Microwave Spectrum, Structure, and Quadrupole Coupling Constant of *s-cis* *o*-Chlorophenol-*d*

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The microwave spectrum of *o*-chlorophenol-*d* has been observed in the frequency range 17—34 GHz. The rotational and centrifugal distortion constants have been obtained. The analysis of the hyperfine structure has given the following nuclear quadrupole coupling constants for the ^{35}Cl species: $\chi_{aa}=-67.1$, $\chi_{bb}=33.1$, and $\chi_{cc}=34.0$ (MHz). The spectrum assigned has been attributed to the *s-cis*-form (the hydroxyl hydrogen pointed toward the chlorine) from the consideration of the r_s-coordinates of hydrogen and chlorine atoms. The non-bonded Cl···H distance is 2.373±0.001 Å.

In the previous paper,[1] we suggested that the intense lines observed in the microwave spectrum of *o*-chlorophenol should be attributed to the *s-cis* form. In this paper, we report the spectrum of *o*-chlorophenol-*d*. Using the r_s-coordinates of the hydrogen and chlorine atoms, we have confirmed the *s-cis*-structure of the molecule, and determined the structural parameters which reproduce the observed rotational constants and the H···Cl non-bonded distance. We have also obtained the Cl quadrupole coupling constants.

Experimental

o-Chlorophenol-*d* was produced by mixing the normal species with D_2O. The obtained sample was dried over anhydrous calcium chloride, followed by trap-to-trap distillation *in vacuo*. The content of the *d*-species in the sample was estimated to be about 50% from the intensity ratio of the same rotational transition of the deuterated and normal species. The microwave spectrum was measured with a conventional spectrometer with 100 kHz square-wave Stark modulation. The D_2O vapor was introduced into the waveguide and pumped out for several hours, and then the sample was introduced. Measurements were made at *ca.* −20 °C with a sample pressure of 0.6—7 Pa.

Results and Discussion

Analysis of the Spectrum. The frequencies of the spectral lines were predicted from the structural models for both the regular and the distorted hexagonal skeleton structure of *s-cis* *o*-chlorophenol.[1] The initial step of the assignment was made for b-type Q-branch transitions with high-J values. The lines of several Q-branch series are the most intense in our observed frequency region. Their hyperfine structure is a clean doublet in which the separation of lines is a few MHz. The separation varies smoothly according as the J-value changes. The center of the doublet was taken as the unperturbed frequency, since only the first order perturbation was taken into account in the analysis of the hyperfine structure. To confirm the assignment of the Q-branch lines, the splitting widths observed were compared with the ones calculated from the χ-values obtained for *o*-$^{35}ClC_6H_4OH$[1] and the model structure.

The frequencies of the R-branch transitions were predicted from the values of κ and $(A-C)/2$ obtained from the analysis of the Q-branch transitions, together with an assumption of the molecular planarity. The hyperfine structure for the R-branch transitions, however, was not expected to be observed, because the magnitude of the hyperfine splitting was predicted to be smaller than the resolution of the spectrometer. A group of the a- and b-type transitions $J_{0,1}\leftarrow J-1_{1,J-1}$, $J_{1,J}\leftarrow J-1_{1,J-1}$, $J_{0,J}\leftarrow J-1_{0,J-1}$, and $J_{1,J}\leftarrow J-1_{0,J-1}$ was observed as a quartet for $J=9$ and 10. In the quartet, the intensities of a- and b-type transitions are comparable to each other. This indicates that the components of the dipole moment, μ_a and μ_b, of this molecule are comparable in magnitude, as observed for the normal species. The assigned transitions are given in Table 1. The rotational constants, and the centrifugal distortion constants constrained by the planarity conditions among $\tau_{aa\beta\beta}$'s, were obtained by the least-squares fitting and are given in Table 2. The values of the distortion constants obtained are fairly close to those for the normal species, but are smaller than those for most of the aromatic molecules studied.

Molecular Structure. The inertia defect for the isotopic species, *o*-$^{35}ClC_6H_4OD$, was almost the same as that for the normal species, *o*-$^{35}ClC_6H_4OH$,[1] and was found to be of very small positive value compared with those of other planar aromatic molecules. This fact is a strong indication of the planar configuration of this molecule. The isotopic substitution at the hydroxyl group, from H to D, reduces further the magnitude of the inertia defect. Therefore, a negative contribution to the inertia defect can be interpreted as coming from the OH torsion. The Kraitchman's equation was used to calculate the coordinates of the hydrogen atom. The values obtained are given in Table 3, where the errors come from those in the moments of inertia. A very small value of the c-coordinate has been obtained with a large error and it seems rather reasonable to consider that the hydrogen atom practically lies in the A-B plane. On the other hand, a very small imaginary value of the c-coordinate for the chlorine atom was obtained by applying the Kraitchman's equation for the two species, *o*-$^{35}ClC_6H_4OH$ and *o*-$^{37}ClC_6H_4OH$.[1] Therefore, the chlorine atom also lies effectively in the A-B plane. The planar structure of this molecule is plausible. No ambiguity in the sign of r_s-coordinates arises in this case, since the other choice of the sign of the H-coordinates leads to an impossible configuration, with too small a distance between the H atom and C–C bond of the

TABLE 1. OBSERVED FREQUENCIES AND QUADRUPOLE SPLITTING OF *s-cis* *o*-$^{35}ClC_6H_4OD$ (MHz)

Transition	Observed	Centrifugal correction	$\Delta\nu$(I)[a]	*hfs*	
				Obsd	$\Delta\nu$(II)[b]
$8_{0,8}-7_{1,7}$	17144.74	−0.06	−0.12		
$8_{1,8}-7_{1,7}$	17153.15	−0.06	0.04		
$8_{0,8}-7_{0,7}$	17166.35	−0.06	−0.06		
$8_{1,8}-7_{0,7}$	17174.77	−0.06	0.10		
$9_{0,9}-8_{1,8}$	19171.55	−0.09	−0.01		
$9_{1,9}-8_{1,8}$	19174.61	−0.09	−0.04		
$9_{0,9}-8_{0,8}$	19179.94	−0.09	0.12		
$9_{1,9}-8_{0,8}$	19183.11	−0.09	0.19		
$10_{0,10}-9_{1,9}$	21192.93	−0.12	0.01		
$10_{1,10}-9_{1,9}$	21194.07	−0.12	0.02		
$10_{0,10}-9_{0,9}$	21196.10	−0.12	0.09		
$10_{1,10}-9_{0,9}$	21197.14	−0.12	−0.00		
$9_{1,8}-8_{2,7}$	21041.50	−0.13	0.20		
$9_{2,8}-8_{2,7}$	21155.67	−0.13	−0.30		
$9_{1,8}-8_{1,7}$	21298.95	−0.13	0.08		
$9_{2,8}-8_{1,7}$	21413.54	−0.13	−0.00		
$11_{0,11}-10_{1,10}$	23212.22	−0.16	−0.02		
$11_{1,11}-10_{1,10}$	23212.72	−0.16	0.07		
$11_{0,11}-10_{0,10}$	23213.34	−0.16	−0.02		
$11_{1,11}-10_{0,10}$	23213.68	−0.16	−0.10		
$10_{1,9}-9_{2,8}$	23154.89	−0.17	0.05		
$10_{2,9}-9_{2,8}$	23203.49	−0.17	−0.02		
$10_{1,9}-9_{1,8}$	23269.46	−0.17	−0.05		
$10_{2,9}-9_{1,8}$	23318.17	−0.17	−0.01		
$12_{0,12}-11_{1,11}$	25230.90	−0.20	0.08		
$12_{1,12}-11_{1,11}$	25230.90	−0.20	−0.06		
$12_{0,12}-11_{0,11}$	25230.90[c]	−0.20	−0.32		
$12_{1,12}-11_{0,11}$	25230.90[c]	−0.20	−0.47		
$13_{0,13}-12_{1,12}$	27249.15	−0.25	0.01		
$13_{1,13}-12_{1,12}$	27249.15	−0.25	−0.04		
$13_{0,13}-12_{0,12}$	27249.15	−0.25	−0.13		
$13_{1,13}-12_{0,12}$	27249.15	−0.25	−0.18		
$14_{0,14}-13_{1,13}$	29267.39	−0.31	−0.00		
$14_{1,14}-13_{1,13}$	29267.39	−0.31	−0.02		
$14_{0,14}-13_{0,13}$	29267.39	−0.31	−0.05		
$14_{1,14}-13_{0,13}$	29267.39	−0.31	−0.07		
$15_{0,15}-14_{1,14}$	31285.71	−0.38	0.08		
$15_{1,15}-14_{1,14}$	31285.71	−0.38	0.08		
$15_{0,15}-14_{0,14}$	31285.71	−0.38	0.07		
$15_{1,15}-14_{0,14}$	31285.71	−0.38	0.06		
$16_{0,16}-15_{1,15}$	33303.64[c]	−0.46	−0.23		
$16_{1,16}-15_{1,15}$	33303.64[c]	−0.46	−0.23		
$16_{0,16}-15_{0,15}$	33303.64[c]	−0.46	−0.23		
$16_{1,16}-15_{0,15}$	33303.64[c]	−0.46	−0.24		
$24_{9,15}-24_{8,16}$	17029.17[d]	−2.01	0.06	−0.82	0.01
$24_{10,14}-24_{9,15}$	22299.30[d]	−2.54	−0.06	−2.27	0.08
$25_{10,15}-25_{9,16}$	20384.23[d]	−2.52	−0.03	−1.97	−0.03
$26_{10,16}-26_{9,17}$	19060.69[d]	−2.58	−0.01	−1.35	−0.02
$27_{10,17}-27_{9,18}$	18751.80[d]	−2.79	0.06	−0.69	−0.05
$28_{10,18}-28_{9,19}$	19684.25	−3.19	0.21		
$29_{10,19}-29_{9,20}$	21842.22[d]	−3.79	−0.10	0.36	−0.15
$30_{10,20}-30_{9,21}$	24958.86[d]	−4.56	−0.04	0.77	−0.00
$28_{11,17}-28_{10,18}$	21925.35[d]	−3.38	0.18	−1.76	−0.04
$29_{11,18}-29_{10,19}$	20641.42[d]	−3.47	−0.04	−1.12	0.01
$30_{11,19}-30_{10,20}$	20480.91[d]	−3.76	−0.32	−0.37	0.10

Table 1. (Continued)

Transition	Observed	Centrifugal correction	$\Delta\nu$(I)[a]	*hfs*	
				Obsd	$\Delta\nu$(II)[b]
$31_{11,20}-31_{10,21}$	21639.38	−4.30	−0.11		
$32_{11,21}-32_{10,22}$	24052.96[d]	−5.08	0.10	0.66	0.09
$31_{12,19}-31_{11,20}$	23423.99[d]	−4.41	−0.10	−1.51	0.01
$32_{12,20}-32_{11,21}$	22210.68[d]	−4.55	0.04	−0.82	0.13
$33_{12,21}-33_{11,22}$	22225.44	−4.95	0.13		
$34_{12,22}-34_{11,23}$	23626.73	−5.65	0.07		
$34_{13,21}-34_{12,22}$	24890.65[d]	−5.63	0.05	−1.32	0.04
$35_{13,22}-35_{12,23}$	23776.85[d]	−5.83	−0.01	−0.76	0.04
$36_{13,23}-36_{12,24}$	23990.67	−6.37	−0.08		

a) $\Delta\nu$(I) = observed − calculated, for the rotational transition. b) $\Delta\nu$(II) = observed − calculated, for the splitting. c) Not included in the least-squares fitting. d) Corrected for the quadrupole effect.

Table 2. Rotational constants(MHz), centrifugal distortion constants(kHz), and inertia defect (amu Å^2) of *s-cis* o-$^{35}ClC_6H_4OD$

A	2930.937±0.009[b]
B	1539.217±0.004
C	1009.203±0.002
τ_{aaaa}	−2.0±0.3
τ_{bbbb}	−0.36±0.03
τ_{aabb}	−0.1±0.2
τ_{abab}	−0.46±0.07
$I_c-I_a-I_b$	0.006±0.002
σ[a]	0.007

a) Standard deviation in frequencies(MHz) for lines fitted. b) Standard deviation.

benzene ring. The non-bonded H···Cl distance was obtained from the r_s-coordinates of Cl[1] and H, as shown in Table 3. The obtained H···Cl distance, 2.373 Å, implies that the assigned spectrum is of the *s-cis*-form of this molecule. As discussed in the previous paper,[1] the a- and b-components of the dipole moment for the *s-cis*-form are comparable in magnitude to each other. Therefore, the comparable intensities of the observed a- and b-type transitions also support the *s-cis*-form of the molecule studied here.

Assuming the rigid planar structure of this molecule, five structural parameters have been obtained from the three isotopic species, $^{35}ClC_6H_4OH$, $^{37}ClC_6H_4OH$, and $^{35}ClC_6H_4OD$. Here, the benzene ring was assumed to be of the same distorted skeleton as obtained for chlorobenzene from its complete r_s-coordinates analysis.[2] The parameters obtained are given in Table 4. These parameters reproduce the observed nine moments of inertia within 0.1 amu Å^2 and the r_s-non-bonded distance (Cl···H) within 0.01 Å. The structural parameters around the OH group are similar to those of phenol. The small differences in r_{OH}, $\angle C_1C_2O$, and $\angle C_2OH$, *i.e.*, the slightly longer bond length r_{OH} and the slightly narrower angles of the $\angle C_1C_2O$ and $\angle C_2OH$, where C_1 is bonded to Cl and C_2 to O, compared with those of phenol, suggest the existence of an intra-molecular hydrogen bonding.

Quadrupole Coupling Constants. The apparent splitting of the doublet was measured for each of the high-J b-type Q-branch transitions listed in Table 1. The hyperfine structures due to ^{35}Cl were analyzed, based on the first-order quadrupole correction computation using the rotational constants in Table 2. The quadrupole coupling constants in the principal inertia axis system, χ_{aa}, χ_{bb}, and χ_{cc}, were obtained using the least-squares method, as shown in Table 5. In this procedure, a quantity, the inverse of the squared standard deviation (in the measurements) for the splitting divided by the splitting width, was taken as the weight for each line. The uncertainties of the values in Table 5 were estimated from the error in the frequency measurements of the unresolved F components. Assuming that the principal z-axis of the χ-tensor lies along the C–Cl bond, the values of χ_{zz} and χ_{yy} are calculated as given in Table 5. The χ_{xx}, the component perpendicular to the molecular plane, is the same as χ_{cc}. The χ_{gg}-values (g=x,y, and z) of $^{35}ClC_6H_4OH$ was recalculated for the molecular structure obtained in this work. The ambiguity of the angle of θ_{za} was within ±0.1° when estimated from the structure in Table 4. The χ-values calculated for the normal and deuterated species coincide within the error limits. The value of χ_{zz}(−68.7 MHz) in this molecule is larger than that in chlorobenzene[3] ($\chi_{zz}=-71.10\pm0.50$ MHz) by 2.4 MHz. This difference suggests an increase of ionicity of the Cl atom compared with that

Table 3. Principal axis coordinates of H and Cl (Å)

	$\|a\|$	$\|b\|$	$\|c\|$
H	1.4863±0.0003[b]	1.7874±0.0003	0.065 ±0.007
Cl[a]	2.0672±0.0001	0.5136±0.0005	$(-0.0004)^{1/2}$±0.011
H···Cl (in plane)		2.373±0.001	

a) Ref. 1. b) The errors came from those in the moments of inertia.

Table 4. Structural parameters[a]

	s-cis *o*-ClC_6H_4OH[b]	C_6H_5Cl[c]	C_6H_5OH[d]
r_{C-Cl} (Å)	1.721±0.001	1.7248	—
r_{C-O} (Å)	1.37±0.005	—	1.364
r_{O-H} (Å)	0.97±0.01	—	0.956
$\angle C_1C_2O$ (°)	121.0±0.5	—	122.2
$\angle C_2OH$ (°)	108.0±0.5	—	109.0

a) A distorted hexagon shape of the chlorobenzene molecule was assumed; Ref. 2. b) This work. c) Ref. 2. d) Ref. 4.

in chlorobenzene. The double bond character of the C–Cl bond should be negligible because the η-value is vanishingly small. This situation appears also in other chlorobenzene derivatives.[5]

Judging from the quadrupole coupling constant alone, the interaction between chlorine and hydrogen atoms is rather weak. The small difference in the χ_{zz} between *o*-chlorophenol and monochlorobenzene reveals no clear effect of hydrogen bonding on the nuclear quadrupole coupling constant of chlorine. The same conclusion had been obtained for 2-chloroethanol.[6]

Table 5. Quadrupole coupling constants of ^{35}Cl(MHz)

	$^{35}ClC_6H_4OH$[a]	$^{35}ClC_6H_4OD$[b]
χ_{aa}	−67.6±0.3	−67.1±2.0
χ_{bb}	33.3±0.1	33.1±0.2
χ_{cc}	34.3±0.4	34.0±2.2
θ_{za}[c]	5.87°	6.84°
χ_{zz}	−68.7±0.3	−68.6±2.0
χ_{yy}	34.4±0.1	34.6±0.2
χ_{xx}[d]	34.3±0.4	34.0±2.2
η[e]	0.00	0.01

a) Ref. 1. b) This work. c) θ_{za} is the angle between the principal inertial a-axis and the C-Cl bond axis. d) χ_{xx} is the component perpendicular to the molecular plane. e) $\eta=(\chi_{xx}-\chi_{yy})/\chi_{zz}$.

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