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BARRIER TO INTERNAL ROTATION OF 4-BROMOPHENOL BY MICROWAVE SPECTRUM AND AB INITIO CALCULATION

Takashi MOTODA, Masao ONDA,* and Ichiro YAMAGUCHI
Department of Chemistry, Faculty of Science and Technology,
Sophia University, Tokyo 102

Microwave spectra of 4-bromophenol(^{79}Br and ^{81}Br species) were observed. An analysis of the doublets due to internal rotation of the hydroxyl group was made on the basis of the pseudo-symmetric internal rotor model. The doublet splitting of the b-type Q-branch transitions, 139.18 MHz, gave a barrier height V_2=14.23 kJ mol^{-1}. The barrier height V_2 for six 4-X-phenols was calculated by means of ab initio MO (4-31G).

Recently, we have reported the microwave spectrum and the barrier height V_2 for the internal rotation of hydroxyl group in 4-chlorophenol.$^{1)}$ The V_2 was estimated according to Kojima's approximation in which the hydroxyl group was assumed to be a pseudo-symmetric internal rotor.$^{2)}$ In this paper, we will report microwave spectra of two isotopic species of 4-bromophenol and compare the experimental (microwave) and theoretical (ab initio calculation) values of V_2 for 4-X-phenol.

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. Measurements were made at room temperature. The accuracy of the measured frequency was better than 0.1 MHz except broadened ones with hyperfine components due to bromine nucleus.

The assigned a-type R-branch and b-type Q-branch transitions are given in Table 1. All the b-type Q-branch transitions were observed as doublets with nearly equal separation as given in Table 2. The doublet was expected due to the internal rotation as observed for phenol.$^{2)}$ The observed splittings width

Table 1. Transition Frequency of 4-Bromophenol$^{a)}$ (in MHz)

	4-^{79}BrC$_6$H$_4$OH		4-^{81}BrC$_6$H$_4$OH	
Transition	obsd	o-c	obsd	o-c
13(0,13)-12(0,12)	15479.40	0.05	15333.46	0.12
13(1,13)-12(1,12)	15222.95	-0.04		
14(0,14)-13(0,13)	16638.37	0.00	16482.08	0.03
14(1,14)-13(1,13)	16385.99	-0.19	16231.16	0.01
14(1,13)-13(1.12)	17271.81	-0.14		
14(2,13)-13(2,12)	16854.18	0.18	16689.71	-0.15
14(2,12)-13(2,11)			16941.00	0.29
15(0,15)-14(0,14)	17792.83	0.40	17626.11	0.15
15(1,15)-14(1,14)	17548.09	0.14	17381.94	-0.21
15(1,14)-14(1,13)	18491.37	-0.20		
15(2,14)-14(2,13)	18050.62	0.19	17874.93	0.08
15(2,13)-14(2,12)	18363.88	0.68	18176.51	-0.28
16(1,16)-15(1,15)			18531.87	0.10
29(1,28)-28(1,27)	35069.09	-0.03	34743.25	0.09
29(2,28)-28(2,27)			34283.03	-0.12
29(2,27)-28(2,26)	35819.75	-0.08	35463.36	0.06
30(0,30)-29(0,29)			34554.50	0.25
30(1,30)-29(1,29)	34830.22	-0.08	34506.01	-0.13
30(1,29)-29(1,28)	36212.92	0.35		
30(2,29)-29(2,28)	35780.08	0.17	35440.76	0.04
30(2,28)-29(2,27)	37041.85	-0.04	36674.32	-0.36
31(0,31)-30(0,30)			35682.36	0.05
31(1,31)-30(1,30)	35975.91	0.13	35641.23	0.07
31(1,30)-30(1,29)	37352.32	0.32		
31(2,30)-30(2,29)	36946.30	0.31	36596.45	0.06
31(2,29)-30(2,28)	38258.63	0.03	37880.82	-0.14
32(0,32)-31(0,31)	37154.45	-0.06	36810.54	-0.28
32(1,32)-31(1,31)	37120.70	-0.12	36775.59	-0.15
32(1,31)-31(1,30)	38488.22	0.13	38133.99	0.07
32(2,31)-31(2,30)	38110.51	0.33	37750.23	0.03
32(2,30)-31(2,29)	39469.69	0.02		
33(0,33)-32(0,32)	38293.93	-0.11	37939.83	0.09
33(1,33)-32(1,32)	38265.48	0.02	37909.95	0.04
33(1,32)-32(1,31)	39621.59	0.09	39257.88	0.18
33(2,32)-32(2,31)	39273.09	0.57	38902.30	0.08
33(2,31)-32(2,30)	40674.83	0.02		
34(0,34)-33(0,33)	39433.88	-0.05	39069.03	0.00
34(1,34)-33(1,33)	39409.81	0.06	39043.73	-0.01
34(2,33)-33(2,32)	40433.52	0.41		
34(2,32)-33(2,31)	41873.55	-0.21		
28(2,26)-28(1,27)	16039.85	-0.16	15852.78	-0.12
29(2,27)-29(1,28)	16790.86	0.14	16572.97	-0.07
30(2,28)-30(1,29)	17620.13	0.09	17370.49	0.04
31(2,29)-31(1,30)	18526.55	-0.07	18244.23	0.15

a) Center frequency of doublet for b-type Q-branch transition.

Table 2. Observed Splitting of b-Type Q-Branch Transitions (in MHz)

Transition	$4\text{-}^{79}BrC_6H_4OH$ obsd	$4\text{-}^{79}BrC_6H_4OH$ split	$4\text{-}^{81}BrC_6H_4OH$ obsd	$4\text{-}^{81}BrC_6H_4OH$ split
28(2,26)-28(1,27)	15970.49 16109.21	138.71	15783.12 15922.46	139.34
29(2,27)-29(1,28)	16721.19 16860.53	139.34	16503.35 16642.59	139.24
30(2,28)-30(1,29)	17550.43 17689.82	139.38	17300.83 17440.14	139.31
31(2,29)-31(1,30)	18456.92 18596.19	139.27	18174.54 18313.92	139.38

are given in Table 2. Each component of the b-type Q-branch transitions listed was weak and broad due to perturbation of the quadrupole coupling.

The rotational constants in Table 3 were obtained by least-squares fitting of the transition frequencies listed in Table 1. The barrier height V_2 was calculated from the parameters(I_a and I_1) in Table 4 and using the perturbation coefficients by Lin and Swalen.$^{3)}$ The value of I_1 was assumed to be the same as for 4-chlorophenol which was calculated from the r_s b-coordinate of hydroxyl hydrogen.$^{1)}$

To compare the V_2 value with those of 4-X-phenols, the same approximation was applied to three molecules (X=H, F, Cl) as given in Tables 4 and 5. Campagnero and Wood 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.$^{4)}$

Table 3. Rotational Constants and Inertia Defect of 4-Bromophenol$^{a)}$

	$4\text{-}^{79}BrC_6H_4OH$	$4\text{-}^{81}BrC_6H_4OH$
A/MHz	5628.3(19)	5628.9(10)
B/MHz	635.72(2)	629.25(2)
C/MHz	571.33(1)	565.995(7)
τ_{aaaa}/MHz	-0.88(76)	0.98(33)
τ_{bbbb}/MHz	0.00010(5)	-0.00010(3)
τ_{aabb}/MHz	-0.003(5)	-0.004(3)
τ_{abab}/MHz	0.014(6)	-0.006(4)
Δ/ uA^2 $^{b)}$	-0.207	-0.023
σ/ MHz $^{c)}$	0.38	0.15

a) Figures in parentheses indicate the uncertainty involved in the last significant digits calculated as the standard deviation. b) $\Delta = I_c - I_a - I_b$. c) Standard deviation for lines fitted.

According to their theory, the experimental V_2 values in Table 5 indicate the following order of the π donor ability in halogen,

4-F > 4-Cl > 4-Br > 4-H.

Table 4. Internal Rotation Parameters

	$4\text{-}^{79}BrC_6H_4OH$	$4\text{-}^{81}BrC_6H_4OH$	$4\text{-}^{35}ClC_6H_4OH$[a]	C_6H_5OH
Split/MHz	139.18	139.30	158.99	111.998[b]
I_a/uA^2	88.792	88.782	89.721	89.439[b]
I_1/uA^2 [c]	0.743	0.743	0.743	0.743
s	51.9	51.9	50.9	53.7
V_2/kJ mol^{-1}	14.23	14.23	13.98	14.71

a) Ref.1. b) Ref.5. c) The moment of inertia of the hydroxyl group about the internal rotation axis.

The obtained barrier heights for 4-substituted phenols are compared with ones from MO calculation in Table 5. The MO calculation of the total energy of the molecules was made by using the 4-31G basis set without geometry optimization. The energy difference between the planar and orthogonal structures was taken as the theoretical barrier height.[1] The theoretical barriers are lower than the experimental ones. However, it is interesting to note the almost constant ratio of 1.5 for the four molecules.

The ab initio calculation was carried out in the Computer Center of the University of Tokyo by using the GSCF2 programmed by N. Kosugi.

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Table 5. Comparison of Barrier Heights in 4-X-C_6H_4OH (in kJ mol^{-1})

Molecule	Experimental	ab initio[a]	Ratio[b]
C_6H_5OH	14.71[c]	9.75	1.51
4-F-C_6H_4OH	12.22[d]	7.95	1.52
4-Cl-C_6H_4OH	13.98[e]	9.33	1.49
4-Br-C_6H_4OH	14.23[f]	9.46	1.50
4-CN-C_6H_4OH	(18.07)[g]	12.05	
4-CH_3-C_6H_4OH	(12.56)[g]	8.37	

a) Calculation on the 4-31G basis set. b) Ratio=experimental/ab initio.c) Ref.5. d) data from Ref.6. e) Ref.1. f) This work. g) predicted value=1.5*ab initio

References

1) M. Onda, T. Motoda, and I. Yamaguchi, Bull. Chem. Soc. Jpn., 58,242(1985).
2) T. Kojima, J. Phys. Soc. Jpn., 15, 284(1960).
3) C. C. Lin and J. D. Swalen, Rev. Mod. Phys., 31,841(1959).
4) G. E. Campagnero and J. L. Wood, J. Mol. Struct., 6,117(1970).
5) E. Mathier, D. Welti, A. Bauder, and Hs. H. Günthard, J. Mol, Spectrosc., 37, 63(1971).
6) N. W. Larsen and F. M. Nicolaisen, J. Mol. Struct., 22, 29(1974).

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