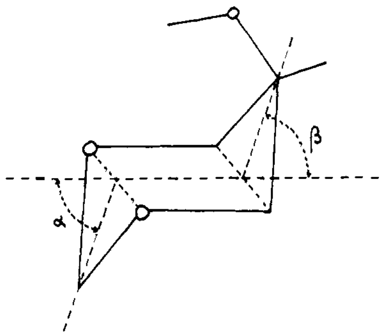

Figure 2. Ring-bending angles in 1,3-dioxan-5-ol.

Table V. Relative Intensities at Room Temperature for Some of the Rotational Transitions of 1,3-Dioxan-5-ol in Excited Vibrational States

transition[b] $J'_{K'_{-1}K'_{+1}}-J''_{K''_{-1}K''_{+1}}$	I/I_0[a] $v_a = 1$	$v_b = 1$
$4_{4,0} \leftarrow 3_{3,0}$	0.51	0.39
$5_{5,0} \leftarrow 4_{4,0}$	0.44	0.32
$12_{12} \leftarrow 12_{11}$	0.50	
$13_{13} \leftarrow 13_{12}$	0.44	
$16_{12,4} \leftarrow 16_{11,5}$	0.47	
$16_{14} \leftarrow 16_{13}$		0.31
$17_{14} \leftarrow 17_{13}$		0.32
$17_{15} \leftarrow 17_{14}$		0.31
$18_{15} \leftarrow 18_{14}$	0.52	0.35
$19_{15} \leftarrow 19_{14}$	0.41	0.36
av rel intensity	0.47 (0.04)	0.34 (0.03)
height above the ground state, cm^{-1}	159 ± 19	226 ± 19

[a] Intensities I_0 for the ground vibrational state. [b] Unresolved asymmetry doublets labeled by limiting prolate quantum number only.

Table VI. Comparison of Calculated and Observed Principal Moments for 1,3-Dioxan-5-ol[a]

	obsd, amu Å^2	calcd axial, amu Å^2	calcd equatorial, amu Å^2
I_a	129.137	128.522	107.964
I_b	172.910	172.668	203.731
I_c	230.407	232.520	284.140
κ	−0.1519	−0.1433	−0.5162
P_{aa}	137.090	138.333	189.953
P_{bb}	93.316	94.187	94.187
P_{cc}	35.820	34.335	13.777

[a] $P_{aa} = \Sigma m_i a_i^2$; $P_{bb} = \Sigma m_i b_i^2$; $P_{cc} = \Sigma m_i c_i^2$; $\kappa = (2B - A - C)/(A - C)$.

The assumed structural parameters for 1,3-dioxan-5-ol are given in Table VIII. The fit is shown in Table IX.

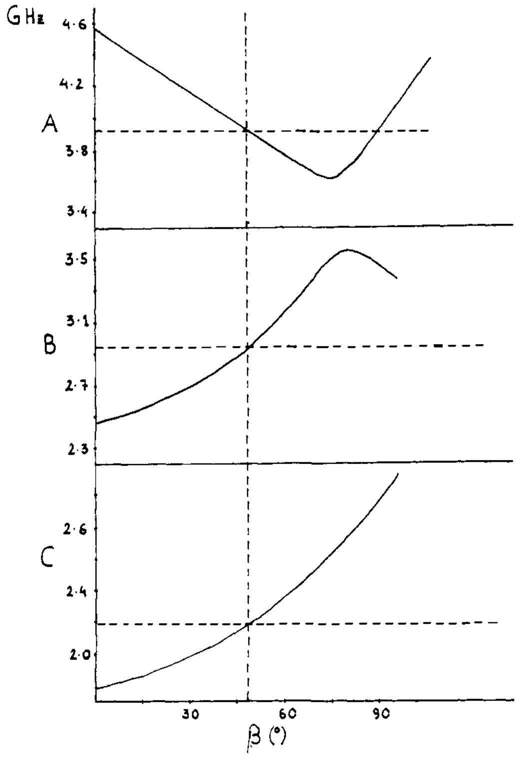

Figure 3. Calculated rotational constants of 1,3-dioxan-5-ol for various values of the angle β ($\alpha = 57°$). Observed rotational constants are indicated by the horizontal broken lines.

Table VII. Observed and Calculated Dipole Moment in 1,3-Dioxan-5-ol (D)

	μ_a	μ_c	μ_a/μ_c
calcd equatorial	0.17	2.61	0.06
calcd axial	1.35	1.99	0.68
obsd	1.61	2.09	0.77

Table VIII. Assumed Structural Parameters

Bond Lengths (Å)		Bond Angles (deg)	
C-C	1.53	∠CCC	110.0
C-O	1.41	∠OCO	112.0
C-H	1.10	∠COC	111.0
O-H	1.00	∠HCH	109.0
Dihedral Angles (deg)		Nonbonded Lengths (Å)	
α[a]	57.0	O···H	2.59
β	47.0	O(H)···O	2.94
		(ring) O···O	1.71
Nonbonded Angles (deg)			
∠O-H···O	100.4		
∠O···H···O	38.5		

[a] See Figure 2.

Intramolecular Hydrogen Bond

Using Kraitchman's equations[17] and the two sets of rotational constants for the normal and deuterated species given in Table II, the absolute values of the Cartesian coordinates of the hydroxyl hydrogen were calculated resulting in substitution coordinates (referred to the principal axis system of the former) $|a| = 1.0652$ (0.0008), $|b| = 0.267i$ (0.003), and $|c| = 1.4799$ (0.0005). The anomalous imaginary value of the b coordinate is noticeable. Studies of molecules such as 2-dimethylaminoethanol,[10] 2-aminoethanol, and 1-aziridineethanol[11] have suggested that this anomaly may be due to large systematic errors in the hydrogen r_s coordinates caused by small changes in the molecular structure upon deuteration. The decrease in the hydrogen-bonded O-(H)···O distance was obtained by postulating that the hydroxyl group is entirely normal, with $r_{OH} = 0.95$ Å and ∠COH = 108°, but that upon deuteration the O(H)···O distance decreases, causing a large error in the coordinates of the hydrogen atom as deduced from Kraitchman's equations. The changes in inertial moments accompanying deuteration are the net result of an increase due to the increase in isotopic mass of the hydroxy hydrogen and changes due to the change in molecular structure.

The planar moment for the normal and deuterated 1,3-dioxan-5-ol has the values $P_{bb} = 93.3167$, $P'_{bb} = 93.2444$ amu Å^2, showing a decrease in the planar inertial moment upon deuteration. In this situation it is reasonable to suppose that

Table IX. Comparison of the Observed and Calculated Values of the Rotational Constants and Deuterium Kraitchman Coordinates of 1,3-Dioxan-5-ol

rotational constants, MHz	obsd	calcd
A	3913.5	3932.2
B	2922.8	2926.8
C	2193.4	2173.5
Kraitchman coordinates, Å	**obsd**	**calcd**
a	1.0652 (0.0008)[a]	1.149
b	0.267i(0.003)	0.000
c	1.4799 (0.0005)	1.488

[a] Imaginary; see text.

the hydroxyl group is in the symmetry plane and the net change in the inertial planar moment is solely caused by the shrinkage in the O···O (ring) distance because the remaining atoms involved in the intramolecular hydrogen bond do not contribute to P_{bb}. Correcting the r_s structure for the inertial moment changes (assuming the b coordinate of the hydrogen to be zero) the required decrease in the O···O ring distance is 0.0019 Å. This shrinkage is of the same order as that obtained in the O(H)···O distances in other molecules.[10,11]

The 1,3-dioxan-5-ol molecule has a bifurcated intramolecular hydrogen bond with the hydroxyl hydrogen equidistant from the two oxygen atoms in the ring. The position of the hydroxyl hydrogen lying in the plane of symmetry supports this. The intramolecular hydrogen bond has been found to be significantly nonlinear with an O-H···O angle of ~100° and an O···H···O angle of ~38° assuming an O-H distance of 1.0 Å.

One of the most interesting applications of microwave spectroscopy to the study of hydrogen-bonded molecules is as a probe of the hydrogen bond potential surface. Pickett[4] was able to show that 6-hydroxy-2-formylfulvene had a symmetrical single minimum hydrogen bond potential function. Rowe et al. have shown that malonaldehyde[5] has a symmetrical double minimum potential surface with an intermediate barrier between the two minima. Experimental data obtained in 1,3-dioxan-5-ol would seem to rule out (a) a symmetrical double minimum potential with high barrier because in this case the hydroxyl hydrogen position should be out of the symmetry plane with an increase in the planar inertial moment P_{bb} upon deuteration, (b) a symmetrical double minimum potential with a barrier intermediate in height because two low-lying vibrational states should result from the quantum-mechanical mixing of the wave functions showing two different spectra. In this case, the molecule has a symmetrical structure with a single potential minimum or a symmetrical double minimum with a low barrier between the two minima so that rapid tunneling occurs between the two asymmetric forms of 1,3-dioxan-5-ol.

Experimental Section

The sample of normal 1,3-dioxan-5-ol was prepared according to the method of Hibbert and Carter[12] by reaction of formaldehyde and glycerol with simultaneous formation of the five- and six-membered acetals. The separation of the two compounds was carried out by the isolation of the benzoates from which, upon hydrolysis, the acetals were obtained. Spectra for the deuterated species were obtained by D_2O exchange in the waveguide cell. Microwave spectra were recorded on a Hewlett-Packard 8460 A MRR spectrometer. The viscous 1,3-dioxan-5-ol (bp ~190 °C) sample, having a low vapor pressure, had to be pumped through the cell frequently. The spectrum once obtained is dense and strong. All observations were taken at room temperature with sample pressures in the range 10-50 μ.

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