Determination of the heavy atom structure of bromobenzene by rotational spectroscopy

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Determination of the heavy atom structure of bromobenzene by rotational spectroscopy

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Abstract

The rotational spectra of ^{79}Br and ^{81}Br-bromobenzene have been remeasured, and spectra for eight singly substituted ^{13}C isotopomers have been measured for the first time using Fourier-transform microwave spectroscopy. This has made possible a determination of the heavy atom structure using both Kraitchman substitution (r_s) and inertial fit analyses (r_0). The experimental structures have been compared with ab initio calculations at the MP2/6-311++G (2df,2p) level as a means of confirming the experimental results. The experimental rotational constants were found to be $A = 5667.750(52)$ MHz, $B = 994.9018(2)$ MHz, and $C = 846.2567(2)$ MHz for ^{79}Br bromobenzene and $A = 5667.730(54)$ MHz, $B = 984.7084(2)$ MHz, and $C = 838.8702(2)$ MHz for ^{81}Br bromobenzene. The quadrupole coupling constants were further refined to $\chi_{aa} = 556.700(16)$ MHz, $\chi_{bb} = -292.86(8)$ MHz, and $\chi_{cc} = -263.84(3)$ MHz for the ^{79}Br species and $\chi_{aa} = 465.039(17)$ MHz, $\chi_{bb} = -244.63(8)$ MHz, and $\chi_{cc} = -220.41(6)$ MHz for the ^{81}Br species.
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1. Introduction

Studies of rare gas complexes of aromatic compounds have long provided a useful means for probing the electronic charge distributions in aromatic species. Recently, studies have been made of a series of halobenzenes with neon and argon [1–4]. A logical continuation of this series are the rare gas complexes of Ar and Ne with bromobenzene. A search for the microwave spectrum of the Ar–bromobenzene complex was therefore initiated leading to the location of

many weak transitions which are almost certainly attributable to this dimer, but a definite assignment has not yet been made; further searching (currently in progress) is required to check our current tentative assignments.

In the process of searching for Ar–bromobenzene transitions, it was necessary to have a thorough knowledge of the spectrum of the bromobenzene monomer, since predicted dimer lines lie in the same region as many of the monomer transitions. Previous microwave studies of bromobenzene did not include measurements of any of the ^{13}C spectra [5,6], meaning that unambiguous identification of monomer ^{13}C transitions was not possible. Since the intensity of dimer transitions was expected to be similar to

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the intensity of ^{13}C monomer transitions, it was readily apparent that a thorough knowledge of the ^{13}C spectra was essential before further progress could be made on assignment of the Ar–bromobenzene dimer spectrum.

The lack of isotopic substitution data for bromobenzene means that the shape of the benzene ring is not accurately known, with previous structural determinations of bromobenzene either assuming a regular hexagon or fitting some (but not all) of the angles in the ring [5]. In order to catalog the ^{13}C-bromobenzene lines and to obtain further insight into the deviation of the benzene ring from a regular hexagon, assignment of the eight ^{13}C substituted isotopomers of bromobenzene (four isotopomers for each of the two isotopes of bromine) was undertaken. These substitutions correspond to single ^{13}C substitution at C_1, C_2, C_3 and C_4 (Fig. 1) for both the [79]Br and the [81]Br isotopomers. This isotopic substitution data provided the information necessary to obtain a heavy atom substitution (r_s) structure for bromobenzene. It was hoped that combination with previously existing d_5-bromobenzene data [5] would provide enough information to perform a full inertial (r_0) fit that included the hydrogen atom structural parameters. Unfortunately this proved unsuccessful. Both substitution and inertial fits (with and without inclusion of the hydrogen atom structural parameters) will be explored further in Section 3.2 of this paper.
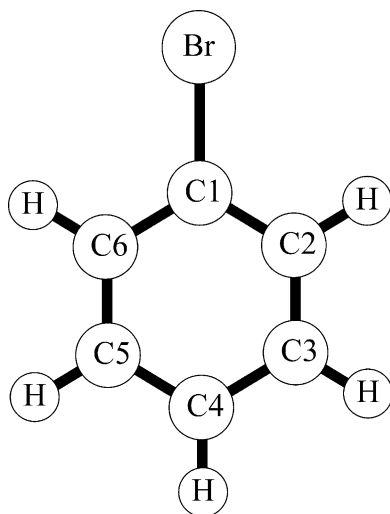

Fig. 1. Bromobenzene monomer showing the atom numbering scheme used to describe the structural parameters.

In addition to the spectroscopic data, ab initio calculations using Gaussian 98W [7] have been performed on bromobenzene, and the structure derived from an MP2/6-311++G(2df,2p) level calculation will be compared with the experimental results.

Since both isotopes of bromine ([79]Br, 50.7% and [81]Br, 49.3%) are quadrupolar (i.e. they have a nuclear spin quantum number $I = 3/2$) nuclear quadrupole coupling constants (χ) are obtainable from the rotational spectra for all observed isotopic species. Each of the rotational transitions is split into an intense quartet of hyperfine components by the coupling of the nuclear spin angular momentum with the overall rotational angular momentum. These quartets were typically spread out over 5–30 MHz. Ab initio values for the quadrupole coupling constants (available from the electric field gradient at the bromine atom) have also been calculated and will be compared with our experimental values in Section 4.

2. Experimental

The rotational spectra of the two isotopomers of bromobenzene ([79]Br and [81]Br) and of the four unique ^{13}C species for each bromine isotopomer were measured (in natural abundance) using Fourier-transform microwave (FTMW) spectroscopy. These correspond to single ^{13}C substitution at C_1, C_2, C_3 and C_4 (Fig. 1) in each bromine isotopomer. A Balle-Flygare type FTMW spectrometer located at Eastern Illinois University was used to measure the spectra [8,9]. This spectrometer has been described in detail previously [9] and the current configuration uses a General Valve Series 9 pulsed nozzle with an 0.8 mm orifice and a repetition rate of about 10 Hz. This spectrometer uses software and hardware modifications from the University of Kiel group [10].

The primary difficulty in observing the rotational spectra is attributable to the relatively low vapor pressure of bromobenzene (observed to be no more than a few torr). The usual procedure of placing a small amount of liquid sample in a glass bulb and filling it with Ar to a backing pressure of 1–3 bar apparently provides insufficient bromobenzene in the gas phase to observe spectra of consistently strong intensity. (Spectra appear strong at first, but

the bromobenzene in the vapor phase seems to be depleted faster than it is replenished, leading to diminishing signal intensity over the course of several hours). To overcome the problems of low vapor pressure a sample 'cell' in which Ar flows over a small liquid sample of bromobenzene was constructed. This cell consists of a piece of 1/4 in. stainless steel Swagelok® tubing (about 15–20 cm total length) that is bent into a U shape and located adjacent to the solenoid valve. The tubing holds about 0.2 ml of liquid (sufficient for 3–4 days of averaging), and the backing pressure of the Ar is maintained at 1.0–1.3 bar. With this setup, normal bromobenzene transitions typically have a signal-to-noise ratio (S/N) of 50 in 10 gas pulses, and the intensity remains consistent until the bromobenzene sample has been exhausted.

Spectra of the ^{13}C transitions for substitution at the C_2 and C_3 atoms of bromobenzene (2.2% abundant due to symmetry allowing substitution at two equivalent locations) typically had a S/N of about 10 after 1000 gas pulses for the most intense transitions. Substitution of atoms C_1 and C_4 on the C_2 symmetry axis of the molecule gave considerably weaker spectra (1.1% abundant), since these substitutions are unique within the molecule. These species typically had S/N of five in about 2000 gas pulses.

An additional (and the most troublesome) difficulty in the assignment of the on-axis ^{13}C isotopomers arose due to the very small isotopic shifts of these species. In particular, the carbon at the C_1 position is very close to the center of mass of the molecule, leading to shifts in the transition frequency of about 1 MHz or less from the spectrum of the parent species. Due to the significantly more intense spectra of the parent isotopomer, it was very difficult to extract the ^{13}C spectrum from beneath the normal species' spectrum. The vertical scale of the spectrum had to be magnified by 50–100 times, to allow the $^{13}C_1$ spectra to be observed and measured. More details on the spectra and the larger uncertainty associated with the measurement of these spectra are given in Section 3. An example of one of the four intense quadrupole components of a ^{79}Br bromobenzene transition along with the corresponding transition for $^{13}C_1$-bromobenzene is shown in Fig. 2 where it can be seen readily how the close proximity of the normal isotopomer transition hinders the measurement of the ^{13}C spectrum.
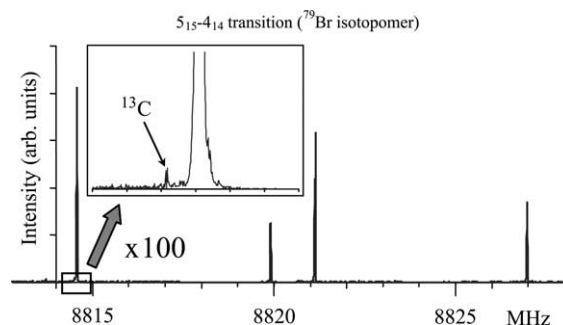

Fig. 2. The 5_{15}–4_{14} transition for the ^{79}Br isotopomer of bromobenzene showing the four hyperfine components for this transition. This figure is a composite of several data files. Each observed rotational transition was split into four intense components. The inset covers the region 8813–8816 MHz and shows the result of magnifying the lowest frequency hyperfine component by a factor of 100, allowing identification of the ^{13}C transition to the low frequency side of the parent isotopic species transition.

3. Results

3.1. Spectra

As described in Section 2, rotational spectra for a total of 10 isotopomers of bromobenzene have been measured, and nuclear quadrupole coupling constants and rotational constants were determined for each. The rotational transitions were fit using the SPFIT program of Pickett [11] employing a Watson A-reduced Hamiltonian in the I^r representation [12]. A summary of the spectroscopic constants of all isotopomers is given in Tables 1 and 2. It should be noted that the A rotational constant carries a larger uncertainty than the other constants for all of the species because only A-type rotational transitions were measured. (These transitions depend mainly on the values of B and C, with only a very small contribution from A). In four of the isotopomers (corresponding to ^{13}C substitution at C_2 and C_3 for each of the two bromobenzene isotopes) the μ_b component of the dipole moment is non-zero due to slight rotation of the principal axes upon isotopic substitution, but attempts to confirm the existence of b-type transitions failed. Since the predicted μ_b component of the dipole moment is on the order of 0.001 D, (and past experience has led us to expect the sensitivity of the spectrometer to be limited to species with $\mu = 0.1$ D or higher), failure to see these b-type transitions was not surprising. A list of

Table 1
Spectroscopic constants for the ^{79}Br monomer species

Parameter	^{79}Br	^{79}Br^{13}C$_1$	^{79}Br^{13}C$_2$	^{79}Br^{13}C$_3$	^{79}Br^{13}C$_4$	MP2/6-311++G(2df,2p)
A (MHz)	5667.750(52)	5668.041(154)	5576.135(82)	5578.268(88)	5667.877(112)	5700.8
B (MHz)	994.9018(2)	994.8320(4)	993.2026(3)	984.3452(3)	977.2438(20)	996.4
C (MHz)	846.2567(2)	846.2130(2)	842.9561(3)	836.6156(3)	833.4525(2)	848.2
Δ_J (kHz)	0.0251(24)	0.0250[a]	0.0308(46)	0.0214(47)	0.0250[a]	–
Δ_{JK} (kHz)	0.191(21)	–	–	–	–	–
$1.5\chi_{aa}$ (MHz)[b]	835.050(24)	835.313(139)	835.085(80)	834.742(78)	834.838(110)	–
$0.25(\chi_{bb} - \chi_{cc})$ (MHz)[b]	$-7.255(26)$	$-7.245(52)$	$-7.222(32)$	$-7.262(35)$	$-7.265(35)$	–
χ_{aa} (MHz)	556.700(16)	556.88(9)	556.72(5)	556.49(5)	556.56(7)	–
χ_{bb} (MHz)	$-292.86(8)$	$-292.93(24)$	$-292.81(14)$	$-292.77(15)$	$-292.81(18)$	–
χ_{cc} (MHz)	$-263.84(6)$	$-263.95(15)$	$-263.92(9)$	$-263.73(10)$	$-263.75(11)$	–
η (MHz)[c]	$-0.0521(2)$	$-0.0520(4)$	$-0.0519(2)$	$-0.0522(2)$	$-0.0522(2)$	–
Δ (u Å^2)	0.0573(8)	0.0571(24)	0.0615(14)	0.0613(15)	0.0553(18)	–
N[d]	76	20	38	38	34	–
$\Delta\nu_{rms}$ (kHz)[e]	2.81	6.99	3.40	3.18	2.73	–

[a] Fixed at the ^{79}Br monomer value.
[b] Fitted parameters taken directly from the output of Pickett's SPFIT program. The actual derived values of the coupling constants (χ_{aa}, χ_{bb} and χ_{cc}) and of the asymmetry parameter (η) are given below.
[c] η is the asymmetry parameter (defined as $\eta = \chi_{bb} - \chi_{cc})/\chi_{aa}$.
[d] N = Number of transitions fitted.
[e] $\Delta\nu_{rms} = [\Sigma(\nu_{obs} - \nu_{calc})^2/N]^{1/2}$.

transition frequencies for selected transitions for the ^{79}Br and ^{81}Br isotopes is given in Table 3; a comprehensive list of measured transition frequencies is available upon request from the authors.

The ratios of the nuclear quadrupole coupling constants ($\chi_{cc}(^{79}$Br$)/\chi_{cc}(^{81}$Br$)$) can be calculated for pairs of isotopomers with substitution at each of the four unique carbon atoms (Table 4) and can be

Table 2
Spectroscopic constants for the ^{81}Br monomer species

Parameter	^{81}Br	^{81}Br^{13}C$_1$	^{81}Br^{13}C$_2$	^{81}Br^{13}C$_3$	^{81}Br^{13}C$_4$	MP2/6-311++G(2df,2p)
A (MHz)	5667.730(54)	5667.807(165)	5576.045(112)	5578.433(112)	5668.103(118)	5700.8
B (MHz)	984.7084(2)	984.6193(3)	982.9684(3)	974.1838(3)	967.1737(3)	986.2
C (MHz)	838.8702(2)	838.8137(3)	835.5719(3)	829.2635(3)	826.1161(2)	828.0
Δ_J (kHz)	0.0265(24)	0.0250[a]	0.0186(49)	0.0263(5)	0.0250[a]	–
Δ_{JK} (kHz)	0.185(21)	–	–	–	–	–
$1.5\chi_{aa}$(MHz)[b]	697.559(26)	697.057(170)	697.449(92)	697.449(65)	697.33(11)	–
$0.25(\chi_{bb} - \chi_{cc})$(MHz)[b]	$-6.054(27)$	$-6.150(61)$	$-6.058(33)$	$-6.07(3)$	$-6.10(4)$	–
χ_{aa} (MHz)	465.039(17)	464.71(11)	464.97(6)	464.97(4)	464.89(8)	–
χ_{bb} (MHz)	$-244.63(8)$	$-244.65(29)$	$-244.60(16)$	$-244.63(13)$	$-244.65(19)$	–
χ_{cc} (MHz)	$-220.41(6)$	$-220.05(18)$	$-220.37(10)$	$-220.34(8)$	$-220.24(11)$	–
η (MHz)[c]	$-0.0521(2)$	$-0.0529(5)$	$-0.0521(3)$	$-0.0522(3)$	$-0.0525(3)$	–
Δ (u Å^2)	0.0571(9)	0.0525(26)	0.0605(18)	0.0643(18)	0.0592(19)	–
N[d]	75	18	34	38	29	–
$\Delta\nu_{rms}$ (kHz)[e]	3.00	7.05	2.75	4.21	3.01	–

[a] Fixed at the ^{79}Br monomer value.
[b] Fitted parameters taken directly from the output of Pickett's SPFIT program. The actual derived values of the coupling constants (χ_{aa}, χ_{bb} and χ_{cc}) and of the asymmetry parameter (η) are given below.
[c] η is the asymmetry parameter (defined as $\eta = \chi_{bb} - \chi_{cc})/\chi_{aa}$.
[d] N = Number of transitions fitted.
[e] $\Delta\nu_{rms} = [\Sigma(\nu_{obs} - \nu_{calc})^2/N]^{1/2}$.

Table 3
Selected transition frequencies for the [79]Br and [81]Br isotopomers of bromobenzene. Full lists of frequencies for all isotopic species are available from the authors upon request

$J_{K_aK_c'} \leftarrow J_{K_aK_c''}$	$2F'$	$2F''$	[79]Br		[81]Br	
			ν_{obs} (MHz)	$\Delta\nu$ (MHz)[a]	ν_{obs} (MHz)	$\Delta\nu$ (MHz)[a]
$4_{14} \leftarrow 3_{13}$	11	9	7052.7280	0.000	6989.5274	0.001
	5	3	7058.3979	−0.004	6994.4169	−0.005
	9	7	7065.9366	0.001	7000.6395	−0.005
	7	5	7072.7939	0.001	7006.3656	−0.001
$4_{23} \leftarrow 3_{22}$	5	3	7320.8712	−0.001	–	–
	11	9	7342.1867	0.005	7275.1521	0.003
	7	5	7378.5574	0.001	7305.4974	−0.002
	9	7	7396.7319	0.002	7320.8604	−0.002
$4_{22} \leftarrow 3_{21}$	5	3	7355.4541	0.003	7290.8381	−0.004
	11	9	7376.7804	0.003	7308.4274	0.005
	7	5	7413.4619	0.000	7339.0265	0.001
	9	7	7431.6672	0.000	7354.4165	0.005
$4_{04} \leftarrow 3_{03}$	9	7	7325.5084	0.000	7257.2493	−0.004
	11	9	7325.9640	0.003	7257.6130	0.005
	7	5	7340.9995	−0.006	7270.2956	0.005
	5	3	7341.9372	0.000	7270.9854	0.001
$4_{13} \leftarrow 3_{12}$	11	9	7646.8170	0.002	7572.4367	0.006
	5	3	7653.5119	−0.002	7578.1496	−0.005
	9	7	7660.0973	0.003	7583.6015	0.004
	7	5	7667.9073	−0.001	7590.0989	−0.004
$5_{15} \leftarrow 4_{14}$	13	11	8814.5717	0.002	8735.0313	0.004
	7	5	8819.9090	−0.004	8739.5640	−0.004
	11	9	8821.1276	−0.001	8740.5501	0.002
	9	7	8826.9699	−0.002	8745.4378	−0.002
$5_{05} \leftarrow 4_{04}$	11	9	9133.4641	0.000	9048.7579	−0.001
	13	11	9133.9448	0.005	9049.1387	0.001
	9	7	9142.6614	−0.002	9056.4941	−0.002
	7	5	9143.3089	−0.004	9056.9938	−0.004
$5_{24} \leftarrow 4_{23}$	7	5	9181.3979	−0.002	9096.6370	0.000
	13	11	9186.4889	0.003	9100.7479	0.003
	9	7	9210.2477	−0.001	9120.5972	0.003
	11	9	9213.5570	0.005	9123.4481	−0.002
$5_{14} \leftarrow 4_{13}$	13	11	9556.5893	−0.001	9463.0991	0.003
	7	5	9562.5264	0.000	9468.1180	−0.001
	11	9	9563.1695	−0.002	9468.6349	0.004
	9	7	9569.5678	−0.002	9473.9770	0.000
$6_{16} \leftarrow 5_{15}$	15	13	10571.1881	0.000	10475.6677	0.005
	13	11	10574.8894	0.001	10478.7787	0.001
	9	7	10575.4732	−0.002	10479.2865	−0.004
	11	9	10579.4186	−0.002	10482.5773	0.001
$6_{06} \leftarrow 5_{05}$	13	11	10924.4957	0.004	10824.0225	−0.001
	15	13	10925.0133	0.005	10824.4402	0.002
	11	9	10930.7068	−0.002	10829.2471	0.000
	9	7	10931.2776	−0.003	10829.6975	−0.004

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

Table 4

Comparison of calculated and experimental nuclear quadrupole coupling constants, asymmetry parameters (η) and ratios of the nuclear quadrupole moments (Q) for the ^{79}Br and ^{81}Br isotopic species

Parameter	This work	MP2/6-311++G(2df,2p)[a]	Caminati et al. [6]
^{79}Br			
χ_{aa} (MHz)	556.700(16)	561.92	558.9(13)
χ_{bb} (MHz)	$-292.86(8)$	-289.13	$-292.5(5)$
χ_{cc} (MHz)	$-263.84(6)$	-272.78	$-266.4(2)$
η (MHz)	$-0.0521(2)$	-0.029	$-0.046(4)$
^{81}Br			
χ_{aa} (MHz)	465.039(17)	468.55	464.1(18)
χ_{bb} (MHz)	$-244.63(8)$	-241.09	$-242.7(7)$
χ_{cc} (MHz)	$-220.41(6)$	-227.46	$-221.4(3)$
η (MHz)	$-0.0521(2)$	-0.029	$-0.046(7)$
$Q(^{79}$Br$)/Q(^{81}$Br$)$[b]	1.1970(7)	1.199	1.2033(7)
$Q(^{79}$Br^{13}C$_1)/Q(^{81}$Br^{13}C$_1)$	1.1995(17)	–	–
$Q(^{79}$Br^{13}C$_2)/Q(^{81}$Br^{13}C$_2)$	1.1976(9)	–	–
$Q(^{79}$Br^{13}C$_3)/Q(^{81}$Br^{13}C$_3)$	1.1969(9)	–	–
$Q(^{79}$Br^{13}C$_4)/Q(^{81}$Br^{13}C$_4)$	1.1975(6)	–	–
$Q(^{79}$Br$)/Q(^{81}$Br$)$ from BrCl[c]	1.197048(3)	–	–

[a] Calculated using Eq. (1) and the calculated values for the electric field gradient at the Br nucleus. Values for the nuclear quadrupole moment of the nucleus were taken from Ref. [15] ($Q(^{79}$Br$) = +33.1(4)$ fm^2, $Q(^{81}$Br$) = +27.6$ fm^2).

[b] Calculated using the ratio of the χ_{cc} components of the nuclear quadrupole coupling constants for the ^{79}Br and ^{81}Br species. See text for discussion.

[c] Literature value for this quantity (taken from Ref. [13]) derived from the coupling constants of BrCl.

compared with the literature value for the ratio of the nuclear quadrupole moments (Q) of the two isotopes of bromine ($Q(^{79}$Br$)/Q(^{81}$Br$) = 1.197048(3)$ [13]). The fact that these numbers are similar for all of the pairs of isotopomers studied serves as a confirmation of the quality of the fits. Another indication of the consistency of the spectral fits can be seen by examination of the inertial defects for each species. In planar molecules only two of the three moments of inertia are independent and a zero value for the inertial defect ($\Delta = I_c - I_a - I_b$) is expected. It can be seen from Tables 1 and 2 that all inertial defects are small and close to zero (and in good agreement with each other), consistent with low frequency, small amplitude out-of-plane vibrations that would be expected for a rigid ring compound of this type. Finally, the treatment of centrifugal distortion in the spectral analysis should be explained. For the normal (^{79}Br and ^{81}Br) species, the Δ_J and Δ_{JK} distortion constants were included in the fit and were necessary for fits that gave residuals consistent with the uncertainties in experimental measurement (typically about 4 kHz or less). For the ^{13}C species (where significantly smaller

bodies of data were available), only Δ_J was fitted for the ^{13}C substitution at the C$_2$ and C$_3$ atoms. For the much less intense spectra belonging to the species with ^{13}C isotopic substitution at the C$_1$ and C$_4$ atoms, the value of Δ_J was fixed at the ^{79}Br monomer value. In all cases where the Δ_J constant was fit it can be seen from Tables 1 and 2 that the value is small and agrees within the tabulated uncertainty for all species. Since this is an aromatic ring compound and likely to be relatively rigid, these small values of distortion constants are to be expected.

In earlier work on bromobenzene, an asymmetry parameter ($\eta = (\chi_{bb} - \chi_{cc})/\chi_{aa}$) was determined along with the quadrupole coupling constants [6]. This parameter gives a measure of the asymmetry of the electronic distribution around the Br nucleus. Experimental values for this quantity are tabulated in Tables 1 and 2, and Table 4 contains theoretical values from the MP2 calculation and previous experimental values (see Section 4 for more details). Rotational constants calculated at the MP2/6-311++G(2df,2p) level are included in the last columns of Table 1 (^{79}Br) and Table 2 (^{81}Br). Further

discussion of calculated structures and comparison with experiment appears in Section 3.2.

3.2. Structure

The heavy atom structure of bromobenzene has been determined using three approaches: (i) via a Kraitchman single isotopic substitution analysis [14]; (ii) via fits of atomic principal axis coordinates to experimental moments of inertia; and (iii) from ab initio calculations. A summary of fitted values of the structural parameters derived using these three methods is given in Table 5, and comparisons of the resulting principal axis coordinates of the heavy atoms are given in Table 6. In the inertial fits, only I_b and I_c were used since a planar molecule only has two independent moments of inertia. Attempts at using I_a and I_b or I_a and I_c in the inertial fits failed, probably because I_a is poorly determined due to the pure a-type spectrum measured. In the inertial fits, the positions of the H atoms are not fitted (the details of the various fits are given below). Attempts at including C–H bond lengths and C–C–H angles as adjustable parameters

in these fits were unsuccessful given the current body of data. The moments of inertia of the isotopomers studied depend very little on these parameters, probably since the H atoms are very light compared to the total mass of the molecule, hence the moments of inertia are relatively insensitive to small changes in their positions. The least-squares fitting routine is therefore not capable of determining the locations of the H atoms accurately and large fluctuations can be seen in the H atom parameters during the least-squares fitting process. Inclusion of d_5-bromobenzene rotational constants from the earlier studies of Rosenthal and Dailey [5] did not help to alleviate this problem. It is likely that the only way to allow successful inclusion of the hydrogen parameters in the fit is to assign spectra for the singly (or doubly) deuterated bromobenzene monomers, which is beyond the scope of this study. Since attempts at including the H atoms in the least-squares fit were unsuccessful, several inertial fits were carried out with the H atom parameters fixed at different values to get a quantitative estimate of the effects of the hydrogen parameters on the heavy atom structure. Inertial fits

Table 5
Fitted structural parameters for the bromobenzene monomer

Parameter[a]	Kraitchman fit[b]	Inertial fit[c]	Inertial fit[d]	Ab initio[e]	Previous Expt.[f]
$R(C_1–C_2)/\text{Å}$	1.424(4), 1.425(4)	1.404(5)	1.404(5)	1.391	1.42(2)
$R(C_2–C_3)/\text{Å}$	1.401(2), 1.401(2)	1.393(4)	1.393(4)	1.393	1.375(11)
$R(C_3–C_4)/\text{Å}$	1.395(1), 1.394(1)	1.398(13)	1.399(13)	1.393	1.4010(3)
$R(C_1–Br)/\text{Å}$	1.822(8), 1.823(7)	1.871(8)	1.871(8)	1.885	1.85(3)
$\angle(Br–C_1–C_2)/°$	121.2(3), 121.0(3)	120.1(4)	120.1(4)	119.3	–[g]
$\angle(C_1–C_2–C_3)/°$	121.2(3), 121.1(3)	119.9(6)	119.9(6)	119.9	117.4(26)
$\angle(C_2–C_3–C_4)/°$	120.4(1), 120.5(1)	120.3(4)	120.2(4)	120.5	117.4(26)
$\angle(C_3–C_4–C_5)/°$	119.70(6), 119.72(6)	119.9(8)	120.0(8)	119.8	117.4(26)
$\angle(C_6–C_1–C_2)/°$	117.0(6), 117.0(5)	119.9(8)	119.8(8)	121.4	–[g]

[a] The atom numbering refers to Fig. 1.

[b] The parameters referred to as Kraitchman fit are those obtained using the single substitution equations of Kraitchman [14]. For each parameter, two values are listed; these correspond to Kraitchman determinations using the ^{79}Br isotopomer (first value) and the ^{81}Br isotopomer as the parent during the single substitution calculations. Note that since the principal axis coordinate of C_1 is small, any parameters involving that atom in the Kraitchman column are likely to be susceptible to larger errors than the others.

[c] The inertial fit data refer to the parameters obtained from a least squares fit of the I_b and I_c moments of inertia to the heavy atom structural parameters, using the ^{79}Br isotopomer as parent. In this case the C–H bond lengths and angles were held fixed at 1.081 Å and 120.0° respectively. ΔI_{rms} for this fit was 0.0088 u Å^2.

[d] Inertial fit using the C–H bond angles and lengths from the ab initio calculation (in the fifth column: C_2–H = 1.080 Å; C_3–H and C_4–H = 1.081 Å; H–C_2–C_1 = 120.19°; H–C_3–C_2 = 119.35°; H–C_4–C_3 = 120.13°). The ^{79}Br isotopomer was used as the parent species. ΔI_{rms} for this fit was 0.0087 u Å^2.

[e] Calculated using GAUSSIAN 98W at MP2/6-311++G(2df,2p) level.

[f] From Ref. [5].

[g] These parameters were undetermined in the cited study.

Table 6
Principal axis coordinates (Å) for the bromobenzene monomer (heavy atoms only) from different structural determinations

Atom	a	b	c
Br	|1.6326|	|0.0100|	|0.0070|
	1.6318	−0.0001	0.0000
	1.6319	0.0000	0.0000
C_1	|0.1888|	|0.0000|	|0.0100|
	−0.2393	0.0001	0.0000
	−0.2585	0.0000	0.0000
C_2	|0.9332|	|1.2144|	|0.0000|
	−0.9429	1.2154	0.0000
	−0.9404	1.2127	0.0000
C_3	|2.3340|	|1.2064|	|0.0000|
	−2.3361	1.2110	0.0000
	−2.3335	1.2046	0.0000
C_4	|3.0341|	|0.0000|	|0.0300|
	−3.0365	−0.0007	0.0000
	−3.0326	−0.0000	0.0000
C_5	|2.3340|	|1.2064|	|0.0000|
	−2.3364	−1.2102	0.0000
	−2.3335	−1.2046	0.0000
C_6	|0.9332|	|1.2144|	|0.0000|
	−0.9432	−1.2149	0.0000
	−0.9404	−1.2127	0.0000

The three lines for each coordinate correspond to Kraitchman fit (Kraitchman's equations give the squares of the principal axis coordinates and thus only the absolute values of the coordinates themselves are known); an inertial fit (obtained with all H-C-C angles set at 120° and C-H distances set at 1.081 Å, giving the parameters listed in column 3 of Table 4); and an MP2 ab initio calculation (MP2/6-311++G(2df,2p) using GAUSSIAN 98W), repectively. All Structures use 79Br as the parent.

with all C–H distances equal to either 1.081 Å (the average distance from our ab initio calculations) or 1.072 Å (from Rosenthal and Dailey [5]), in both cases with $\theta_{C-C-H} = 120°$, were carried out. In addition, a fit using the computed C–H distances and angles from the ab initio calculations was performed. (In all fits, C–C–H angles are defined as H–C_4–C_3, H–C_3–C_2 and H–C_2–C_1). All three inertial fits led to heavy atom structures that differed by amounts well within the calculated uncertainties.

Table 5 shows that the different approaches to the structure determination generally give good agreement between the various parameters although

the structural parameters involving C_1 are a notable exception. These parameters differ significantly between the Kraitchman and inertial fits because of the proximity of C_1 to the center of mass of bromobenzene. Since the substitution structure analysis involves determination of the squares of the principal axis coordinates of the substituted atom, calculation of the coordinate itself magnifies the uncertainty if the square of a coordinate is less than about 1.0 Å^2. The smaller the coordinate, the more pronounced the effect, and for principal axis coordinates less than 0.5 Å or so, the results are known to be unreliable. For this reason, the principal axis coordinates of C_1 are undependable and give values for R_{C-Br} and θ_{Br-C-C} that do not compare well with the inertial fit values. (see Table 6 for a summary of the principal axis coordinates for the compound). Examination of the MP2 ab initio results shows that all structural parameters, including the C–Br distance and Br–C–C angle, are in good agreement with the inertial fit. This lends credence to the fact that the discrepancy observed between the two experimentally determined structures arises from the uncertainty in the Kraitchman analysis and not from a problem with the inertial analysis. However, it should be noted that the ab initio and inertial fit values are comparing slightly different parameters; the ab initio parameters are strictly equilibrium (r_e) values and the inertial fit values are ground state (r_0) values. Nevertheless, the differences are expected to be small (~0.01 Å and 0.5°) and the ab initio calculations serve to illustrate that there is good agreement in most cases (except, as described, for the parameters involving C_1).

4. Discussion

The first fact that is apparent from inspection of the heavy atom structural parameters is that the carbon ring structure of bromobenzene deviates by only a small amount from a regular hexagon. In the Kraitchman fit, the angle that differs most from 120° is $\theta(C_6-C_1-C_2) = 117.0(6)°$. This large deviation is due, however, to the poorly determined coordinates of C_1, as discussed above. In the inertial fit, no angle differs from 120° by more than 0.3°. This is in contrast with the ab initio results, which predict a $\theta(C_6-C_1-C_2)$ of 121.4°, by far the largest C–C–C

angle in the compound. There does not seem to be any obvious explanation of this behavior. Other ab initio angles agree (to within 1°) with the inertial fit values (and with the substitution values that do not involve C_1). Distances are all in agreement to less than 0.01 Å for the three structures, again with the exception of parameters involving C_1.

The structural parameters from the previous microwave studies [5] of bromobenzene are included in the last column of Table 5. Since the earlier work was based on only the ^{79}Br and ^{81}Br isotopomers and d_5 data, there was insufficient information for either a complete heavy-atom inertial fit or a substitution structure determination. However, the structure from the current study is in relatively good agreement with the earlier data with only one parameter (the C_2–C_3 distance) falling slightly outside the experimental uncertainty.

Further information is available from ab initio calculations which we can compare with our experimental data. The electric field gradient at the bromine nucleus was calculated at the MP2/6-311++G(2df,2p) level using GAUSSIAN 98W and used to determine quadrupole coupling constants for bromobenzene via the conversion formula

$$\chi_{gg} \approx -2.3496 \times 10^{30} \times \left(\frac{Q}{m^2}\right) \times \left(\frac{V_{gg}}{\text{a.u.}}\right) \qquad (1)$$

where Q is the nuclear quadrupole moment [15] and V_{gg} is the electric field gradient in atomic units ($g = x, y, z$). Nuclear quadrupole coupling constants calculated using Eq. (1) are listed in Table 4 where they are compared with the current and previous [6] experimental values. These calculated constants can then be used to calculate an asymmetry parameter ($\eta = -0.029$ MHz). Experimental values for the asymmetry parameters for all isotopomers are listed in Tables 1 and 2. The previous experimental work gives a value of $-0.046(4)$ MHz [6] and our current value is $-0.0521(2)$ MHz (for both ^{79}Br and ^{81}Br isotopomers). These values are in reasonable agreement although the ab initio values of the actual coupling constants agree significantly better with experiment than the values of the asymmetry parameter do. The calculated coupling constants differ at worst by about 3% from our current experimental values, seeming to indicate that the ab initio calculations are describing the electronic

distribution in this molecule quite well. This information will be useful in application of ab initio calculations at a similar level to the structure of the Ar–bromobenzene dimer, where accurate prediction of the coupling constants will be an important aspect of spectral assignment.

Finally the ab initio calculations also furnished a value for the dipole moment of the compound. The best structural calculations in the current work (MP2/6-311++G(2df,2p)) predict a dipole moment of 1.74 D. This is in excellent agreement with the experimental value of 1.7 D from earlier work [16]. We can interpret this once again as the ab initio calculations providing a relatively reliable description of the bromobenzene monomer at this level of calculation. The dipole moment was not remeasured in the current work because our laboratory does not currently have access to a power supply for measuring Stark effects.

5. Conclusions

Microwave rotational spectra have been remeasured for the ^{79}Br and ^{81}Br isotopomers of the bromobenzene monomer leading to refined values for the rotational, centrifugal distortion and nuclear quadrupole coupling constants. The rotational spectra of eight ^{13}C isotopomers have also been measured, to our knowledge for the first time on an FTMW machine, thereby allowing a heavy atom structure to be determined for this monomer. Comparisons of the single isotopic substitution structures with both inertial fit data and ab initio calculations have shown good agreement with the exception of those parameters involving C_1, the carbon atom attached to bromine. The poor agreement in this case can be ascribed to the proximity of this atom to the center of mass, the resulting small coordinates leading to larger uncertainties in the Kraitchman fit. The ab initio calculations have provided a means of identifying areas of poor agreement between the Kraitchman and inertial fit values for this molecule as well as furnishing additional molecular properties of interest. Having shown a reasonable ability for reproducing the monomer properties it is hoped that this level of calculation will be helpful in predictions of

the Ar–bromobenzene dimer structure and serve as an aid in the assignment of its rotational spectrum.

References

[1] R.A. Appleman, S.A. Peebles, R.L. Kuczkowski, J. Mol. Struct. 446 (1998) 55.

[2] R.J. Wilson, S.A. Peebles, S. Antolínez, M.E. Sanz, R.L. Kuczkowski, J. Phys. Chem. A. 102 (1998) 10630.

[3] J.J. Oh, I. Park, S.A. Peebles, R.L. Kuczkowski, E. Kraka, D. Cremer, J. Chem. Phys. 113 (2000) 9051.

[4] J.J. Oh, I. Park, S.A. Peebles, R.L. Kuczkowski, J. Mol. Struct. 599 (2001) 15.

[5] E. Rosenthal, B.P. Dailey, J. Chem. Phys. 43 (1965) 2093.

[6] W. Caminati, A.M. Mirri, Chem. Phys. Lett. 12 (1971) 127.

[7] GAUSSIAN 98W (Revision A.11), M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[8] T.J. Balle, W.H. Flygare, Rev. Sci. Instrum. 52 (1981) 33.

[9] This spectrometer was transported from the University of Michigan. Specific details of the design may be found in. K.W. Hillig II, J. Matos, A. Scioly, R.L. Kuczkowski, Chem. Phys. Lett. 133 (1987) 359 and references therein.

[10] J.-U.Grabow, PhD Thesis, University of Kiel, 1992.

[11] H.M. Pickett, J. Mol. Spectrosc. 148 (1991) 371.

[12] J.K.G. Watson, J. Chem. Phys. 46 (1969) 1935.

[13] A.C. Legon, J.C. Thorn, Chem. Phys. Lett. 215 (1993) 554.

[14] J. Kraitchman, Am. J. Phys. 21 (1953) 17.

[15] I. Mills, T. Cvitaš, K. Homann, N. Kallay, K. Kuchitsu, Quantities, Units and Symbols in Physical Chemistry, second ed., Blackwell Scientific Publications, Oxford, 1993.

[16] R.J.W. Le Fevre, D.A.A.S. Narayana Rao, Aust. J. Chem. 8 (1955) 140.