Microwave Spectrum and Barrier to Internal Rotation of 4-Chlorophenol

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Microwave spectra of 4-chlorophenol were observed in the frequency ranges 8—18 and 26.5—40 GHz. Rotational constants were obtained for the ground vibrational states of three isotopic species, $^{35}ClC_6H_4OH$, $^{37}ClC_6H_4OH$, and $^{35}ClC_6H_4OD$, and for the first excited state of C–Cl out-of-plane bending mode for $^{35}ClC_6H_4OH$. All the b-type Q-branch transition lines of the OH species split into doublets, but those of the OD species do not. The separation of doublets is 158.99±0.16 MHz for the ground state of $^{35}ClC_6H_4OH$. An analysis of the doublets on the basis of the pseudo-symmetric internal rotor model gives the barrier height to the internal rotation of hydroxyl group as $V_2=13.98\pm0.37$ kJ mol^{-1} for the ^{35}Cl species. The V_2 value obtained is compared with the theoretical V_2 value calculated for 4-X-phenols (X=H, F, Cl) by means of *ab initio* MO with the 4-31G basis set.

The microwave spectrum of phenol was reported for the first time by Kojima.[1] The barrier height V_2 was determined to be 13.16±1.20 kJ mol^{-1} from the observed splitting. In his method the hydroxyl group was assumed to be a pseudo-symmetric internal rotor. Following Kojima's paper, many theoretical and experimental articles on phenol have appeared.[2–6] One of them is the article on a strict Rotation-Internal Rotation (RIR) treatment by Mathier *et al.* and a more reliable V_2 value is given.[5]

The molecule of 4-fluorophenol has the same symmetry as that of phenol with respect to the overall and internal rotations. The far IR spectra of 4-fluorophenol were analyzed with the exact RIR treatment by Larsen and Nicolaisen.[7] In this paper, we report microwave spectra of three isotopic species of 4-chlorophenol and the value of V_2 as estimated according to Kojima's approximation.[1]

Experimental

The sample was obtained commercially and distilled *in vacuo*. The deuterated species (OD) was produced by mixing the normal species with D_2O in a wave-guide cell. The content of the *d*-species thus produced was estimated to be about 30% from the intensity ratio between the same rotational transitions of the deuterated and normal species. The microwave spectrum was measured with a conventional spectrometer using 100 kHz square-wave Stark modulation. The measured frequency regions were 8—18 and 26.5—40 GHz. The microwave sources for them were a synthesizer (HP-8672A) and a YIG tuned GaAs oscillator (Watkins-Johnson 5610-302FD), respectively. Measurements were made at room temperature with sample pressures of 3—7 Pa. The accuracy of the measured frequency was better than 0.1MHz for all lines except broadened ones with hyperfine components due to chlorine nucleus.

Results and Discussion

Analysis of Spectrum. Frequencies of spectral lines were predicted from a structural model which was constructed with structural parameters transferred from chlorobenzene[8] and phenol.[9] The components of the dipole moment were estimated as $\mu_a=1.65$ D and $\mu_b=1.22$ D from those of the two molecules mentioned above. From these predictions it was expected that the a-type transitions would be observed strongly for this molecule. This is in contrast to the case of phenol where $\mu_a=0.133$ D and $\mu_b=1.217$ D.[9] The spectrum consisted of many lines in the observed region. This complexity of the spectrum comes from the existence of two chlorine isotopic species in their ground and low frequency excited vibrational states. The initial step of assignment was made for the a-type R-branch transitions which were expected to appear as singlets with the assumed barrier to internal rotation of hydroxyl group. Some of the transitions with high K_{-1} were observed as doublets due to nuclear quadrupole coupling of chlorine. For $8_{3,6}$—$7_{3,5}$, $8_{3,5}$—$7_{3,4}$, $7_{2,6}$—$6_{2,5}$, and $7_{2,5}$—$6_{2,4}$, the separations of the doublets were about 1 MHz, which is consistent with those predicted by using χ-values obtained for chlorobenzene.[10] The assigned a-type R-branch transitions are given in Tables 1 and 2.

The b-type Q-branch transitions were expected to be doublets due to the internal rotation as seen in the b-type transitions of phenol.[1] The separation of the doublets depends on the barrier height of the internal rotor. It was predicted to be 27.6 to 467 MHz for $V_2=18$ to 12 kJ mol^{-1}. The upper and lower components of the doublets were searched for in the frequency region, which are located at the same distances from the predicted unperturbed frequencies as calculated from the results of analysis of the a-type R-branch transitions. The observed separations of the doublets were about 159 MHz. The observed b-type Q-branch transition frequencies and their splitting widths are given in Tables 1 and 2 and Table 3, respectively. Each component of b-type Q-branch transitions listed in the tables was observed as single line despite the perturbation of quadrupole coupling.

The rotational constants were obtained by least-

TABLE 1. OBSERVED FREQUENCIES IN MHz OF a-TYPE R-BRANCH AND b-TYPE Q-BRANCH[a] TRANSITIONS[b] FOR 4-$^{35}ClC_6H_4OH$

Transition	$v=0$	$v=1$	Transition	$v=0$	$v=1$
$7_{0,7}-6_{0,6}$	12472.11(8)		$19_{1,19}-18_{1,18}$	32404.05(−4)	32433.55(3)
$7_{1,7}-6_{1,6}$	12106.60(−3)		$19_{1,18}-18_{1,17}$	c)	34436.62(−13)
$7_{1,6}-6_{1,5}$	13108.16(−1)		$19_{2,18}-18_{2,17}$	c)	33788.00(−1)
$7_{2,6}-6_{2,5}$	12625.28(23)		$19_{2,17}-18_{2,16}$	35532.14(−7)	35555.93(7)
$7_{2,5}-6_{2,4}$	12803.44(−8)		$19_{3,17}-18_{3,16}$	34454.65(13)	34480.70(−19)
$8_{0,8}-7_{0,7}$	14195.25(4)		$19_{3,16}-18_{3,15}$	35171.11(−20)	35201.42(−27)[d]
$8_{1,8}-7_{1,7}$	13822.18(3)		$19_{4,16}-18_{4,15}$	34561.53(14)	
$8_{1,7}-7_{1,6}$	14961.63(−13)		$19_{4,15}-18_{4,14}$	34648.55(−15)	
$9_{0,9}-8_{0,8}$	15899.96(−5)		$20_{0,20}-19_{0,19}$	34133.82(1)	34163.79(−3)
$9_{1,9}-8_{1,8}$	15532.83(−7)		$20_{1,20}-19_{1,19}$	34074.65(−3)	34105.68(−7)
$9_{1,8}-8_{1,7}$	16806.49(−27)		$20_{1,19}-19_{1,18}$	36077.78(−6)	36098.75(−3)
$9_{2,8}-8_{2,7}$	16206.03(−2)		$20_{2,19}-19_{2,18}$	35480.72(8)	35507.82(19)
$9_{2,7}-8_{2,6}$	16570.57(−4)		$20_{2,18}-19_{2,17}$	37367.60(15)	37391.92(37)[d]
$10_{0,10}-9_{0,9}$	17587.85(−2)		$20_{3,18}-19_{3,17}$	36249.75(−16)	
$10_{1,10}-9_{1,9}$	17238.81(2)		$20_{3,17}-19_{3,16}$	37117.40(−2)	37149.35(12)
$10_{2,9}-9_{2,8}$	17989.60(3)		$20_{4,17}-19_{4,16}$	36396.21(12)	
$15_{1,14}-14_{1,13}$	27596.35(6)	27613.14(7)	$20_{4,16}-19_{4,15}$	36519.19(4)	
$15_{2,14}-14_{2,13}$	c)	26840.19(−5)	$21_{0,21}-20_{0,20}$	35789.31(−45)[d]	
$15_{2,13}-14_{2,12}$	28032.49(−9)	28053.45(−8)	$21_{1,21}-20_{1,20}$	35743.58(−13)	
$15_{3,13}-14_{3,12}$	27223.12(−1)	27244.45(−2)	$21_{1,20}-20_{1,19}$	37726.64(−18)	
$15_{3,12}-14_{3,11}$	27484.18(−9)	27507.61(2)	$21_{2,20}-20_{2,19}$	37192.45(2)	
$15_{4,12}-14_{4,11}$	27232.60(26)		$21_{3,19}-20_{3,18}$	38039.11(10)	
$15_{4,11}-14_{4,10}$	27249.24(−23)		$21_{3,18}-20_{3,17}$	39066.46(11)	
$16_{0,16}-15_{0,15}$	27526.57(4)	27549.21(3)	$21_{4,18}-20_{4,17}$	38230.80(10)	
$16_{1,16}-15_{1,15}$	27379.74(10)	27404.71(45)[d]	$21_{4,17}-20_{4,16}$	38400.41(1)	
$16_{1,15}-15_{1,14}$	29331.47(4)	29349.03(9)	$22_{0,22}-21_{0,21}$	37446.88(−21)	
$16_{2,15}-15_{2,14}$	28565.89(1)	28587.73(−0)	$22_{1,22}-21_{1,21}$	37411.26(−20)	
$16_{2,14}-15_{2,13}$	29927.67(−11)	29949.53(−1)	$22_{1,21}-21_{1,20}$	39367.42(3)	
$16_{3,14}-15_{3,13}$	29037.07(8)	29059.77(13)	$13_{2,11}-13_{1,12}$	12034.91(6)	
$16_{3,13}-15_{3,12}$	29386.55(−22)	29411.98(4)	$14_{2,12}-14_{1,13}$	12321.63(5)	
$16_{4,13}-15_{4,12}$	29062.50(18)	29085.93(28)[d]	$15_{2,13}-15_{1,14}$	12757.88(−0)	
$16_{4,12}-15_{4,11}$	c)	29112.79(−10)	$16_{2,14}-16_{1,15}$	13354.09(−14)	
$17_{0,17}-16_{0,16}$	29176.09(18)	29200.40(2)	$17_{2,15}-17_{1,16}$	14119.14(11)	
$17_{1,17}-16_{1,16}$	29057.13(19)	29083.15(1)	$18_{2,16}-18_{1,17}$	15058.12(10)	
$17_{1,16}-16_{1,15}$	31045.70(−20)	31064.12(−3)	$19_{2,17}-19_{1,18}$	16173.40(1)	
$17_{2,16}-16_{2,15}$	30305.17(11)	30328.23(3)	$20_{2,18}-20_{1,19}$	17462.97(−3)	
$17_{2,15}-16_{2,14}$	31810.81(10)	31833.17(−2)	$20_{3,17}-20_{2,18}$	18136.89(8)	
$17_{3,15}-16_{3,14}$	30847.26(−9)	30871.26(−1)	$23_{3,20}-23_{2,21}$	18256.52(−22)	
$17_{3,14}-16_{3,13}$	31302.87(−27)	31329.92(−21)	$35_{5,30}-35_{4,31}$		31521.43(−11)
$17_{4,14}-16_{4,13}$	30894.38(33)[d]	30918.98(13)	$36_{5,31}-36_{4,32}$	31041.11(−5)	30740.84(9)
$17_{4,13}-16_{4,12}$	30935.05(11)		$37_{5,32}-37_{4,33}$	30366.79(17)	30083.00(9)
$18_{0,18}-17_{0,17}$	30826.83(3)	30853.12(0)	$38_{5,33}-38_{4,34}$	29841.79(−7)	29577.32(−7)
$18_{1,18}-17_{1,17}$	c)	30759.50(6)	$39_{5,34}-39_{4,35}$	c)	c)
$18_{1,17}-17_{1,16}$	32740.52(8)	32759.46(−1)	$40_{5,35}-40_{4,36}$	29344.07(−2)	
$18_{2,17}-17_{2,16}$	32037.10(−7)	32061.58(−0)	$41_{5,36}-41_{4,37}$	29412.62(−4)	
$18_{2,16}-17_{2,15}$	33679.39(−4)	33702.64(11)	$42_{5,37}-42_{4,38}$	29713.73(−1)	29544.02(−5)
$18_{3,16}-17_{3,15}$	32653.54(10)	32678.51(−10)	$43_{5,38}-43_{4,39}$	30257.70(−1)	30114.03(5)
$18_{3,15}-17_{3,14}$	33232.36(26)	33260.84(−1)	$44_{5,39}-44_{4,40}$	31050.52(−1)	
$18_{4,15}-17_{4,14}$	32727.40(19)		$45_{5,40}-45_{4,41}$	32093.57(4)	
$18_{4,14}-17_{4,13}$	32787.65(−6)		$46_{5,41}-46_{4,42}$	c)	33314.26(−2)
$19_{0,19}-18_{0,18}$	32479.44(−0)	32507.58(−3)	$47_{5,42}-47_{4,43}$	c)	34862.94(1)

a) Center frequency of doublet. b) Figures in parentheses indicate the last digits of the difference: the observed minus calculated frequency. c) Overlapped by other lines. d) Not included in the least-squares fitting.

TABLE 2. OBSERVED FREQUENCIES IN MHz OF a-TYPE R-BRANCH AND b-TYPE Q-BRANCH TRANSITION[a)]

Transition	4-^{35}ClC$_6$H$_4$OD	4-^{37}ClC$_6$H$_4$OH	Transition	4-^{35}ClC$_6$H$_4$OD	4-^{37}ClC$_6$H$_4$OH
$15_{1,14}-14_{1,13}$		26956.47(5)	$18_{1,17}-17_{1,16}$		32008.16(−6)
$15_{2,13}-14_{2,12}$	27359.91(−22)	27325.11(20)	$18_{2,17}-17_{2,16}$	31317.75(29)	
$15_{3,13}-14_{3,12}$	26590.05(−3)		$18_{2,16}-17_{2,15}$		32846.58(−1)
$15_{3,12}-14_{3,11}$	26825.77(−11)	26792.29(−0)	$18_{3,16}-17_{3,15}$	31897.33(−16)	31870.10(−2)
$15_{4,12}-14_{4,11}$	26595.87(4)		$18_{3,15}-17_{3,14}$	32424.40(−19)	32378.40(16)
$15_{4,11}-14_{4,10}$	26610.76(8)		$18_{4,15}-17_{4,14}$	31960.94(9)	
$16_{0,16}-15_{0,15}$		26926.84(8)	$18_{4,14}-17_{4,13}$	32013.33(−11)	
$16_{1,16}-15_{1,15}$		26770.45(−2)	$19_{0,19}-18_{0,18}$		31769.65(6)
$16_{2,15}-15_{2,14}$	27920.45(4)		$19_{1,19}-18_{1,18}$		31686.79(6)
$16_{2,14}-15_{2,13}$	29213.07(24)		$19_{2,17}-18_{2,16}$		34661.16(−14)
$16_{3,14}-15_{3,13}$	28362.61(6)		$20_{1,20}-19_{1,19}$		33321.13(−9)
$16_{3,13}-15_{3,12}$	28679.19(2)	28641.34(−12)	$20_{1,19}-19_{1,18}$		35286.98(4)
$16_{4,13}-15_{4,12}$	28382.58(4)		$37_{4,33}-37_{3,34}$	26908.73(−12)	
$16_{4,12}-15_{4,11}$	28405.66(−19)		$38_{4,34}-38_{3,35}$	28191.52(−2)	
$17_{0,17}-16_{0,16}$	28542.77(−17)	28539.67(−4)	$39_{4,35}-39_{3,36}$	29679.95(−5)	
$17_{1,17}-16_{1,16}$	28418.78(−14)	28411.64(−6)	$40_{4,36}-40_{3,37}$	31360.71(7)	
$17_{1,16}-16_{1,15}$		30343.34(4)	$33_{5,28}-33_{4,29}$	34065.50(16)	
$17_{2,16}-16_{2,15}$	29622.31(4)	29606.15(1)	$34_{5,29}-34_{4,30}$	33129.36(−10)	
$17_{2,15}-16_{2,14}$	31054.75(24)	31017.82(−1)	$35_{5,30}-35_{4,31}$	32228.38(−35)	
$17_{3,15}-16_{3,14}$		30105.32(−15)	$36_{5,31}-36_{4,32}$	31393.66(−11)	
$17_{3,14}-16_{3,13}$	30545.65(−5)		$37_{5,32}-37_{4,33}$	30655.46(23)	
$17_{4,14}-16_{4,13}$	30171.14(17)	30141.47(11)	$39_{5,34}-39_{4,35}$	29582.68(0)	
$17_{4,13}-16_{4,12}$	30206.47(−1)	30174.63(−14)	$40_{5,35}-40_{4,36}$	29299.98(29)	
$18_{0,18}-17_{0,17}$		30153.92(5)			

a) Figures in parentheses indicate the last digits of the difference: the observed minus calculated frequency.

TABLE 3. OBSERVED SPLITTING IN MHz OF b-TYPE Q-BRANCH TRANSITIONS FOR ^{35}ClC$_6$H$_4$OH

Transition $K_{-1}=2-1$	$v=0$	Transition $K_{-1}=5-4$	$v=0$	$v=1$
$13_{2,11}-13_{1,12}$	159.03	$36_{5,31}-36_{4,32}$	158.21	159.23
$14_{2,12}-14_{1,13}$	158.85	$37_{5,32}-37_{4,33}$	158.33	159.44
$15_{2,13}-15_{1,14}$	158.75	$38_{5,33}-38_{4,34}$	158.29	159.22
$16_{2,14}-16_{1,15}$	159.01	$39_{5,34}-39_{4,35}$	a)	a)
$17_{2,15}-17_{1,16}$	159.02	$40_{5,35}-40_{4,36}$	158.26	a)
$18_{2,16}-18_{1,17}$	158.89	$41_{5,36}-41_{4,37}$	158.31	a)
$19_{2,17}-19_{1,18}$	158.88	$42_{5,37}-42_{4,38}$	158.31	159.31
$20_{2,18}-20_{1,19}$	158.79	$43_{5,38}-43_{4,39}$	158.25	159.43
		$44_{5,39}-44_{4,40}$	158.25	a)
		$45_{5,40}-45_{4,41}$	158.25	a)
		$46_{5,41}-46_{4,42}$	a)	159.14
		$47_{5,42}-47_{4,43}$	a)	159.20
average	158.90(15)		158.27(6)	159.28(16)

a) Overlapped by other lines.

squares fitting of the transition frequencies listed in Tables 1 and 2. The values derived for the parameters are given in Table 4. Satellites which formed a series of lines with decreasing intensity were observed for low K_{-1} transitions near the ground vibrational lines. The most intense satellite lines were assigned to the transitions in the first excited state as specified in Table 1. On the basis of their intensity and inertia defect, this excited state is ascribed to the out-of-plane mode with the lowest vibrational frequency, namely, the C–Cl out-of-plane bending (165 cm^{-1}).[11] A search for the lines due to the OH torsional excited state was not successful.

Barrier to Internal Rotation. The splitting in the b-type Q-branch transitions was analyzed by using the same approximation as assumed for phenol molecule; a pseudo-symmetric internal rotor was assumed for O–H group.[1] The observed splittings of the doublets were almost independent of J for each $K_{-1}-K'_{-1}$ series as seen in Table 3. However, the observed splittings for the two series of transitions, $J_{2,J-2}-J_{1,J-1}$ and $J_{5,J-5}-J_{4,J-4}$ of ^{35}ClC$_6$H$_4$OH ($v=0$), indicate that the splitting of the doublet varies depending on the K_{-1} values. Mathier *et al.*[5] pointed out the same K_{-1} dependency for phenol and gave an empirical formula for this dependency. Their empirical formula* was applied to the present analysis of 4-chlorophenol, and a virtual value of splitting independent of K_{-1} was obtained as 158.99±0.16 MHz (Table 5).

For the evaluation of barrier height the most uncertain parameter is I_1, the moment of inertia of the

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* Split/MHz=158.99(16)−0.0175(25)×($K_{-1}^2+K'^2_{-1}$) for $J_{K-1,K+1}-J_{K'-1,K'+1}$ of 4-^{35}ClC$_6$H$_4$OH. The virtual splitting was obtained by means of the least-squares method using the splitting widths in Table 3.[5]

TABLE 4. ROTATIONAL CONSTANTS, INERTIA DEFECT, AND INTERNAL ROTATION SPLITTING OF 4-CHLOROPHENOL[a)]

	$4\text{-}^{35}ClC_6H_4OH$		$4\text{-}^{35}ClC_6H_4OD$	$4\text{-}^{37}ClC_6H_4OH$
	$v=0$	$v=1$	$v=0$	$v=0$
A/MHz	5632.78(7)	5598.80(54)	5591.03(2)	5632.86(63)
B/MHz	975.573(4)	976.142(7)	951.854(3)	950.485(4)
C/MHz	831.655(4)	832.511(7)	813.505(3)	813.352(4)
τ_{aaaa}/MHz	−0.011(24)	−0.027(60)	−0.011[b)]	−0.011[b)]
τ_{bbbb}/MHz	−0.00011(2)	−0.00007(4)	−0.00011[b)]	−0.00011[b)]
τ_{aabb}/MHz	0.0004(5)	0.0009(11)	0.0004[b)]	0.0004[b)]
τ_{abab}/MHz	−0.00029(18)	−0.00047(35)	−0.00029[b)]	−0.00029[b)]
Δ/uÅ^2[c)]	−0.076(6)	−0.943(17)	−0.096(4)	−0.073(15)
σ/MHz[d)]	0.121	0.082	0.162	0.096
Split/MHz[e)]	158.99	159.28	<0.2	—

a) Figures in parentheses indicate the uncertainty involved in the last significant digits calculated as 2.5 times the standard deviation. b) Assumed. c) $\Delta = I_c - I_a - I_b$. d) Standard deviation for lines fitted. e) Average value of the splittings in the b-type Q-branch transitions.

TABLE 5. INTERNAL ROTATION PARAMETER

	$4\text{-}^{35}ClC_6H_4OH$	C_6H_5OH
Split/MHz	158.99(16)	111.998[a)]
I_a/uÅ^2	89.721(1)	89.439[a)]
I_1/uÅ^2	0.740(18)	0.743[a)]
F/GHz	688(16)	686
s	50.9(2)	53.7
V_2/kJ mol^{-1}	13.98(37)	14.71 [14.44][a),b)]

a) Ref. 5. b) Obtained by RIR analysis.

hydroxyl group about the internal rotation axis. In the present analysis the following approximation is adopted: The a-axis coincides with the internal rotation axis and the center of mass of the hydroxyl group lies on the a-axis. The first moment equation was used to calculate the I_1 value, together with using the r_s b-coordinate of hydroxyl hydrogen (0.833±0.002 Å). The values of I_1 for the two molecules coincided well with each other as shown in Table 5.

The barrier height V_2 was calculated from the parameters in Table 5 by using the perturbation coefficients given by Lin and Swalen.[12] The error for I_1 arises from the ambiguity in the b-coordinate of the hydrogen atom, ±0.01 Å, which seems to be in the maximum allowable range. The b-type Q-branch transitions for $^{35}ClC_6H_4OD$ were not observed as doublet. The splittings, if any, were smaller than 0.2 MHz because no line broadening was recognized. They were predicted to be 0.41 MHz from the V_2 value obtained. The smaller splittings than 0.2 MHz of the transitions correspond to the higher V_2 than 15 kJ mol^{-1}. This result that the V_2 value for the OD species is higher than that of the OH species, is apparently the same as those in the case of phenol and 4-fluorophenol.[7]

To compare the V_2 value of 4-chlorophenol with that of phenol, the same approximation was applied to phenol; I_1 was calculated from the r_s coordinate of hydroxyl hydrogen because I_1 was roughly estimated in Kojima's paper. The V_2 value of phenol obtained on this approximation coincides with the value based on the RIR treatment within 2% as shown in Table 5.

Campagnero and Wood[13] assumed that the barrier height of 4-X-phenols is dependent mainly on the degree of double bond character in the C–O bond; if substituent X at 4-position is a strong π donor, the double bond character will decrease and thus the barrier height will decrease.[13] Larsen and Nicolaisen[7] explained the lower barrier height of 4-fluorophenol than that of phenol by the above theory. According to their theory, our result may be taken to indicate that the ability of chlorine as a π donor is lower than that of fluorine in 4-X-phenol.

Recently, the barrier in phenol has been calculated for a fully-optimized structure based on the STO-3G basis set[14] and also based on 4-31G for a rigidly rotating structure.[15] To compare the experimentally obtained barrier heights of 4-substituted phenols with MO theoretical ones, we calculated the total energies of the molecules with standard geometry and rigidly rotating hydroxyl group by using the 4-31G basis set without geometry optimization. The benzene ring was assumed as a regular hexagon in which the C–C bond length is equal to the mean value for the r_s length in phenol, 1.3912 Å. The other assumptions adopted were that the C–O bond lies on the C_{2v} axis of the ring and that the hydroxyl group rotates about the axis rigidly. The energy difference between the planar and orthogonal structures was taken as the theoretical barrier height. The results are given in Table 6. The MO theoretical barriers in Table 6 are lower than the experimental ones. However, it is interesting to have almost a constant ratio 1.5 of the experimental to theoretical value for the three molecules.

The *ab initio* calculation was carried out at the

Table 6. Comparison of barrier heights in kJ mol^{-1} in para-substituted phenols

Molecule	Experimental	*ab initio*a)	Ratiob)
Phenol	14.44c)	9.75	1.48
4-fluorophenol	12.05d)	7.95	1.52
4-chlorophenol	13.98e)	9.33	1.52

a) Calculation on the 4-31G basis set. b) Ratio= experimental/*ab initio*. c) Ref. 5. d) Ref. 7. e) This work.

Computer Center of the University of Tokyo by using the GSCF2 programmed by N. Kosugi.

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