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Geometrical structure of benzene and naphthalene: Ultrahigh-resolution laser spectroscopy and *ab initio* calculation

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Geometrical structures of the isolated benzene and naphthalene molecules have been accurately determined by using ultrahigh-resolution laser spectroscopy and *ab initio* calculation in a complementary manner. The benzene molecule has been identified to be planar and hexagonal (D_{6h}) and the structure has been determined with accuracies of 2×10^{-14} m (0.2 mÅ; $1 \text{ \AA} = 1 \times 10^{-10}$ m) for the C–C bond length and 1.0×10^{-13} m (1.0 mÅ) for the C–H bond length. The naphthalene molecule has been identified to be symmetric with respect to three coordinate axes (D_{2h}) and the structure has been determined with comparable accuracies. We discuss the effect of vibrational averaging that is a consequence of zero-point motions on the uncertainty in determining the bond lengths.

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I. INTRODUCTION

It is quite difficult to determine accurately the structural parameters such as bond lengths and bond angles for an isolated large polyatomic molecule. Although the direct method of electron diffraction can be utilized, the accuracy is normally 10 mÅ and the identification of each chemical bond is impossible. The rotational constants obtained by ultrahigh-resolution laser spectroscopy provide three structural parameters although they do not permit the calculation of each bond length and bond angle in a large molecule. In this study, we attempted to utilize *ab initio* theoretical calculation to complement ultrahigh-resolution laser spectroscopy. In order to verify the reliability of *ab initio* calculation, we compared rotational constant values that had been accurately determined by ultrahigh-resolution laser spectroscopy with the precisely calibrated transition wavenumbers of a large number of rotational lines. We performed calculations with various methods and basis sets, and found that one of them yielded rotational constant values that were nearly identical to those obtained experimentally for benzene and naphthalene.

The benzene molecule is considered to be planar and hexagonal (D_{6h}) in the ground state. We can determine only one structural parameter from the rigid rotor rotational constants because the relation $A = B = 2C$ holds for a planar oblate symmetric-top molecule. The bond lengths, therefore, were determined by assuming the same geometrical struc-

ture for both C_6H_6 and C_6D_6 and by solving the simultaneous equations for rotational constants.^{1,2} The experimentally obtained rotational constants are, however, the averaged values over zero-point vibrations. The averaged bond length at the zero-vibrational level (r_0) is generally longer than the equilibrium bond length at the potential minimum (r_e) because of anharmonicity in the potential energy of C–H stretching vibration. The $r_0(\text{C–D})$ is also supposed to be shorter than the $r_0(\text{C–H})$ because the zero-point energy of C–D is smaller than that of C–H. For benzene, however, it has been shown that the $r_0(\text{C–H})$ is rather shorter than the $r_e(\text{C–H})$ by means of the mass dependence method,^{3,4} in which the results of ultrahigh-resolution laser spectroscopy are simultaneously analyzed for the isotopes, C_6H_6 , C_6D_6 , and $^{13}C_6H_6$. We tried to determine the bond lengths by complementarily using *ab initio* theoretical calculation.

The naphthalene molecule $C_{10}H_8$ is symmetric with respect to three coordinate axes (D_{2h}). A minimum of nine parameters are needed to represent the molecular structure. It is therefore impossible to determine the geometrical structure by three rotational constants. We examined *ab initio* theoretical calculations for the rotational constants in the ground state and found that the second-order Møller-Plesset (MP2) method provided excellent agreement with the accurate experimental values. In this article, we present these experimental and calculational results for the geometrical structures of the isolated benzene and naphthalene molecules and discuss the uncertainty in determining the structural parameters due to the effect of vibrational averaging that is a consequence of zero-point motions.

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II. EXPERIMENTAL AND *AB INITIO* CALCULATION

For benzene (C_6H_6) and perdeuterated benzene (C_6D_6), the rigid rotor rotational constants A , B , and C at the zero-vibrational level in the ground state were accurately determined by ultrahigh-resolution laser spectroscopy using the technique of a molecular beam.^{1,2} The relative wavenumber of each observed rotational transition was calibrated with the accuracy of 0.00005 cm^{-1} using a Doppler-free spectrum of tellurium molecule, of which the absolute wavenumber of a spectral line was determined by the tellurium atlas,⁵ and frequency marks generated with a stabilized etalon (Burleigh CFT-500, FSR = 150 MHz) and an E-O modulator (New Focus 4001). The cavity length of the etalon was locked using a single-mode cw laser (InnoLight, Prometheus 20, 532 nm, 20 mW, linewidth of 1 kHz/100 ms) of which the wavelength was tuned to a hyperfine line of the iodine molecule. The obtained rotational constants are reliable to 0.0000003 cm^{-1} , as the transition wavenumbers of all rotational lines were precisely calibrated and more than 1000 transitions were incorporated in a least-squares fit for the constant determination.

The rotational constants of naphthalene ($C_{10}H_8$) were accurately determined by ultrahigh-resolution laser spectroscopy using the technique of a pulsed supersonic jet.⁶ The rotational constants of perdeuterated naphthalene ($C_{10}D_8$) have been determined in the present work. A part of the ultrahigh-resolution fluorescence excitation spectrum is shown in Fig. 1. We recorded a Doppler-free saturation spectrum of the iodine molecule and frequency marks of the

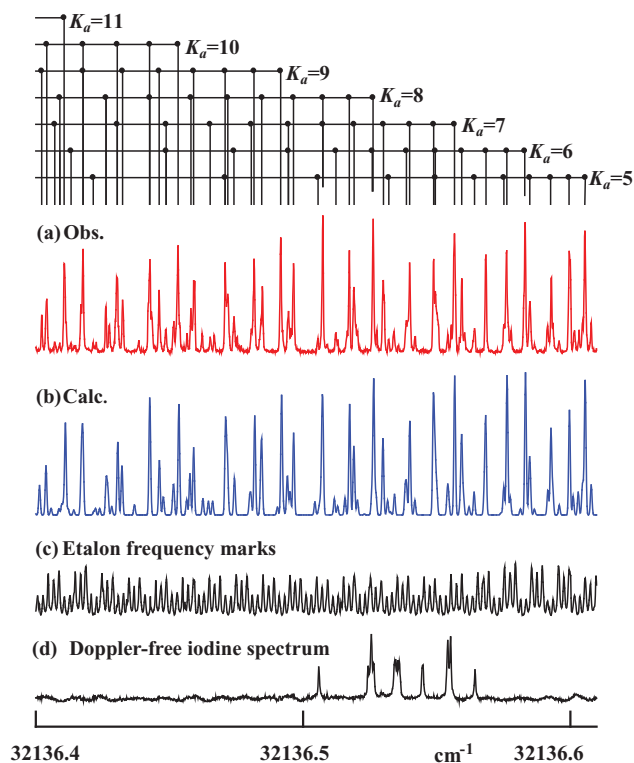


FIG. 1. (a) A part of the ultrahigh-resolution fluorescence excitation spectrum of perdeuterated naphthalene ($C_{10}D_8$). (b) Calculated spectrum using the determined rotational constants. (c) Frequency marks at every 0.002 cm^{-1} obtained by a stabilized etalon. (d) Doppler-free saturation spectrum of the iodine molecule.

TABLE I. Rigid rotor rotational constants (cm^{-1}) of benzene obtained by experiment and *ab initio* calculations with the 6-31+G(2d, 2p) basis set.

	A	B	C
C_6H_6			
experiment	0.189772	0.189772	0.0948858
RHF	0.192709	0.192709	0.0963546
MP2	0.189781	0.189781	0.0948906
CCSD	0.189121	0.189121	0.0945604
CCSDT	0.187840	0.187840	0.0939196
CISD	0.192014	0.192014	0.0960074

stabilized etalon together with the naphthalene spectrum. The absolute wavenumber of each hyperfine line of the iodine molecule was determined with the accuracy of 0.0002 cm^{-1} using the Doppler-free high-resolution iodine atlas.⁷ The obtained rotational constants are reliable to 0.0000001 cm^{-1} .

We performed *ab initio* theoretical calculation of geometry optimization, which provided us the rotational constants at the potential minimum, using the GAUSSIAN 09 program package.⁸ For benzene, we examined calculational methods of restricted Hartree-Fock (RHF), MP2, coupled cluster singles and doubles (CCSD), coupled cluster singles, doubles and triples (CCSDT), and configuration interaction singles and doubles (CISD) with different basis sets retaining D_{6h} symmetry. We also performed the similar procedure for naphthalene retaining D_{2h} symmetry.

III. RESULTS AND DISCUSSION

The calculated rotational constants for benzene (C_6H_6) using the 6-31+G(2d, 2p) basis set with several calculational methods are listed in Table I. The results of calculations for naphthalene ($C_{10}H_8$) using the 6-31G(d, p) basis set are listed in Table II. In Table III, the experimentally obtained rigid rotor rotational constants of C_6H_6 are compared with the calculated values which are the closest values to the experimental ones in the examined calculational methods. The MP2/6-31+G(2d, 2p) calculation yielded approximately the same values of rotational constants as those obtained experimentally within an error of 0.006%. The optimized bond lengths are shown in Fig. 2. We next calculated the rotational constants of C_6D_6 with the same geometrical structure. The resultant values are shown in Table III together with those of C_6H_6 , which are also approximately the same as the experimental values

TABLE II. Rigid rotor rotational constants (cm^{-1}) of naphthalene obtained by experiment and *ab initio* calculations with the 6-31G(d, p) basis set.

	A	B	C
$C_{10}H_8$			
experiment	0.104052	0.0411269	0.0294838
RHF	0.105481	0.0415496	0.0298081
MP2	0.104058	0.0411351	0.0294810
CCSD	0.104089	0.0410332	0.0294311
CCSDT	0.103485	0.0406861	0.0292042
CISD	0.105628	0.0416469	0.0298699

TABLE III. Experimental and calculated rotational constants (cm^{-1}) of C_6H_6 and C_6D_6 .

	A	B	C
C_6H_6			
experiment	0.189772	0.189772	0.0948858
MP2/6-31+G(2d, 2p)	0.189781	0.189781	0.0948906
C_6D_6			
experiment	0.157013	0.157013	0.0785065
MP2/6-31+G(2d, 2p)	0.157000	0.157000	0.0785000

within an error of 0.008%. We consider, therefore, that the calculated geometrical structure is true for the isolated benzene molecule. The actual errors for the determined bond lengths were estimated by comparing these calculated values with the experimental ones, which were obtained by solving simultaneous equations for the rotational constants of C_6H_6 and C_6D_6 assuming the same bond lengths and by high-resolution infrared spectroscopy. The results are listed in Table IV. We finally conclude that the isolated benzene molecule is planar and hexagonal (D_{6h} symmetry) with $r(\text{C}-\text{C}) = 1.3969$ 0.0002 Å and $r(\text{C}-\text{H}) = 1.0817$ 0.0010 Å.

We carried out the same procedure for naphthalene (C_{10}H_8), retaining D_{2h} symmetry. The MP2/6-31G(d, p) calculation yielded rotational constant values that were nearly the same as the experimental ones as shown in Table V. The calculated bond lengths and bond angles are presented in Fig. 3. The rotational constants of C_{10}D_8 calculated with the same geometrical structure are also shown in Table V together with those of C_{10}H_8 . The difference between the calculated and experimental rotational constants was a maximum of 0.0000072 cm^{-1} for the C value of C_{10}D_8 . We evaluated the change in rotational constants with C–C and C–H bond lengths. The C value varies by 0.00001 and 0.000008 cm^{-1} with the change in C–C and C–D bond lengths by 0.2 mÅ and 1.0 mÅ, respectively. These values are considered to be the actual accuracies of this method.

We have thus demonstrated that it is possible to determine accurately the geometrical structure of a large polyatomic molecule by comparing the values of experimentally determined rotational constants to those obtained via *ab initio* theoretical calculation. Although this method could

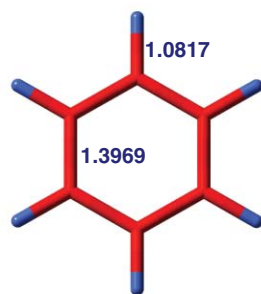


FIG. 2. Geometrical structure of the benzene molecule determined by ultrahigh-resolution laser spectroscopy and *ab initio* calculation. Bond lengths are in units of Å (10^{-10} m).

TABLE IV. Bond lengths (Å) obtained in the present work compared with the experimental values.

	$r(\text{C}-\text{C})$	$r(\text{C}-\text{H})$
Present work ^a	1.3969	1.0817
Doi <i>et al.</i> ^b	1.3971	1.0807
Pliva <i>et al.</i> ^c	1.3969	1.0815

^a*Ab initio* calculation at the MP2/6-31+G(2d, 2p) level.

^bUltrahigh-resolution laser spectroscopy (Ref. 2).

^cHigh-resolution infrared spectroscopy (Ref. 3).

be applied to various molecules in principle, the accuracy is highly dependent on molecular size and symmetry. Benzene and naphthalene are typical stable aromatic hydrocarbons and the theoretical calculation is thus relatively easy and reliable. In general, rotational constants obtained through *ab initio* calculation differ from experimentally obtained values by more than 1%. It is extremely surprising that the MP2 method gives very close values (with an error of less than 0.03%) even for naphthalene. We also achieved excellent results for anthracene with the same MP2/6-31G(d, p) calculation.⁹

There are two significant problems in the determination of molecular structure. The first is the effect of zero-point vibrations on rotational constants at the zero-vibrational level. The experimentally obtained rotational constants correspond to effective bond lengths r_0 , which are the averaged values over zero-point vibrations and are normally longer than the equilibrium bond lengths r_e at the potential minimum.^{10,11} The “ r_0 structure” is obtained in this manner so as to enable us to select a calculational method that provides rotational constant values that are nearly identical to the experimentally obtained ones, although *ab initio* calculation yields the “ r_e structure.” For example, the equilibrium and effective bond lengths of the CH radical have been accurately determined by a global fit of vibrational and rotational level energies. The equilibrium bond lengths of C–H and C–D are almost identical ($r_e(\text{C}-\text{H}) = 1.11979$ Å and $r_e(\text{C}-\text{D}) = 1.11888$ Å), whereas the effective bond lengths at the zero-vibrational level differ by 3.8 mÅ ($r_0(\text{C}-\text{H}) = 1.13030$ Å and $r_0(\text{C}-\text{D}) = 1.12655$ Å).¹²⁻¹⁴ It is known that the difference between $r_0(\text{C}-\text{H})$ and $r_0(\text{C}-\text{D})$ is 3 to 5 mÅ in small molecules.^{15,16} However, the benzene molecule does not conform to this rule. The “ r_m structure,” which is the equilibrium structure determined by the mass dependence method and is approximately the same as r_e structure,⁴ has been reported to be $r_m(\text{C}-\text{H}) = 1.0859$ Å by the simultaneous analysis of the results for

TABLE V. Experimental and calculated rotational constants (cm^{-1}) of C_{10}H_8 and C_{10}D_8 .

	A	B	C
C_{10}H_8			
experiment	0.104052	0.0411269	0.0294838
MP2/6-31G(d, p)	0.104058	0.0411351	0.0294810
C_{10}D_8			
experiment	0.0872880	0.0365063	0.0257480
MP2/6-31G(d, p)	0.0872842	0.0365065	0.0257406

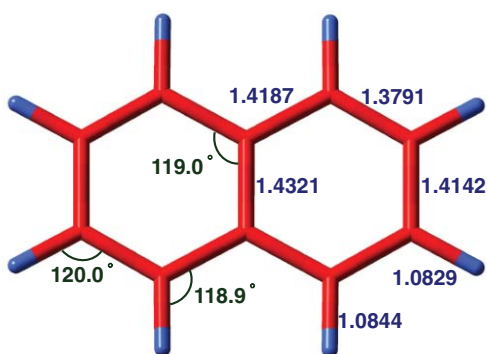


FIG. 3. Geometrical structure of the naphthalene molecule determined by ultrahigh-resolution laser spectroscopy and *ab initio* calculation. Bond lengths are in units of Å (10^{-10} m).

C_6H_6 , C_6D_6 , and $^{13}C_6H_6$.³ This value is rather longer than $r_0(C-H) = 1.0815$ Å (Table IV). It strongly suggests that the increase of the C–H bond length with zero-point vibration is small and the $r_0(C-H)$ is not different much from the $r_0(C-D)$ in benzene. This increase is the result of vibrational averaging over all normal modes of C–H stretching. Almost all of them include anti-phase stretching motions, that is, stretching and shrinking of C–H bonds, so that the bond lengthening by vibrational averaging, which arises from anharmonicity in the potential energy, becomes smaller than that of a single C–H bond (12.51 mÅ).¹⁴ Consequently, the difference between $r_0(C-H)$ and $r_0(C-D)$ is considered to be small in the planar aromatic hydrocarbons with several C–H bonds, and to be less than 1 mÅ in benzene and naphthalene, which is relatively smaller than that of a small aliphatic molecule. This is the reason why the calculated rotational constants assuming $r_0(C-H) = r_0(C-D)$ are very close to the experimental values for both C_6H_6 and C_6D_6 , and both $C_{10}H_8$ and $C_{10}D_8$. In order to determine the r_0 structure, it is necessary to obtain the accurate r_e structure by *ab initio* calculation with geometry optimization and to evaluate the effect of zero-point motions along all coordinates. However, this procedure is actually impossible for large polyatomic molecules with a large number of normal modes such as benzene and naphthalene. We therefore adopted the calculated geometrical structure as the approximated r_0 structure, and estimated the errors in bond lengths by calculating the change in rotational constants with the change in each C–C and C–H bond length.

The second problem in the determination of molecular structure is the inertial defect $\Delta = I_c - I_b - I_a$, which is zero for a frozen planar molecule but is actually nonzero due to change in the effective rotational constants as a result of zero-point motions.^{17,18} For large planar molecules, the Δ value has been shown to be small and negative,¹⁹ for example, -0.1 amu Å² in naphthalene,⁶ -1.1 amu Å² in anthracene,⁹ and -0.6 amu Å² in pyrene.²⁰ This is considered to be the limit of accuracy in determining the geometrical structure of a large planar molecule. The inertial defect of -0.1 amu Å² in naphthalene corresponds to the change in bond lengths of 0.1 mÅ and 1.0 mÅ for $r_0(C-C)$ and $r_0(C-H)$, respectively, which are considered to be the limits of accuracies in determining bond lengths. The benzene and naphthalene molecules

are planar, so that all of their out-of-plane normal modes are anti-symmetric with respect to the equilibrium positions. The displacement of each atom by zero-point motions is, therefore, expected to be very small. In this case, the difference between the r_e structure and r_0 structure is dominated by vibrational averaging along in-plane normal coordinates. It is essentially necessary to estimate the contributions of all in-plane and out-of-plane normal modes.¹⁷ However, it has been found by Oka that the inertial defect at the zero-vibrational level is dominated by the wavenumber of the lowest out-of-plane vibration (ν_1) and the following empirical relation holds for many planar aromatic molecules:¹⁹

$$\Delta = -\frac{33.715}{\nu_1} + 0.0186\sqrt{I_c}. \quad (1)$$

In consequence, the effect of vibrational averaging by in-plane and out-of-plane modes can be considered separately in determining the structural parameters. The accuracies are strongly dependent on low-frequency out-of-plane modes.

In conclusion, the geometrical structures of benzene and naphthalene have been accurately determined by *ab initio* calculation, which yields rotational constant values that are nearly identical to determined accurately the experimental values. We conclude that these structures are approximately true for the actual molecules at the zero-vibrational level in the ground state. The difference between the C–H and C–D effective bond lengths is considered to be less than 1.0 mÅ. The aromatic hydrocarbon possesses several C–H bonds and the most of normal C–H stretching modes include anti-symmetric motions. The lengthening of C–H bond by vibrational averaging, therefore, becomes smaller and the deuterium effect on the averaged bond length is considered to be small in benzene and naphthalene.

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