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We observed microwave absorption spectra of some deuterated benzenes and accurately determined the rotational constants of all H/D isotopomers in the ground vibrational state. Using synthetic analysis assuming that all bond angles are 120°, the mean bond lengths were obtained to be $r_0(C–C) = 1.3971$ Å and $r_0(C–H) = r_0(C–D) = 1.0805$ Å. It has been concluded that the effect of deuterium substitution on the molecular structure is negligibly small and that the mean bond lengths of C–H and C–D are identical unlike small aliphatic hydrocarbons, in which $r_0(C–D)$ is about 5 mÅ shorter than $r_0(C–H)$. It is considered that anharmonicity is very small in the C–H stretching vibration of aromatic hydrocarbons. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4937949]

I. INTRODUCTION

Benzene is a key molecule that is of great importance investigating molecular structure and excited-state dynamics. We performed three spectroscopic experiments for jet-cooled deuterated benzenes, and analyzed the results based on theoretical considerations and *ab initio* calculations. In Paper I, we present results on rotational constants of all the H/D isotopomers which were obtained mainly by the analysis of microwave spectra. The main objective of this study is to accurately determine the molecular structure at the zero-vibrational level in the electronic ground state. In Paper II,[1] we present results of high-resolution laser spectroscopy for the $S_1\ ^1B_{2u} − S_0\ ^1A_{1g}\ 6_0^1(e_{2g})$ band and discuss the vibrational and rotational structure in the electronic excited state. In Paper III,[2] we discuss the vibronic structure in the $S_1\ ^1B_{2u}$ state and the radiationless transition in the electronic excited state, including "channel three," which would be observed as a drastic decrease in fluorescence quantum yield for high-vibrational levels. We also present the results of mass-selected resonance enhanced multiphoton ionization (REMPI) spectroscopy.

The structures of all the isotopomers of benzene including H and D atoms are illustrated in Fig. 1. There is only one species for C_6H_6, C_6H_5D, C_6HD_5, and C_6D_6. For $C_6H_4D_2$, there are three isotopomers: o-$C_6H_4D_2$, m-$C_6H_4D_2$, and p-$C_6H_4D_2$, in which a pair of D atoms are substituted at the 1,2-(ortho), 1,3-(meta), and 1,4-(para) positions, respectively. For $C_6H_2D_4$, there are three isomers structured in the reverse manner: o-$C_6H_2D_4$, m-$C_6H_2D_4$, and p-$C_6H_2D_4$. Three isotopomers also exist for $C_6H_3D_3$, which are designated 1,2,3-$C_6H_3D_3$, 1,2,4-$C_6H_3D_3$, and 1,3,5-$C_6H_3D_3$.

The benzene molecule is a planar regular hexagon (D_{6h}) and only two bond lengths, $r(C–C)$ and $r(C–H)$, are necessary to describe the structure. The molecular structure is possibly changed by deuterium substitution. For benzene, one is the change in the bond angles which distorts the regular hexagon. Another is the change in the bond lengths. We carefully discuss the difference between the C–H and C–D bond lengths. One can, however, only obtain one parameter from the rigid rotor rotational constants A, B, and C, because the relationship $A = B = 2C$ holds for the benzene molecules with D_{6h}. A least-squares fit of rotational constants for deuterated molecules is a way to obtain more structural parameters. For C_6H_6 and C_6D_6, the rotational constants were determined precisely,[3–7] and it was possible to evaluate two bond lengths assuming $r(C–H) = r(C–D)$.[6] The equilibrium bond length at the potential minimum is identical for different isotopes in the Born-Oppenheimer approximation, which is $r_e(C–H) = r_e(C–D)$.

However, the actual mean bond length $r_0(C–D)$ at the zero-vibrational level is shorter than $r_0(C–H)$ because of the anharmonicity in the potential energy. The increase in the mean bond length is smaller for the C–D bond because the zero-point energy is smaller than that of the C–H bond. The difference, $\Delta R = r_0(C–H) − r_0(C–D)$, has already been estimated for some small molecules. It was reported to be 5 mÅ in CH,[8] CH_3,[9,10] and CH_4,[11] and 3−5 mÅ in CH_3O[12] and CH_3F.[13] ΔR is, however, suggested to be very small for large aromatic molecules such as benzene,[7] naphthalene,[7] and anthracene.[14] To verify this point, we observed pure rotational transitions of jet-cooled deuterated benzenes using Fourier transform microwave (FTMW) spectroscopy. A small dipole moment arises from the zero-point vibration for isotopomers with low symmetry. The FTMW spectra of C_6H_5D,[15] o-$C_6H_4D_2$, and m-$C_6H_4D_2$[16] have already been observed and the rotational constants were determined by Bauder's group. We have observed the FTMW spectra of 1,2,3-$C_6H_3D_3$, o-$C_6H_2D_4$, m-$C_6H_2D_4$, and C_6HD_5 and determined their rotational constants. In this article, we present the experimental results

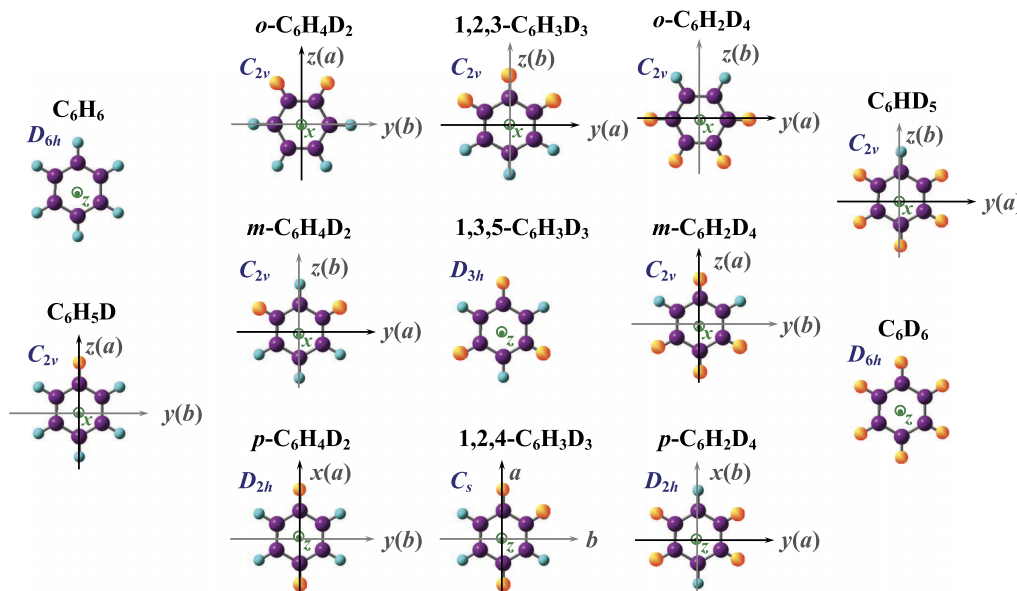a)Author to whom correspondence should be addressed. Electronic mail: baba@kuchem.kyoto-u.ac.jp

FIG. 1. Structure of H/D isotopomers of benzene.

and discuss the molecular structure of benzene, particularly the mean bond lengths, r_0(C–H) and r_0(C–D).

II. EXPERIMENTAL

Deuterated benzenes were synthesized by maintaining the mixture of C_6H_6 and C_6D_6 at 800 K for 7 h with a small amount of aluminum powder. After the exchange reaction, the abundance ratio of isotopomers in the sample mixture became within the statistical limit distribution; as the number of D atoms increases, 1:6:15:20:15:6:1 for the mixture of C_6H_6:C_6D_6 = 1:1. This 1:1 mixture was used in observing excitation spectra as shown in Papers II and III.[1,2] In this microwave experiment, to increase the intensity, the mixture of C_6H_6:C_6D_6 = 1:3 was used in which the abundance ratio

was 1:8:25:40:35:16:3. The sample vapor (2%) was mixed with the Ne gas and the mixed gas was expanded into a vacuum chamber from a pulsed nozzle to generate a supersonic jet.

A Balle-Flygare type FTMW spectrometer[17] was used to observe pure rotational transitions. The microwave cavity was set coaxially to the jet. With this setup, a spectral line splits into two peaks by the Doppler effect (Fig. 2), and the transition frequency was calculated by taking the average.[18]

III. RESULTS AND DISCUSSION

We observed four or more rotational transitions for each isotopomer of 1,2,3-$C_6H_3D_3$, o-$C_6H_2D_4$, m-$C_6H_2D_4$, and C_6HD_5. Typical spectra are shown in Fig. 2, and all
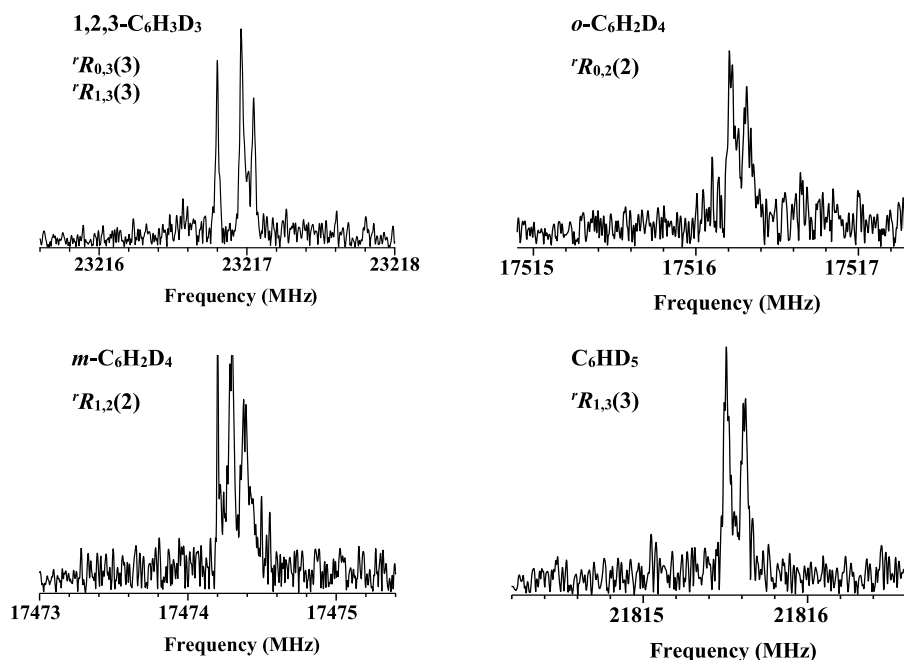

FIG. 2. Observed FTMW spectra of deuterated benzenes. A strong peak near the center is a noise caused by the strong microwave power.

TABLE I. Frequencies and assignments of observed FTMW spectral lines.

Molecule	Assignment	Frequency(MHz)	J'	K'_a	K'_c	J''	K''_a	K''_c
$o\text{-}C_6H_4D_2$	$^rR_{1,3}(3)$	239 62.921(7)	4	1	4	3	1	3
$1,2,3\text{-}C_6H_3D_3$	$^rR_{1,1}(1)$	128 90.602(6)	2	0	2	1	1	1
	$^rR_{0,1}(1)$	129 06.736(3)	2	1	2	1	0	1
	$^rR_{0,2}(2)$	180 57.83(1)	3	1	3	2	0	2
	$^rR_{1,3}(3)$	232 17.000(7)	4	0	4	3	1	3
	$^rR_{0,3}(3)$	232 17.000(7)	4	1	4	3	0	3
	$^rR_{1,1}(2)$	232 42.738(5)	3	2	2	2	1	1
$o\text{-}C_6H_2D_4$	$^rR_{1,1}(1)$	123 16.225(8)	2	0	2	1	1	1
	$^rR_{1,2}(2)$	174 84.496(6)	3	0	3	2	1	2
	$^rR_{0,2}(2)$	175 16.273(2)	3	1	3	2	0	2
	$^rR_{1,3}(3)$	224 98.247(4)	4	0	4	3	1	3
	$^rR_{0,3}(3)$	225 00.116(2)	4	1	4	3	0	3
	$^rR_{1,1}(2)$	229 90.49(2)	3	2	2	2	1	1
$m\text{-}C_6H_2D_4$	$^rR_{1,2}(2)$	174 74.339(3)	3	1	3	2	1	2
	$^rR_{0,2}(2)$	174 99.975(8)	3	0	3	2	0	2
	$^rR_{1,3}(3)$	224 81.543(2)	4	1	4	3	1	3
	$^rR_{0,3}(3)$	224 83.007(3)	4	0	4	3	0	3
C_6HD_5	$^rR_{1,1}(1)$	119 53.075(5)	2	0	2	1	1	1
	$^rR_{0,1}(1)$	122 70.076(7)	2	1	2	1	0	1
	$^rR_{1,3}(3)$	218 15.561(2)	4	0	4	3	1	3
	$^rR_{0,3}(3)$	218 17.101(4)	4	1	4	3	0	3

the transition frequencies are presented in Table I. Because similar experiments were performed previously for C_6H_5D, $o\text{-}C_6H_4D_2$, and $m\text{-}C_6H_4D_2$,[15,16] pure rotational transitions have been observed for all the microwave-active deuterated benzenes except $1,2,4\text{-}C_6H_3D_3$. It was difficult to accurately determine the higher-order rotational constants because of the limited number of observed transitions. However, the least-square fit was not good enough without the centrifugal distortion terms. We, therefore, fixed them to the averaged values of C_6H_6 and C_6D_6 for D_J, D_{JK}, and D_K, and then obtained reliable values of the rigid-rotor rotational constants $A, B,$ and C. The best-fit results are listed in Table II, (b). For $o\text{-}C_6H_4D_2$, we obtained slightly different values from the

reported ones by Oldani *et al.*,[16] because a new transition was incorporated in a least squares fit. Oldani *et al.* fitted the centrifugal distortion constants of $o\text{-}C_6H_4D_2$ separately, and their rotational constants are considered to be more accurate than ours. However, we used our values here because they improved consistency in a synthetic analysis for all isotopomers. Actually, centrifugal distortion constants did not affect the rigid-rotor rotational constants A, B, and C within the experimental error. For C_6H_6 and C_6D_6, we used the values that were previously determined by ultrahigh-resolution laser spectroscopy.[5,6]

The A, B, and C values in Table II, (a) are the calculated rotational constants of all H/D isotopomers, which were

TABLE II. Rotational constants (cm^{-1}) of all benzene H/D isotopomers at the zero-vibrational levels in the S_0 state.

	(a) By R_0 Structure			(b) By Observation		
	A (cm^{-1})	B (cm^{-1})	C (cm^{-1})	A (cm^{-1})	B (cm^{-1})	C (cm^{-1})
C_6H_6	0.189 77	0.189 77	0.094 88	0.189 771 7(3)	0.189 771 7(3)	0.094 885 9(2)
C_6H_5D	0.189 77	0.177 58	0.091 73	0.189 769 4(2)	0.177 587 3(2)	0.091 719 3(2)
$o\text{-}C_6H_4D_2$	0.183 39	0.172 25	0.088 82	0.183 394 6(3)	0.172 259 6(3)	0.088 810 3(2)
$m\text{-}C_6H_4D_2$	0.183 55	0.171 84	0.088 75	0.183 549 2(3)	0.171 854 0(3)	0.088 739 8(3)
$p\text{-}C_6H_4D_2$	0.189 77	0.166 60	0.088 72			
$1,3,5\text{-}C_6H_3D_3$	0.171 84	0.171 84	0.085 92			
$1,2,3\text{-}C_6H_3D_3$	0.172 38	0.171 84	0.086 06	0.172 386 5(5)	0.171 850(2)	0.086 045 5(2)
$1,2,4\text{-}C_6H_3D_3$	0.181 83	0.163 02	0.085 96			
$o\text{-}C_6H_2D_4$	0.172 24	0.161 66	0.083 39	0.172 243 0(2)	0.161 672 3(2)	0.083 384 1(1)
$m\text{-}C_6H_2D_4$	0.171 84	0.161 78	0.083 33	0.171 852(4)	0.161 789(4)	0.083 321(1)
$p\text{-}C_6H_2D_4$	0.177 43	0.157 01	0.083 30			
C_6HD_5	0.166 72	0.157 01	0.080 86	0.166 721(5)	0.157 016(5)	0.080 855(2)
C_6D_6	0.157 01	0.157 01	0.078 50	0.157 012 8(2)	0.157 012 8(2)	0.078 506 4(1)

obtained by assuming the common R_0 *structure*, as described below. We also used the relationship between the A, B, and C values derived by structural considerations. For example, the B value of C_6HD_5 must be identical to the A and B values of C_6D_6, and the B value of m-$C_6H_4D_2$ must be identical to the B value of 1,3,5-$C_6H_3D_3$. The resultant values are in agreement with those obtained by the least-squares fit of each isotopomer, with a standard deviation of 1×10^{-5} cm^{-1}.

We discuss how to accurately determine the geometrical structure of benzene from the rigid rotor rotational constants of deuterated isotopomers, especially the C–H bond length. Several models have been proposed to represent the molecular structure, such as r_e, r_0, r_g, r_s, r_m, and r structures. The r_e *structure* is the equilibrium structure where nuclei are frozen at the potential minimum, which is identical for different isotopomers in the Born-Oppenheimer approximation. An actual molecule takes a slightly different structure because of the zero-point vibration. The mean displacements of normal coordinates are not zero, including those of a C–H stretching mode: $\langle \Delta Q \rangle \neq 0$.[19]

The mean atomic positions are different from the equilibrium positions, which are represented by the r_0 *structure*. The rotational constant is approximately given by

$$B_0 = B_e - \frac{1}{2} \sum_i \alpha_i \qquad (1)$$

$$= B_e - \frac{1}{2} \sum_i \left(\alpha_i^{harm} + \alpha_i^{anharm} \right), \qquad (2)$$

where α_i is the anharmonic constant of the ith normal mode. α_i^{harm} represents anharmonicity which exists in the harmonic potential. Because it is difficult to determine all the α_i values for a large molecule, it is difficult to obtain the r_e *structure*. Another experimental method to accurately determine the geometrical structure is electron diffraction for gas phase molecules.[20] The mean distances between the identical atoms are calculated from the diffraction angles, which lead to the r_g *structure*. The mean bond length is given by

$$r_g = r_e + \langle CRD \rangle + \langle \Delta z \rangle + \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2r_e} + \cdots, \qquad (3)$$

where $\langle CRD \rangle$ is the centrifugal distortion term. $\langle \Delta z \rangle$ is the mean displacement of stretching along the bond axis, and $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ are the perpendicular components of the mean square displacement. $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ include only the harmonic terms, whereas $\langle \Delta z \rangle$ arises from the anharmonic effect. The moment of inertia in the zero-vibrational level can be extracted from Eqs. (2) and (3), and we obtain

$$I_z = I_0 \left(1 - \sum_i \frac{\alpha_i^{harm}}{2B_0} \right) \qquad (4)$$

$$= I_e \left(1 + \sum_i \frac{\alpha_i^{anharm}}{2B_0} \right). \qquad (5)$$

Although this is a favorable way to determine the bond length, the experimental accuracy is not higher than high-resolution spectroscopy. The results of ethylene-h_4 and ethylene-d_4 are not reliable.[21,22]

We then considered the r_s *structure*, which is obtained from the difference of moments of inertia between the isotopomers, ΔI, assuming that the position of nuclei is not changed by isotopic substitution.[19,23] We started from this model to analyze the rotational constants of deuterated benzenes. However, we must take into account the change in the C–H bond length, while the C−C bond length and bond angles are assumed to be identical for all the isotopomers. We define a fitting parameter

$$\Delta R = r_0(C-H) - r_0(C-D) \qquad (6)$$

and search the best-fit value that minimizes the mean-square deviation of the observed rotational constants. We call this the R_0 *structure*. The origin is set to the center of the regular hexagon composed of C atoms. In the intramolecular coordinates of each atomic nucleus $r_i(x_i, y_i, z_i)$, r_0 is given by the moment of inertia and is represented by a tensor whose elements are obtained by[19]

$$I_{xx} = \sum_i m_i \left(y_i^2 + z_i^2 \right) - \frac{\left(\sum_i m_i y_i \right)^2}{\sum_i m_i} - \frac{\left(\sum_i m_i z_i \right)^2}{\sum_i m_i}, \qquad (7)$$

$$I_{xy} = - \sum_i m_i x_i y_i + \frac{\left(\sum_i m_i x_i \right) \left(\sum_i m_i y_i \right)}{\sum_i m_i} - \frac{\left(\sum_i m_i z_i \right)^2}{\sum_i m_i}. \qquad (8)$$

The C_6H_6 structure with the D_{6h} symmetry is assumed to remain in the r_s *structure* of all deuterated isotopomers. There are differences in the moment of inertia around the α axis ($\alpha = x, y, z$) between C_6H_6 and a deuterium-substituted molecule (the molecular weight, M'), and the following relationships are derived from Eqs. (7) and (8):

$$\Delta I_{\beta\beta} = \frac{f_\beta M' - g^2 \Delta m}{M'} \cdot \Delta m \cdot r_s(H)^2, \qquad (9)$$

$$\Delta I_{zz} = f_z \cdot \Delta m \cdot r_s(H)^2, \qquad (10)$$

$$\Delta I_{\alpha\beta} = 0. \qquad (11)$$

Here, Δm is the difference between the atomic masses, $\Delta m = m_D - m_H$, and β is either x or y. f_β, f_z, and g are the parameters that depend on the isotopomer and molecular axis as indicated in Table III. The z axis is in the direction of the symmetry axis. $r_s(H)$ is the distance from the origin to the H atom and it is given by

$$r_s(H) = r_s(C-H) + r_s(C-C). \qquad (12)$$

TABLE III. Coefficients f_x, f_y, f_z, and g for benzene H/D isotopomers.

Molecule	From C_6H_6				From C_6D_6			
	f_x	f_y	f_z	g	f_x	f_y	f_z	g
C_6H_6					-6	-3	-3	0
C_6H_5D	1	1	0	1	-5	-2	-3	1
o-$C_6H_4D_2$	2	3/2	1/2	$\sqrt{3}$	-4	$-3/2$	$-5/2$	$\sqrt{3}$
m-$C_6H_4D_2$	2	1/2	3/2	1	-4	$-5/2$	$-3/2$	1
p-$C_6H_4D_2$	3	3/2	3/2	2	-3	$-3/2$	$-3/2$	2
o-$C_6H_2D_4$	4	3/2	5/2	$\sqrt{3}$	-2	$-3/2$	$-1/2$	$\sqrt{3}$
m-$C_6H_2D_4$	4	5/2	3/2	1	-2	$-1/2$	$-3/2$	1
C_6HD_5	5	2	3	1	-1	-1	0	1
C_6D_6	6	3	3	0				

To search the R_0 *structure* and introduce ΔR, it is useful to calculate the change in the moment of inertia by substituting the R_0 *structure* in Eq. (7). If we assume that $(\Delta R)^2$ is much smaller than $R_0(H)$, the elements of the ΔI tensor are expressed as

$$\Delta I_{\beta\beta} = f_\beta \left[m_D \{R_0(H) - \Delta R\}^2 - m_H R_0(H)^2 \right]$$
$$- \frac{g^2}{M'} [m_D \{R_0(H) - \Delta R\} - m_H R_0(H)]^2 \quad (13)$$

$$= \frac{f_\beta M' - g^2 \Delta m}{M'} \{\Delta m R_0(H)^2 - 2 m_D \Delta R \cdot R_0(H)\}$$
$$+ \frac{m_D}{M'} (f_\beta M' - g^2 m_D)(\Delta R)^2 \quad (14)$$

$$\simeq \frac{f_\beta M' - g^2 \Delta m}{M'} \{\Delta m R_0(H)^2 - 2 m_D R_0(H) \cdot \Delta R\}, \quad (15)$$

$$\Delta I_{zz} = f_z \{\Delta m R_0(H)^2 - 2 m_D R_0(H) \cdot \Delta R + m_D(\Delta R)^2\} \quad (16)$$

$$\simeq f_z \{\Delta m R_0(H)^2 - 2 m_D R_0(H) \cdot \Delta R\}. \quad (17)$$

By comparing these equations with Eqs. (9) and (10), we obtain

$$r_s(H)^2 = R_0(H)^2 - \frac{2 m_D}{\Delta m} R_0(H) \cdot \Delta R. \quad (18)$$

Therefore, the r_s bond length is approximately given by

$$r_s(H) = R_0(H) - \frac{m_D}{\Delta m} \Delta R. \quad (19)$$

I_{yy} which is the moment of inertia along the in-plane axis perpendicular to the symmetry axis can be derived by starting the deuterium substitution from C_6H_6,

$$I_{yy}(C_6H_6) = 3 m_C R_0(C)^2 + 3 m_H R_0(H)^2 \quad (20)$$
$$= 3 m_C R_0(C)^2 + 3 m_H \left[r_s(H)^2 + \frac{2 m_D}{\Delta m} r_s(H) \cdot \Delta R \right]. \quad (21)$$

Conversely, the hydrogen substitution from C_6D_6 leads to

$$I_{yy}(C_6D_6) = 3 m_C R_0(C)^2 + 3 m_D (R_0(H) - \Delta R)^2 \quad (22)$$
$$= 3 m_C R_0(C)^2 + 3 m_D \left[r_s(H)^2 + \frac{2 m_H}{\Delta m} r_s(H) \cdot \Delta R \right]. \quad (23)$$

Because $I_{yy}(C_6H_6)$ and $I_{yy}(C_6D_6)$ were accurately determined by ultrahigh-resolution spectroscopy, it is possible to determine the best-fit value of ΔR. $R_0(C)$ can be determined from $r_s(H)$ and ΔR using Eqs. (21) and (23). $R_0(H)$ can be determined in the same way using Eq. (19). The following square deviation parameter was used as the objective criteria of evaluation:

$$\sigma^2 = \sum \left[\{I_{aa}(\text{calc}) - I_{aa}(\text{obs})\}^2 + \{I_{bb}(\text{calc}) - I_{bb}(\text{obs})\}^2 \right]. \quad (24)$$

We searched for the best R_0 *structure* of deuterated benzenes, using $R_0(C-C)$, $R_0(C-H)$, and ΔR, which minimized the value of this error parameter σ^2. The results with respect to $R_0(C)$ are shown in Fig. 3. Because two $R_0(C)$ values were obtained from Eqs. (21) and (23), we used the averaged values for the least-squares fit, which is expressed as $R_0^A(C)$. We assume this
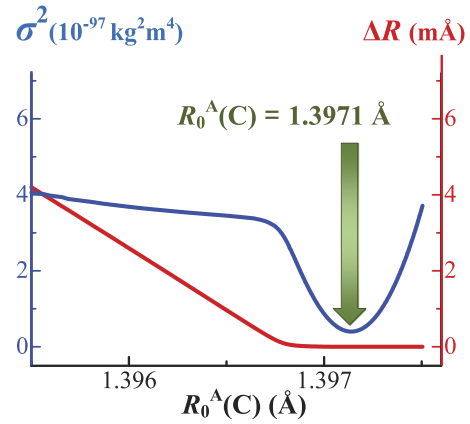

FIG. 3. Change in σ^2 and ΔR with respect to the C–C mean bond length R_0^A(C).

$R_0^A(C)$ to be $R_0(C-C)$. σ^2 showed the minimum at $R_0(C-C)$ = 1.3971 Å and $R_0(C-H)$ = 1.0805 Å, with $\Delta R = 0.0$ mÅ. ΔR was zero in the range of $R_0(C-H) < 1.0821$ Å. We therefore used these value as the best-fit R_0 *structure*. The standard deviation error was estimated to be ±0.3 mÅ for $R_0(C-H)$ by comparing the determined rotational constants and the calculated values using this final structure. In Table IV, this R_0 *structure* is compared with the previously reported structures that were obtained assuming that $r_0(C-H) = r_0(C-D)$ in addition to the results of *ab initio* calculations.[7] All values are in agreement within the error of 1 mÅ for $R_0(C-H)$ and 0.2 mÅ for $R_0(C-C)$. Thus, the mean bond length is approximately the same for C–H and C–D in the benzene molecule.

Finally, we consider the r_e *structure*. Pliva *et al.*[3] proposed a modified model, *r structure*, where the equilibrium rotational constants of an isotopically substituted molecule were derived from the mean rotational constants and a molecular weight of C_6H_6 using an approximate relationship for a symmetric top molecule,

$$B'_0 = B'_e - 1.787 \times 10^{-3} \left(\frac{B'_0}{B_0} \right)^2 \left(\frac{M'_0}{M_0} \right)^{1/2}. \quad (25)$$

Assuming that Eq. (25) holds for an asymmetric top molecule, we obtained the r_e *structure* from the rotational constants of deuterated benzenes. The results are shown in Table V and compared with other experimental results and *ab initio* calculations. It should be noted, however, that $R_e(C-H)$ is not shorter than $R_0(C-H)$ in the analysis, using the method of Pliva *et al.* This r_e *structure* is thus not yet accurate. High level calculations for the vibration-rotation constants should be performed to accurately determine the r_e *structure* of benzene.

TABLE IV. r_0 *structure* of benzene (Å).

	$r_0(C-H) = r_0(C-D)$	$R_0(C-C)$
This work	1.0805	1.3971
Doi *et al.*[6]	1.0807	1.3971
Pliva *et al.*[3]	1.0815	1.3969
Baba *et al.*[7]	1.0817	1.3969

TABLE V. r_e structure of benzene (Å).

	R_e(C–H) = R_e(C–D)	R_e(C–C)
This work	1.0864	1.3892
Pliva *et al.*[3]	1.0857	1.3893
Gauss *et al.* (*ab initio*)[24]	1.0800	1.3911

It should be noted that the anharmonic effect on the C–H bond is suggested to be small, suggesting that R_0(C–D) is approximately identical to R_0(C–H). As a result, our R_0 *structure* is the same as the r_0 *structure* in D_{6h} symmetry. The values of inertial defect, which is attributed to mainly out-of-plane zero-point vibrations,[25,26] are consistent with this result. These effects on the rotational constants are estimated to be less than 0.03%,[4,5] and the obtained R_0 *structure* is substantially identical to the r_0 *structure*. This means that the mean structure of benzene is a planar regular hexagon with r_0(C–H) = r_0(C–D).

IV. CONCLUSIONS

The rotational constants for several deuterated benzenes at the zero-vibrational levels in the ground state were determined using FTMW spectroscopy. We performed a synthetic best-fit analysis to determine the mean bond lengths, and finally obtained r_0(C–C) = 1.3971 Å and r_0(C–H) = 1.0805 Å. We also found that r_0(C–H) = r_0(C–D). This relationship was suggested to be valid also in naphthalene and anthracene. We consider that the negligibly small deuterium effect on the C–H mean bond length is common for aromatic hydrocarbons. It may be attributed to a mixing of the normal modes, which makes the anharmonicity small for the C–H stretching.

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