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Microwave spectrum of benzoic acid

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Abstract

The microwave spectrum of benzoic acid was observed in the frequency range 30 ∼ 40 GHz by using a Stark modulation spectrometer and 6–10 GHz by a molecular beam Fourier-transform microwave spectrometer (MB-FTMW). The rotational and centrifugal distortion constants of the normal and carboxylic deuterated species were obtained for the ground and C_1–COOH torsional state. For the normal species in the ground state the rotational constants were determined by least-squares fitting using low J transitions observed with FTMW: $A = 3872.2741(5)$ MHz, $B = 1227.3128(2)$ MHz, $C = 932.5657(2)$ MHz. The obtained inertial defect ($\Delta = -0.3656(2)$ uÅ^2) indicated that the equilibrium conformation was of the planar structure with large amplitude torsional motion. r_s. Coordinates of the hydroxyl hydrogen were $|a| = 2.91(1)$ Å, $|b| = 1.14(1)$ Å, indicating the hydrogen was located close to the benzene ring. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Benzoic acid; rotational spectrum; MB-FTWM

1. Introduction

The benzoic acid is one of the most important acids in chemistry. Its acid strength is the standard in the Hammet rule. The structure of the carboxylic group is interesting in view of the chemical behavior of the acid.

The structure of benzoic acid had been investigated with X-ray diffraction method by several investigators [1]. Most recent study clearly indicated that the dimer unit existed in crystal [2]. The infrared studies on this molecule in solutions showed the dimer structure [3]. The molecular beam spectroscopy revealed that the dimer structure was dominant in He beam [4]. There have been no structure study so far on the isolated monomeric benzoic acid in the gas phase.

This time we observed benzoic acid by microwave spectroscopy and obtained the molecular constants and the structural information on this molecule.

2. Experimental

The sample of normal benzoic acid was obtained commercially and was used without further purification. The sample of deuterated benzoic acid, C_6H_5COOD, was prepared by the reaction of benzoic anhydride with D_2O [5]. After refluxing the mixture of the anhydride and D_2O for 72 h at 100°C ∽ 110°C without any catalysis, like $SOCl_2$, the deuterated species was obtained with the yield of 80%.

The boiling point of benzoic acid is fairly high (bp:249.2°C at 760 Torr) and it begins to sublime at around 100°C [6]. Therefore it has very low vapor pressure at room temperature. We started the measurement of the spectrum with the sample gas introduced under low sublimation pressure at 100°C.

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Table 1
Molecular constants of benzoic acid

	MB-FTMW	Stark modulation spectrometer		
	C_6H_5COOH ($v = 0$)	C_6H_5COOH ($v = 0$)	C_6H_5COOH ($v = 1$)	C_6H_5COOD ($v = 0$)
A/MHz	3872.2741(5)	3877.94 (3)	3910 (10)	3841.0(11)
B/MHz	1227.3128(2)	1227.390(8)	1227.46(2)	1202.67(8)
C/MHz	932.5657(2)	932.466(8)	932.74(2)	915.88(8)
Δ_J /kHz		− 0.02 (2)		
Δ_{JK} /Khz		0.15 (2)		
Δ_K /kHz		17.9 (3)		
δ_J/kHz		− 0.051(2)		
δ_J/kHz		− 0.28 (5)		
ΔI/uÅ^2	− 0.3659(2)	− 0.091(9)		0.01(9)

The X-band wave guide cell was heated with an usual electrical ribbon heater surrounding the cell. Any microwave absorption, however, was not observed at the cell temperature of 50°C ~ 120°C.

After several attempts were made, we could at last observe the spectrum by adopting the following heating method. The solid sample was mounted at one internal end of the wave guide and the wave guide and the sample handling vacuum system were set together in a glass jacket and both were uniformly heated up by heated air flow of above 100°C. Then the temperature of the wave guide was decreased slowly to 50°C so that the sample was deposited on the whole inner surface of the wave guide. Then the whole system was held at 50 ±; 1°C and sample pressure was maintained at 0.01 ∽ 0.02 Torr under flow condition.

The microwave spectrum was observed with a conventional 100 kHz Stark modulated spectrometer in the frequency region 8 ∽ 40 GHz. The accuracy of the measured frequency was 0.1 MHz for intense line of the normal species and 0.5 MHz or less for the torsionally excited state and deuterated species. This poor accuracy came from the broadening of the line widths of 1 ∽ 3 MHz, presumably because of the inhomogeneity of the Stark field by deformation of Stark septum on heating and by the condensation of solid sample on the septum. The other reason was that the measured lines overlapped with many vibrationally excited lines because benzoic acid had many low lying vibrational modes.

Low-*J* transitions were observed with MB-FTMW spectrometer in the 6–10 GHz region. The direction of the molecular beam was perpendicular to the microwave propagation. We designed several model of heated nozzles, modified versions of NIST group [7]. The sample was heated 90°C in the nozzle pocket and the stagnation pressure was 500 Torr with argon.

3. Results and discussion

3.1. Wave guide spectrum

The spectrum was observed as a bush of lines throughout the observed frequency region. Many intense transitions accompanied by several satellites which could be assigned to the low frequency vibrationally excited state lines. We assigned 60 a-type R-branch and 30 b-type Q-branch lines of the normal species in the ground state. The lists of the observed frequencies have been deposited with the B.L.L.D. as Supplementary Publication No. SUP26611. The rotational and centrifugal distortion constants were obtained as shown in Table 1.

A series of clear progression with decreasing intensity was assigned to the torsional state of C_1-carboxyl group which had the lowest vibrational frequency in this molecule. The 29 a-type R-branch lines of the first excited state were assigned and the rotational constants were determined as shown in Table 1. For the deuterated species, 32 transitions were assigned and the rotational constants were determined also as shown in Table 1.

The small inertial defect indicates the planar structure of this molecule. The r_s-coordinates of the hydroxyl hydrogen were calculated as follows: $|a| = 2.91(1)$ Å, $|b| = 1.14(1)$ Å. The absolute values

Table 2
Observed transitions of benzoic acid by MB-FTMW[a]

Transition	OBS (MHz)	O–C (kHz)
3 (2,1)–2 (2,0)	6571.8266	− 0.3
3 (0,3)–2 (0,2)	6387.4461	2.0
3 (1,2)–2 (1,1)	6906.5851	3.2
3 (2,2)–2 (2,1)	6479.6363	0.8
3 (1,3)–2 (1,2)	6023.4953	0.4
4 (3,2)–3 (3,1)	8682.8180	0.7
4 (1,4)–3 (1,3)	8006.7151	− 1.6
4 (2,3)–3 (2,2)	8621.3734	− 1.7
4 (3,1)–3 (3,0)	8689.7113	− 2.3
4 (1,3)–3 (1,2)	9178.8098	1.3
4 (2,2)–3 (2,1)	8845.9184	− 2.3
4 (0,4)–3 (0,3)	8414.9191	− 1.9
2 (1,2)–1 (0,1)	6669.9745	3.1
3 (1,3)–2 (0,2)	8396.9973	2.4
3 (2,1)–3 (1,2)	7623.4144	− 0.4
4 (2,2)–4 (1,3)	7290.5260	− 0.9
5 (2,3)–5 (1,4)	7043.4289	− 0.7

[a] One standard deviation of the fit was 1.9 kHz.

of the coordinate of the hydrogen favor the *syn* position to the carboxylic group.

The average relative intensity of 17 transitions of the vibrationally excited state to the ground state was 0.47 ± 0.05. The value was calculated simply from the relative peak height of less overlapped lines and the energy difference between the two states was calculated as 177 cm^{-1} at 333 K. The frequency may correspond to one of three vibrational modes calculated by Kim et al [3]; C–C in-plane rocking (193 cm^{-1}), C–C torsional + ring torsion (192 cm^{-1}), and ring torsion + C–C out-of-plane deformation (168 cm^{-1}) modes. The last is of the lowest frequency and this must correspond to the most intense satellite lines assigned this time. If the assigned transition is the excited state of C_1–COOH torsional mode, we can also calculate the frequency from their inertial defects. According to the method by Hanyu et al. [8] the approximate torsional frequency was estimated as 184 cm^{-1}. The agreement between calculated and experimental values is well and this supports that the assigned vibrationally excited state is of the C_1–COOH torsional mode.

3.2. MB-FTMW spectrum

The rotational constants were determined by least-squares fitting of 17 low-*J* transitions observed with MB-FTMW (Table 2). Any splitting or broadening of the transition were not observed. The b-type transitions were expected to be splitting as a result of the COOH torsional motion or inversion of hydroxyl hydrogen if their barrier height were low. No splitting means the height may be fairly high. A theoretical calculation about the torsional angle showed the height was above 5 kcal/mol by a single point low level treatment (HF/ 4-31G).

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