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Assignment and analysis of the rotational spectrum of bromoform enabled by broadband FTMW spectroscopy

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ABSTRACT

The rotational spectrum of the bromoform molecule is complicated by overlap of extensive hyperfine splitting structure of three bromine nuclei belonging to four isotopic species of comparable abundance. We have been able to achieve an unambiguous assignment of this spectrum on the basis of complete hyperfine patterns of the lowest-*J* rotational transitions recorded at conditions of supersonic expansion with chirped-pulse, broadband Fourier transform microwave spectroscopy. The mm-wave rotational spectrum was then also studied up to J = 131 and 318 GHz, and extensive measurements are reported for four isotopic species of HCBr₃ and four DCBr₃ species. Precise values of many spectroscopic constants have been determined from global fits of all measurements for a given isotopic species and have been substantiated by comparisons among the various isotopic species and with results of *ab initio* calculations. The experimental measurements allowed determination of the axial rotational constant *C* for the symmetric top species, evaluation of nuclear quadrupole hyperfine splitting constants in the principal quadrupole axes of the bromine nucleus, and extension of the range of known values of the *h*₃ splitting constant. The *r_z* geometry of HCBr₃ was also determined.

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1. Introduction

The deceptively simple halogenated methane derivatives are some of the most studied molecules by high-resolution molecular spectroscopy. In spite of this, the members of this family containing multiple heavy halogen nuclei pose sufficiently severe assignment problems that the rotational spectrum of CH₂I₂ was only assigned in 1996 [1], and the hyperfine structure of CHCl₃ was assigned even more recently, in 2006 [2]. The rotational spectrum of the bromoform molecule, HCBr₃ (see Fig. 1) was, in fact, first studied more than half a century ago [3,4]. The results of the two studies proved sufficiently different to stimulate further discussion in the literature [5,6], but no additional measurements. Bromoform poses additional complications since ⁷⁹Br and ⁸¹Br isotopes have comparable natural abundance, so that this compound will consist of a mixture of four equally abundant isotopic species. Two of those, HC⁷⁹Br₃ and HC⁸¹Br₃, are oblate symmetric top species of $C_{3\nu}$ symmetry, whereas the remaining two species, $HC^{79}Br_2^{81}Br$ and $HC^{79}Br^{81}Br_2$, are oblate asymmetric tops of C_s symmetry, in

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which the unique atom lies in the symmetry plane. For the lowest *J* rotational transitions the magnitude of the hyperfine splitting is greater than the differences in frequencies arising from isotopic changes in the rotational constants. In consequence the hyperfine patterns of all four isotopic species of bromoform are overlapped, as shown in Fig. 2.

One possible solution to such a problem is to first study the high-*J* millimeter wave rotational spectrum, in which the hyperfine splitting structure will be mostly collapsed. In the present case this spectrum was found to be rather weak ($\mu_c \approx 1D$, [7]) and was not a good starting point for the analysis due to the uncertainty arising from the mixture of isotopic species, transitions in vibrationally excited states, and the uncertainty concerning the published spectroscopic constants. A much more promising approach appeared to be through the assignment of hyperfine structure in the low-*J* transitions, providing that this could be measured efficiently, and preferably in its entirety.

A recently designed low-frequency chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer at the University of Virginia was ideal for this purpose. The instrument used in these studies operates from 2 to 8 GHz covering the spectral range of the three lowest-*J* rotational transitions. The full spectrum over this bandwidth was captured on each experimental repetition cycle, allowing for efficient data collection [8–10]. Assignment of this

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Fig. 1. The orientation of the bromoform molecule in the inertial axes. In the symmetric top and the ⁷⁹Br₂⁸¹Br species there is a bromine atom in the *ac* inertial plane (top), while in the ⁷⁹Br⁸¹Br₂ species the unique bromine atom is positioned in the *bc* inertial plane (bottom). The determinable angles and the r_z geometry determined in this work are marked. The discrepancy $\delta \theta$ between the direction of the CBr₁ bond and the quadrupolar *z* axis is exaggerated for clarity.

spectrum then made a study of the MMW spectrum feasible. In consequence we are able to report the results of a comprehensive study of the rotational spectrum of the bromoform molecule resolving, at the same time, the long standing questions concerning its assignment.

2. Experimental

The supersonic expansion spectrum of bromoform at frequencies 2–8 GHz was obtained with a direct digital chirped-pulse Fourier transform microwave spectrometer at the University of Virginia. In this instrument, high-speed electronics are used to directly generate the polarizing pulse and detect the molecular emission without any mixing steps. This leads to a simple and flexible spectrometer design.

The operating principles of chirped-pulse spectrometers [8–10] and of this instrument in particular [11] have been described previously. A high-speed arbitrary waveform generator with a sampling rate of 20 Gs/s (Tektronix AWG7102) is used to generate a linear frequency sweep from 2 to 8 GHz with a total duration of 9 μ s. This chirped-pulse is amplified by a 200 W travelling wave tube amplifier (Amplifier Research 200T2G8A), sent into the vacuum chamber, and broadcast into the microwave–molecule interaction region by a standard gain horn antenna (Advanced Technical Materials 250-441-C3). Molecular emission is collected with a second horn antenna, amplified, and detected by a fast oscilloscope (40 Gs/s, Tektronix TDS6124C) with an 8-bit digitizer and a hardware bandwidth of 12 GHz. The molecular sample (0.3% bromoform in a 20:80 mixture of helium and neon) is pulsed through



Fig. 2. Comparison of the chirped-pulse Fourier transform microwave spectrum of the complete $J = 2 \leftarrow 1$ transition of HCBr₃ with calculation based on final fitted constants. The nuclear quadrupole hyperfine splitting patterns of the different bromine isotopic species overlap to such an extent that only the central patterns of the two asymmetric species are distinguishable.

two General Valve Series 9 pulsed nozzles oriented perpendicularly to the axis connecting the two horn antennas. The backing pressure was 1 atm and the overall repetition rate was 3.5 Hz. In these measurements, molecular emission was collected for 40 μs and the spectra of HCBrC₃ and DCBr₃ were obtained by FFT of time-domain signals averaged over 2 \times 10⁵ repetition cycles.

Additional measurements of selected hyperfine components in the $J = 3 \leftarrow 2$ and $J = 4 \leftarrow 3$ rotational transitions for some isotopic species of HCBr₃ were carried out with the Warsaw cavity FTMW spectrometer [12], which is a coaxial microwave component version of the original Balle-Flygare (BF-FTMW) design [13]. In this case the carrier gas was either Ar or a mixture of He and Ar, which allows an increase in signal amplitude without increasing the Doppler splitting [14].

The room-temperature rotational spectrum of HCBr₃ was measured up to 318 GHz using the BWO-based broadband millimetre wave (MMW) spectrometer in Warsaw [15,16]. Analysis of data recorded on all spectrometers was aided by the graphical display and assignment tools available in the AABS package for Assignment and Analysis of Broadband Spectra [17,18]. This package has mechanisms for rapid setting up of spectroscopic data sets by graphical comparison of appropriate predictions with the measured broadband spectra, and it allows keeping track of already assigned lines in complex spectra. The AABS package has already been applied in several studies of rotational spectra consisting of many overlapped spectroscopic species, most recently in analyses of FASSST spectra of $S(CN)_2$ [19] and $CIONO_2$ [20]. Z. Kisiel et al./Journal of Molecular Spectroscopy 257 (2009) 177-186

3. The Hamiltonian

The Hamiltonian for fitting the rotational spectrum of bromoform is a sum of the rotational Hamiltonian, H_r , and the nuclear quadrupole splitting Hamiltonian, H_Q . The symmetric top species of bromoform are oblate symmetric tops, while the asymmetric top species are oblate asymmetric tops with the asymmetry parameter $\kappa \approx + 0.934$. The closest correspondence between constants for the symmetric top and the asymmetric top isotopic species is therefore obtained by using Watson's *S*-reduced asymmetric rotor Hamiltonian in representation III^{*I*} [21] for the ⁷⁹Br₂⁸¹Br and ⁷⁹Br⁸¹Br₂ isotopologs.

Nuclear quadrupole hyperfine splitting is the major factor determining the nature of the low-frequency rotational spectrum of bromoform. Efficient treatment of this effect is, therefore, key to the assignment of the spectrum. We use the techniques that were developed for the analysis of the hyperfine structure in methylchloroform [22], and more recently also used for chloroform [2]. The construction of the Hamiltonian and subsequent numerical analysis are carried out with the SPFIT/SPCAT program package [23,24], which provides tensorial coupling mechanisms used in the nuclear quadrupole part of the Hamiltonian. The F_1 , I, F coupling scheme was used to couple the rotational and the three nuclear spin angular momenta, such that $F_1 = J + I_1$, $I = I_2 + I_3$, and $F = F_1 + I$. The key feature of the present approach is that it is possible to take advantage of the features of SPFIT for declaring linear combinations of constants dependent on the actual parameters of fit so that the very complex triple nucleus nuclear quadrupole splitting in the symmetric top species of bromoform can be completely described by means of only three independent parameters of fit.

In the C_{3v} symmetry, oblate symmetric top species of bromoform the three equivalent bromine nuclei are positioned off the symmetry axis, which is colinear with the *c* inertial axis. The orientation of the two principal inertial planes containing the *c* axis is arbitrary, so that one of the three bromine nuclei can be placed on a selected principal plane (see Fig. 1). If a bromine atom is placed on the *ac* inertial plane then its quadrupole tensor

$$\chi(\mathrm{Br}_1) = \begin{pmatrix} \chi_{aa} & 0 & \chi_{ac} \\ 0 & \chi_{bb} & 0 \\ \chi_{ac} & 0 & \chi_{cc} \end{pmatrix}.$$
 (1)

consists of only the diagonal elements and one off-diagonal element. The quadrupole tensors for the remaining two nuclei, Br_2 and Br_3 , are obtained by $\pm 120^\circ$ rotation about the *c* inertial axis of the tensor in Eq. (1) and, in terms of tensor elements for nucleus Br_1 , are given by

$$\chi(Br_{2,3}) = \begin{pmatrix} \frac{1}{4}(\chi_{aa} + 3\chi_{bb}) & \pm\frac{\sqrt{3}}{4}(\chi_{bb} - \chi_{aa}) & -\frac{1}{2}\chi_{ac} \\ \pm\frac{\sqrt{3}}{4}(\chi_{bb} - \chi_{aa}) & \frac{1}{4}(3\chi_{aa} + \chi_{bb}) & \pm\frac{\sqrt{3}}{2}\chi_{ac} \\ -\frac{1}{2}\chi_{ac} & \pm\frac{\sqrt{3}}{2}\chi_{ac} & \chi_{cc} \end{pmatrix}$$
(2)

where, in the case of the ± sign, the upper sign refers to Br₂ and the lower sign to the Br₃ nucleus. Owing to the Laplace condition $\chi_{aa} + \chi_{bb} + \chi_{cc} = 0$, there are only two determinable diagonal tensor elements and for nucleus Br₁ in the present oblate symmetric top case these are $\chi_{bb} - \chi_{aa}$ and χ_{cc} . For nuclei Br₂ and Br₃ the diagonal tensor elements, expressed in terms of those of nucleus Br₁, are $-(\chi_{bb} - \chi_{aa})/2$ and χ_{cc} , while the off-diagonal tensor elements for Br_{2,3} are as given in Eq. (2). All parameters for Br₂ and Br₃ are thus dependent parameters of Br₁. We note that the three bromine nuclei are in fact identical and diagonalisation of each of the three tensors in Eqs. (1) and (2) will lead to an identical result for the se-

lected bromine nucleus is positioned in the bc inertial plane, then an alternative to Eqs. (1) and (2) is possible:

$$\chi(Br_1) = \begin{pmatrix} \chi_{aa} & 0 & 0\\ 0 & \chi_{bb} & \chi_{bc}\\ 0 & \chi_{bc} & \chi_{cc} \end{pmatrix},$$
(3)

and

$$\chi(\mathrm{Br}_{2,3}) = \begin{pmatrix} \frac{1}{4}(\chi_{aa} + 3\chi_{bb}) & \pm \frac{\sqrt{3}}{4}(\chi_{bb} - \chi_{aa}) & \pm \frac{\sqrt{3}}{2}\chi_{bc} \\ \pm \frac{\sqrt{3}}{4}(\chi_{bb} - \chi_{aa}) & \frac{1}{4}(3\chi_{aa} + \chi_{bb}) & -\frac{1}{2}\chi_{bc} \\ \pm \frac{\sqrt{3}}{2}\chi_{bc} & -\frac{1}{2}\chi_{bc} & \chi_{cc} \end{pmatrix}.$$
 (4)

For the asymmetric top species of bromoform the orientation of the inertial planes is no longer arbitrary but is determined by the relative masses of the three bromine nuclei. All such species are of C_s symmetry and for $HC^{79}Br_2^{81}Br$ and $DC^{79}Br_2^{81}Br$ the single ⁸¹Br nucleus lies in the *ac* inertial plane. On the other hand, in $HC^{79}Br^{81}Br_2$ and $DC^{79}Br^{81}Br_2$, the single ⁷⁹Br nucleus lies in the *bc* inertial plane. The nuclear quadrupole tensor for the unique Br_1 nucleus in the asymmetric top species of bromoform is, therefore, of the form given by Eq. (1) or Eq. (3), and gives rise to three determinable constants. The quadrupole tensors for the two symmetry equivalent bromine nuclei are now related by reflection across the appropriate symmetry plane and are of the form

$$\chi(\mathbf{Br}_{2,3}) = \begin{pmatrix} \chi'_{aa} & \pm \chi'_{ab} & -\chi'_{ac} \\ \pm \chi'_{ab} & \chi'_{bb} & \pm \chi'_{bc} \\ -\chi'_{ac} & \pm \chi'_{bc} & \chi'_{cc} \end{pmatrix}$$
(5)

for the ⁷⁹Br₂⁸¹Br species, and

$$\chi(\mathrm{Br}_{2,3}) = \begin{pmatrix} \chi'_{aa} & \pm \chi'_{ab} & \pm \chi'_{ac} \\ \pm \chi'_{ab} & \chi'_{bb} & -\chi'_{bc} \\ \pm \chi'_{ac} & -\chi'_{bc} & \chi'_{cc} \end{pmatrix}.$$
(6)

for the ⁷⁹Br⁸¹Br₂ species. Analysis of the asymmetric species thus requires determination of five additional nuclear quadrupole splitting constants comprising of two diagonal, and three off-diagonal ones. The absolute signs of the off-diagonal nuclear quadrupole constants are not determinable, but some phase relationships between them are important. The negative signs of χ'_{ac} in Eq. (5) and of χ'_{bc} in Eq. (6) are in relation to values for χ_{ac} and χ_{bc} in Eqs. (1) and (3). In fact the signs of any two sets of off-diagonal constants in the quadrupole tensors for the three bromine nuclei can be reversed without altering the final result and a more detailed investigation of the possibilities has been given in [22]. The choice of signs made below in reporting the results of the fits has been for consistency of signs between similar quantities among the studied isotopic species.

4. Rotational spectrum

In principle the easiest way to assign the nuclear quadrupole hyperfine structure is to start with the $J = 1 \leftarrow 0$ transition. For bromoform this transition falls in the frequency region 2.35–2.6 GHz and was regrettably heavily contaminated by spurious signals associated with cellular phone communication. For this reason the assignment was based on the $J = 2 \leftarrow 1$ transition and hyperfine components in the remaining rotational transitions were added at a later stage. Fig. 3 shows that the resolution and signal to noise achieved in the CP-FTMW spectrum were more than sufficient for a thorough analysis. Prediction of constants in bromine hyperfine tensors was key to the assignment. We used *ab initio* calculated values for bromoform, which were scaled by the ratio between calculation and experiment determined on the basis of experimental values for CH₃Br [25] and CH₂Br₂ [26]. The calculations were carried

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Fig. 3. Expanded section of the CP-FTMW spectrum of the $J = 2 \leftarrow 1$ rotational transition of bromoform illustrating the excellent signal to noise ratio achieved on averaging the time-domain signal over 200000 gas pulses. Complete resolution of the hyperfine splitting structure is visible. This region is dominated by transitions of HC⁷⁹Br⁸¹Br₂ (black sticks in the prediction), most of which are for K = 0, although the strong line near 4930 MHz is for K = 1. The lines for this species used in the data set for fitting are indicated by the diamond symbols between the two panes, Transitions in the remaining three isotopic species are also present in this region and are indicated in grey.

out at the MP2/6-31G(d,p) level with the PC-GAMESS [27] version of the GAMESS [28] package and the estimate turned out to be accurate to within 2% on average. Matching the patterns of calculated and predicted lines turned out to be reasonably straightforward providing that a start was made on most intense components of the K = 0 transition for each isotopic species. A small problem concerning the symmetric top species was that predictions made with SPCAT generated many spurious lines of appreciable calculated intensity. Such phenomena are often encountered on working with Hamiltonians involving a high density of states and complex labelling schemes, and are the consequence of breakdown in eigenvalue labelling. Comparison with the actual spectrum allowed us to identify and to filter out such lines.

Once a fit of the hyperfine structure was achieved it was possible to study the MMW spectrum. Assignment was made on the basis of predictions based on rotational constants fitted to the CP-FTMW data and quartic centrifugal distortion constants calculated from the *ab initio* harmonic force field with program VIBCA [18]. The compact low-*K* bandheads of the symmetric top species were relatively easy to identify, see Fig. 4. The lines just beyond the bandhead, at intermediate values of *K*, were difficult to assign although this was again possible at much higher values of *K*. Such behaviour appeared to be the consequence of the evolution of line profile from completely collapsed to increasingly broad hyperfine splitting structure, resulting in some self-cancellation effects at intermediate *K*. The asymmetric top species were more difficult

to assign due to the fact that the strongest and most compact lines were for smallest values of K_c. Such lines carried the greatest asymmetry contribution and did not give rise to easily discernible patterns. In addition, even though the spectrum was recorded at an acceptable signal to noise ratio, there was considerable congestion from plethora of weak lines due to transitions in low lying excited vibrational states. Those were expected to be the states associated with \angle (BrCBr) bending motions, and the frequencies of the two lowest normal modes are 154 and 223 cm⁻¹ [29]. The assignment of the ground states for both symmetric and asymmetric species was finally confirmed by Loomis-Wood type display plots of the type shown in Fig. 5, which nicely illustrate the evolution of the hyperfine splitting. Since calculation of triple nucleus splitting patterns at the required high values of J is still prohibitive only the hyperfine free frequencies were determined from the mm-wave spectrum. In cases of resolved hyperfine this was averaged by evaluating the average frequency of components in the identified multiplet.

In the final step of the analysis the data from the CP-FTMW and MMW spectra were fitted in a single global fit for each of the four HCBr₃ species. The SPFIT program allows such a fit to be constructed by treating the spin resolved, and spin unresolved data as two degenerate subsets, distinguished by an additional label. For the asymmetric top isotopologs this would require seven labels per energy level so that, in order to remain within the standard limit of six labels per state, we used symmetric top quantization



Fig. 4. Millimetre wave spectrum of the $J = 90 \leftarrow 89$ rotational transition of the symmetric top HC⁸¹Br₃ bromoform. Nuclear quadrupole splitting is collapsed in the lowest *K* lines, but appears at higher *K* in the form of discernible doublets or quartets.

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Fig. 5. Comparison of nuclear quadrupole splitting patterns of successive *K* components in the J = 90 - 89 rotational transition of the symmetric top HC⁸¹Br₃ species at 218.5 GHz (left) and those in the J = 88 - 87 rotational transition of the asymmetric top HC⁷⁹Br₂⁸¹Br species near 217 GHz (right). In this diagram segments of the actual spectrum are aligned at calculated frequencies for successive *K* or *K_c* transitions in the pertinent isotopic species.

also for these species. The fitted spectroscopic constants resulting from the global fits are collected in Table 1 and the complete results and data files associated with these fits are in Tables S1–S4 of the Supplementary data. The present analysis involves some less frequently used techniques provided by the SPFIT program so that additional explanatory comments have been placed in the Supplementary tables. For the four DCBr₃ species of bromoform only the CP-FTMW spectrum was measured and the results are reported in Table 2, and in Tables S5–S8.

All fits are close to the expected experimental accuracy of each of the spectrometers employed in this work. In the HC⁷⁹Br₃ data set, for example, there are 120 CP-FTMW lines fitted to 6.0 kHz, 22 BF-FTMW lines fitted to 1.4 kHz, and 329 MMW lines fitted to 39.3 kHz. For the asymmetric species the numbers of measured lines are higher and for HC⁷⁹Br₂⁸¹Br are 308, 59, and 348 fitted to 7.2, 2.2, and 42.6 kHz for CP-FTMW, BF-FTMW and MMW, respectively. The data for the three spectrometers were assigned frequency uncertainties of 10, 2 and 50 kHz. These values are probably too high, since the rms deviations in Table 1 are appreciably smaller than unity, but still expected to reflect the relative precision of data obtained with the three spectrometers. The standard deviation of 6-7 kHz for measurements with the 2-8 GHz version of the CP-FTMW is close to the expected accuracy of below 5 kHz benchmarked for this spectrometer [11]. The somewhat higher deviations of 8-9 kHz obtained on fitting the DCBr₃ species probably reflect the neglect of deuterium hyperfine structure in the analysis. Although the chirped-pulse spectrum is known for its intensity fidelity and spin statistical weights for the symmetric species are available, see [30], we have not yet used that information simply because we are not yet sufficiently confident in the accuracy of the intensity calculation at the density and mixing of states that we face in this problem.

5. Rotational and centrifugal distortion constants

It can be seen in Tables 1 and 2 that the axial constant C has been determined also for the symmetric-top species of bromoform. Determination of axial constants in ground states of symmetric top molecules is normally not possible, although in high-resolution infrared spectroscopy several specialized techniques have been used for this purpose, as recently reviewed in [31]. Pure rotational spectra of molecules with nuclear quadrupole coupling offer another route, providing that the quadrupole tensor contains significant off-diagonal elements. Prototype examples of such behaviour were identified in near prolate molecules BrNCO [32] and cyclopropyl bromide [33]. In those molecules $\Delta J = +1, \Delta K_a = -1$ perturbations between rotational energy levels, which were mediated by the single off-diagonal constant χ_{ab} (BrNCO) or χ_{ac} (cyclopropyl bromide), allowed enhanced determination of the values of the A₀ rotational constant. Similar effects for chlorine [34], and even nitrogen nuclei [35] were used to enhance the determination of the χ_{ab} constant. In bromoform all three inertial frame off-diagonal nuclear quadrupole constants are large and lead to a rich off-diagonal structure in the Hamiltonian matrix. Each such matrix is set up for a given value of the total angular momentum quantum number F, is block diagonal in J, and blocks differing in J by 1 are connected by $\Delta K = \pm 1$ terms in χ_{ab} and χ_{ac} , and $\Delta K = \pm 2$ terms in χ_{bc} . The magnitudes of such terms between J = 1 and J = 2 blocks are close to 5% of the diagonal, rotational terms for J = 1. This results in a numerically very stable solution for the value of C and the fitted values are compared in Table 3 with values evaluated from the appropriate planar moment in the asymmetric top species. The agreement between the two different evaluations of C from the most precise evaluation for HC⁷⁹Br₃ is excellent.

The fitted values for the quartic centrifugal distortion constants are expected to be well reproduced by *ab initio* calculation, which is confirmed by the comparison presented in Table 4. We initially needed the computed values for prediction of mm-wave transition frequencies, so that the calculated harmonic force field was scaled for optimum reproduction of the constants for HC⁷⁹Br₃. The good agreement of the resulting predictions for the remaining species of HCBr₃ justified the use of calculated values also for all isotopic species of DCBr₃. The only significant discrepancy between experimental and calculated quartics occurs for the values of d_2 in HC⁷⁹Br₂⁸¹Br. This constant is very small and not very well determined by experiment, but it is also subject to difficulties in calculation. A detailed discussion of the behaviour of the d_2 on off-axis isotopic substitution has been given for the case of 1,1,1-trichloroethane [36], where the change of sign of d_2 between the two asymmetric species has been rationalised. In bromoform it turns that there is considerable mutual cancellation of underlying terms in the evaluation of d_2 (Eq. (1) of Ref. [36]) so that the value of this constant is close to 0.02% of the sum of the magnitudes of the underlying terms, and is thus subject to instabilities in numerical evaluation.

Finally the global fit of the measurements for the asymmetric top species of HCBr₃ resulted in values also for the sextic constant h_3 . In symmetric top molecules this constant is determinable directly from a splitting in K = 3 transitions. Such splitting is only measurable at very high values of J and its observation has been the subject of much research effort, leading to empirical rationali-

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Table 1

Spectroscopic constants for the four protonated isotopic species of bromoform determined from global fits of FTMW and MMW measurements.

		HC ⁷⁹ Br ₃	HC ⁷⁹ Br ₂ ⁸¹ Br	$\mathrm{HC}^{79}\mathrm{Br}^{81}\mathrm{Br}_{2}$	HC ⁸¹ Br ₃
A/MHz B/MHz C/MHz		1247.715120(52) ^a 633.6715(51)	1247.706274(88) 1227.49640(10) 628.4156(10)	1237.58968(12) 1217.39214(12) 623.157(12)	1217.383118(95) 618.035(17)
DJ/kHz D _{JK} /kHz D _K /kHz d ₁ /kHz d ₂ /kHz		$\begin{array}{c} 0.2526886(54) \\ -0.426141(63) \\ [0.1931]^{\rm b} \end{array}$	0.2487668(55) -0.419623(29) [0.1900] ^b 0.002261(13) 0.000357(16)	$\begin{array}{c} 0.2447669(60) \\ -0.412701(24) \\ [0.1870]^{\rm b} \\ 0.0020010(94) \\ -0.0000768(89) \end{array}$	0.2408136(86) -0.406171(23) [0.1841] ^b
H _J /mHz H _{JK} /mHz H _{KJ} /mHz h ₁ /mHz h ₂ /mHz h ₃ /mHz		0.09604(18) -0.3811(21) 0.431(16)	$\begin{array}{c} 0.09688(28) \\ -0.3819(13) \\ 0.4539(48) \\ -0.01181(90) \\ -0.0154(15) \\ 0.01082(54) \end{array}$	$\begin{array}{c} 0.09255(19)\\ -0.36926(86)\\ 0.4651(42)\\ -0.00085(28)\\ -0.01149(22)\end{array}$	0.08868(25) -0.35847(93) 0.4527(31)
$\begin{array}{l} (3/2)\chi_{cc}/\text{MHz} \\ (3/2)\chi_{cc}/\text{MHz} \\ (\chi_{bb} - \chi_{aa})/4/\text{MHz} \\ (\chi_{bb} - \chi_{aa})/4/\text{MHz} \\ \chi_{ac}/\text{MHz} \\ \chi_{ac}/\text{MHz} \\ \chi_{ac}/\text{MHz} \\ \chi_{ab}/\text{MHz} \\ \chi_{bc}/\text{MHz} \end{array}$	Br ₁ Br _{2,3} Br ₁ Br _{2,3} Br ₁ Br _{2,3} Br _{2,3}	$\begin{array}{c} -347.9447(49) \\ -347.9447(49)^6 \\ -213.9369(25) \\ 106.9884(12) \\ -258.522(13) \\ 129.2611(66) \\ \mp 370.5496(44) \\ \mp 223.886(11) \end{array}$	$\begin{array}{c} -290.8671(69) \\ -347.8226(41) \\ -178.7573(34) \\ 106.9882(26) \\ -215.775(56) \\ 129.286(37) \\ \mp 370.4827(51) \\ \mp 224.023(26) \end{array}$	$\begin{array}{c} -347.6966(69) \\ -290.7630(37) \\ 213.8971(30) \\ -89.3491(29) \\ -258.891(36)^{\rm d} \\ 107.907(28)^{\rm d} \\ \mp 309.6045(49) \\ \mp 186.875(18)^{\rm d} \end{array}$	$\begin{array}{c} -290.6652(60)\\ -290.6652(60)\\ -178.7196(29)\\ 89.3598(14)\\ -215.956(21)\\ 107.978(10)\\ \mp 309.5514(50)\\ \mp 187.023(18) \end{array}$
M _{bb} ^e /MHz M _{cc} /MHz	Br ₁ Br ₁	0.00418(26) 0.00157(71)	0.00376(22) 0.00270(58)	0.00332(25) 0.00234(56)	0.00260(53) 0.0024(13)
$N_{ m lines}{}^{ m f}\sigma_{ m ft}{}^{ m f}/ m kHz$ $\sigma_{ m rms}$		142,329 5.52,39.3 0.738	367,348 6.62,42.6 0.819	341,309 7.06,32.7 0.733	139,310 6.41,43.2 0.802

^a Round parentheses enclose standard errors in units of the last quoted digit of the value of the constant.

^b Assumed value, calculated from the *ab initio* force field, which was scaled scaled for optimum reproduction of the determinable quartic constants.

^c The quantities in italics are dependent constants related to those for the Br₁ nucleus by ±120° rotation about the *c* axis. For the symmetric species ($\chi_{bb} - \chi_{aa}$)/4 for Br_{2,3} is equal to $-(\chi_{bb} - \chi_{aa})/8$ for Br₁.

^d Owing to different orientation of this species in the inertial axes (see text), the indicated values are in the order $\chi_{bc}(Br_1)$, $\chi_{bc}(Br_{2,3})$, and $\chi_{ac}(Br_{2,3})$.

^e The values for Br_{2,3} were obtained from those for Br₁ by ±120° rotation about the *c* axis. It was assumed that $M_{aa}(Br_1) = 0$, and the signs of the **M** tensor components are consistent with the definition $H_{sr} = + \mathbf{I} \cdot \mathbf{M} \cdot \mathbf{J}$.

^f The first number refers to the FTMW and the second to the MMW data set.

Table 2

Spectroscopic constants for the four deuterated isotopic species of bromoform determined from global fits of FTMW and MMW measurements.

		DC ⁷⁹ Br ₃	$\mathrm{DC}^{79}\mathrm{Br_2}^{81}\mathrm{Br}$	$\mathrm{DC}^{79}\mathrm{Br}^{81}\mathrm{Br}_2$	DC ⁸¹ Br ₃
A/MHz B/MHz C/MHz		1239.55580(13) 633.704(35)	1239.54405(26) 1219.59411(26) 628.4038(45)	1229.55457(28) 1209.61603(27) 623.2012(87)	1209.60495(13) 618.127(28)
D _J /kHz D _{JK} /kHz D _K /kHz d ₁ /kHz d ₂ /kHz		[0.2473] ^a [-0.4118] [0.1870]	[0.2435] [-0.4053] [0.1841] [0.001961] [0.000423]	[0.2397] [-0.399] [0.1812] [0.001947] [-0.0000730]	[0.2359] [-0.3928] [0.1784]
$(3/2)\chi_{cc}$ /MHz $(3/2)\chi_{cc}$ /MHz $(\chi_{bb} - \chi_{aa})/4$ /MHz $(\chi_{aa} - \chi_{bb})/8$ /MHz χ_{ac} /MHz χ_{ab} /MHz χ_{bc} /MHz	Br ₁ Br _{2,3} Br ₁ Br _{2,3} Br ₁ Br _{2,3} Br _{2,3}	$\begin{array}{c} -348.8563(62) \\ -348.8563(62)^{b} \\ -214.0176(21) \\ 107.0088(10) \\ -257.482(17) \\ 128.7410(89) \\ \mp 370.6895(36) \\ \mp 222.985(15) \end{array}$	$\begin{array}{c} -291.680(10)\\ -348.7021(58)\\ -178.8341(31)\\ 107.0327(26)\\ -214.881(54)\\ 128.786(35)\\ \mp 370.6033(46)\\ \mp 223.111(26)\end{array}$	$\begin{array}{c} -348.5649(97) \\ -291.5386(68) \\ 213.9658(31) \\ -89.3760(31) \\ -257.797(47)^{\rm c} \\ 107.528(40)^{\rm c} \\ \mp 309.7418(46) \\ \mp 186.167(29)^{\rm c} \end{array}$	-291.4213(57) -291.4213(57) -178.7891(23) 89.3945(11) -215.101(19) 107.5505(99) ∓309.6718(40) ∓186.282(17)
$M_{bb}{}^{ m d}/ m MHz$ $M_{cc}/ m MHz$	Br ₁ Br ₁	0.00196(48) 0.0025(11)	0.00211(34) 0.00162(74)	0.00121(33) 0.00364(90)	0.00226(48) 0.0018(11)
$N_{ m lines} \ \sigma_{ m fit}/ m kHz$		169 7.99	475 8.70	449 8.64	174 8.27

^a Square parentheses enclose assumed values, calculated from the scaled *ab initio* force field, which gave optimum reproduction of the determinable quartic constants for the protonated species.

^b The quantities in italics are dependent constants derived from those for Br₁, see Table 1 and text.

^c Owing to different orientation of this species in the inertial axes (see text), the indicated values are in the order $\chi_{bc}(Br_1)$, $\chi_{bc}(Br_{2,3})$, and $\chi_{ac}(Br_{2,3})$.

^d The values for $Br_{2,3}$ were obtained from those for Br_1 by ±120° rotation about the *c* axis. It was assumed that $M_{aa}(Br_1) = 0$, and the signs of the **M** tensor components are consistent with the definition $H_{sr} = + \mathbf{I} \cdot \mathbf{M} \cdot \mathbf{J}$.

Table 3

Comparison of fitted values for the axial rotational constant C (MHz) in the symmetric top species of bromoform with values estimated from the asymmetric top species.

	Exp.	Calc. ^a
HC ⁷⁹ Br ₃	633.6715(51)	633.6702(10) ^a
DC ⁷⁹ Br ₃	633.704(35)	633.659 ^{a,b}
HC ⁸¹ Br ₃	618.035(17)	617.994(12) ^c
DC ⁸¹ Br ₃	618.127(28)	618.038 ^{b,c}

^a Evaluated from $2P_b$ for the ⁷⁹Br₂⁸¹Br isotopic species.

^b Error not estimated due to lack of MMW data for this species and assumption of all quartic constants.

^c Evaluated from $2P_a$ for the ⁷⁹Br⁸¹Br₂ isotopic species.

sation of the observed values of h_3 [37,38]. It has been shown, however, that determination of h_3 in asymmetric top species obtained on off-axis isotopic substitution of a symmetric top parent molecule is much less demanding experimentally [36]. The present results represent such a determination and the opposed signs and similar magnitude of h_3 for the two asymmetric top species in Table 1 are as found for 1,1,1-trichloroethane. The present values are also compared in Fig. 6 with those for molecules of similar symmetry and with the empirical relation [38]

$$h_3 = 2.4 \times 10^{-21} B_x^4 / |B_x - B_z|, \tag{7}$$

where B_z denotes the axial rotational constant, B_x is the rotational constant around an axis perpendicular to the symmetry axis, and all quantities are in units of MHz. The agreement of h_3 for bromoform with expectations concerning the behavior of this constant is very good. The present results extend the range of known values of h_3 for tetratomic and pentatomic molecules by an order of magnitude.

6. Nuclear hyperfine coupling constants

The values derived for the diagonal constants in principal inertial and principal nuclear quadrupole tensors for bromoform are collected in Table 5. There are several useful confirmations of the self- consistency of the data obtained for the various isotopic species. One such check results from the fact that the principal nuclear quadrupole y axis is perpendicular to the plane containing the relevant CBr bond and is parallel to the axis defining the small isotopic rotation between the different bromine species. The χ_{yy} values for a given isotopic bromine nucleus should thus be identical in all species containing such a nucleus. This is indeed found to be the case, as for ^{79}Br in HCBr₃, for example, χ_{yy} is equal to -311.892(5), -311.895(6), -311.895(6) MHz in HC⁷⁹Br₃, HC⁷⁹Br₂⁸¹Br, and HC⁷⁹Br⁸¹Br₂, respectively. The ⁷⁹Br/⁸¹Br ratios of χ_{vv} values are 1.19705(4) for HCBr₃, 1.19702(3) for DCBr₃. These are consistent with best estimates of such isotopic ratios of 1.197048(3) [39] and 1.1970514(32) [40]. We note, however, that the present ground state values are not sufficiently precise to discern any averaging effects relative to the equilibrium values in [39,40], since such effects have been found to be at the level of



Fig. 6. Comparison of the values of the h_3 splitting constant determined for the asymmetric species of bromoform with those for pyramidal molecules and for methane derivatives. The empirical relationship proposed in [37,38] is indicated by the dashed line.

 3×10^{-6} [40]. Furthermore, the very small isotopic rotation of bromoform in its inertial frame on bromine substitution is well reflected by changes in the precisely determined quadrupolar angles. For example, the substitution of one bromine atom in HC⁷⁹Br₃ changes the angle between the corresponding CBr bond and the *c* inertial axis by 0.018°, whereas the difference in the associated θ_{zc} angles, 73.1765(34)°-73.1593(7)°), is equal to 0.0172(35)°.

It thus appears that, at the precision of present measurements, no isotopic effects due to bromine substitution are apparent. Small isotopic changes are visible, however, on deuterium substitution, and the clearest effect of this type is a decrease in the value of χ_{zz} at the level of 0.2 MHz or 0.03%. This is similar to the percentage change in the magnitude of χ_{zz} between CH₂I₂ and CD₂I₂ [41]. Effects of this type were studied in detail for the methyl chloride [42], methyl bromide [43], methyl iodide [44] series, with conclusion that the dominant underlying cause of the isotope effect was the change in the effective carbon hydrogen bond length. The behaviour in bromoform is consistent with this picture as we note from computation that a 0.01 Å decrease in CH bond length leads to a decrease in *ab initio* calculated value of χ_{zz} of 0.03%.

The values of determined principal quadrupole tensor elements for bromoform lead to very small values of the quadrupole asymmetry parameter η for all species. This is similar to chloroform and indicates rather cylindrical symmetry of the field gradient at the bromine nucleus around its principal quadrupole *z* axis. It is intriguing to note that η changes sign between bromoform and chloroform, see Table 6, which indicates that the magnitude of χ_{yy} is now greater than that of χ_{xx} , while the reverse is the case

Table 4

Comparison of experimental and calculated values (kHz) of quartic centrifugal distortion constants for bromoform.

	I		· · · · ·	e				
	HC ⁷⁹ Br ₃		HC ⁷⁹ Br ₂ ⁸¹ Br		HC ⁷⁹ Br ⁸¹ Br ₂		HC ⁸¹ Br ₃	
	Expt.	Calc. ^a	Expt.	Calc. ^a	Expt.	Calc. ^a	Expt.	Calc. ^a
D_J	0.252689(5)	0.2549	0.248767(6)	0.2509	0.244767(6)	0.2469	0.240814(9)	0.2430
D_{IK}	-0.42614(6)	-0.4254	-0.41962(3)	-0.4187	-0.41270(3)	-0.4120	-0.40617(2)	-0.4056
D_K		0.1931		0.1900		0.1870		0.1841
d_1			0.002261(13)	0.002045	0.002001(9)	0.002029		
d_2			0.00036(2)	0.0000376	-0.000077(9)	-0.0000695		

^a Calculated from the 0.86f scaled MP2/6-31G(d,p) harmonic force field, which gave optimum reproduction of the determinable quartic constants for HC⁷⁹Br₃.

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Table 5

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Nuclear quadrupole splitting constants for the bromine nucleus in bromoform, in inertial axes and in principal axes of the quadrupole tensor.

	⁷⁹ Br			⁸¹ Br		
	HC ⁷⁹ Br ₃	HC ⁷⁹ Br ₂ ⁸¹ Br	HC ⁷⁹ Br ⁸¹ Br ₂	HC ⁸¹ Br ₃	HC ⁸¹ Br ₂ ⁷⁹ Br	HC ⁸¹ Br ⁷⁹ Br ₂
χ_{aa}/MHz	543.8554(53)	-98.0355(54)	-311.8953(64)	454.3276(61)	275.6192(59)	454.4703(72)
χ_{bb}/MHz	-311.8922(53)	329.9173(54)	543.6931(64)	-260.5508(61)	-81.7772(59)	-260.5589(72)
χ_{cc}/MHz	-231.9631(33)	-231.8817(27)	-231.7977(46)	-193.7768(40)	-193.8420(25)	-193.9114(46)
χ _{zz} /MHz χ _{xx} /MHz χ _{yy} /MHz	622.1083(87) -310.2161(78) -311.8922(53)	622.1154(171) -310.2202(167) -311.8951(62)	622.1783(208) -310.2830(204) -311.8953(64)	519.6940(129) -259.1432(122) -260.5508(61)	519.6598(130) -259.1063(118) -260.5535(63)	519.7131(317) -259.1542(313) -260.5589(72)
$ heta_{zc}/{ m deg}$	73.1593(7) 0.002694(15)	73.1499(15) 0.002692(29)	73.1348(18) 0.002591(34)	73.1598(13) 0.002709(26)	73.1725(13) 0.002785(26)	73.1765(34) 0.002703(62)
χ _{aa} /MHz χ _{bb} /MHz χ _{cc} /MHz	$\begin{array}{c} DC^{79}Br_{3} \\ 544.3206(47) \\ -311.7498(47) \\ -232.5709(41) \end{array}$	DC ⁷⁹ Br2 ⁸¹ Br -97.8314(56) 330.2994(56) -232.4681(39)	$\begin{array}{c} DC^{79}Br^{81}Br_2\\ -311.7433(70)\\ 544.120(70)\\ -232.3766(65) \end{array}$	$\begin{array}{c} DC^{81}Br_{3} \\ 454.7186(50) \\ -260.4378(50) \\ -194.2809(38) \end{array}$	DC ⁸¹ Br ₂ ⁷⁹ Br 275.9315(66) -81.5725(66) -194.3591(45)	$\begin{array}{c} DC^{81}Br^{79}Br_2\\ 454.8949(70)\\ -260.4415(70)\\ -194.4533(67) \end{array}$
χ _{zz} /MHz χ _{xx} /MHz χ _{yy} /MHz	621.9082(103) -310.1585(101) -311.7498(47)	621.8900(167) -310.1393(163) -311.7507(60)	621.9146(268) -310.1713(267) -311.7433(70)	519.5369(115) -259.0992(107) -260.4378(50)	519.5432(187) -259.1022(180) -260.4410(66)	519.5627(305) -259.1211(304) -260.4415(70)
$ heta_{zc}^{\ a}/deg \eta^{b}$	73.2308(9) 0.002559(18)	73.2211(15) 0.002591(28)	73.2079(24) 0.002528(44)	73.2304(12) 0.002577(23)	73.2405(20) 0.002577(37)	73.2510(33) 0.002541(60)

^a The angle between the axis c of the principal inertial tensor and the axis z of the principal nuclear quadrupole tensor.

^b Nuclear quadrupole asymmetry parameter, $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$.

Table 6

Comparison of experimental and calculated values of the nuclear quadrupole asymmetry parameter η and the difference angle $\delta\theta$ (degrees) between quadrupolar and structural angles for chloroform and bromoform.

	HC ³⁵ Cl ₃		HC ⁷⁹ Br ₃		
	η	$\delta \theta^{a}$	η	$\delta \theta$	
Experiment	$-0.0040(2)^{b}$	0.59(2) ^b	+0.00269(2)	0.80(3) ^c	
MP2/6-31G(d,p) MP2/aug-cc-pVDZ MP2/aug-cc-pVTZ	-0.0021 -0.0024 -0.0016	0.73 0.69 0.50	-0.0059 +0.0060 +0.0085	0.99 0.93 0.70	

^a $\delta \theta = \theta_{zc} - \theta_{BrC.c.}$ ^b Ref. [2].

^c Evaluated using the r_z geometry determined in this work.

for chloroform. The comparison in Table 6 also shows that while the *ab initio* calculation of η for HCCl₃ is relatively satisfactory the values for HCBr₃ show considerable basis set dependence and demonstrate that reliable field gradient calculations for bromine are clearly much more of a challenge than for chlorine.

Table 6 also contains a comparison illustrating the difference, $\delta\theta$ in angular orientation between the principal quadrupole axis *z*, and the axis of the BrCl bond. As discussed in detail in [45] there is systematic, and well calculable behaviour of this quantity. The *z* axis for a given nucleus terminal to a bond will, in the presence of other nuclei carrying considerable electron density, be distorted away from the bond axis towards the heavy nuclei. The situation for bromoform is no different and the distortion (as indicated in Fig. 1) appears to be somewhat greater than for chloroform.

The values of the principal quadrupole splitting constants χ_{zz} for the various halogeno-substituted methanes fall into a systematic pattern, as visible in Table 7. The gradual increase in the magnitude of χ_{zz} with the number of chlorine atoms from CH₃Cl to CHCl₃ has been rationalised in terms of gradually increasing, though small, π -bond character [48]. The behaviour for the bromine series is similar, with the presently determined χ_{zz} for bromoform greater than for CH₂Br₂.

7. Spin-rotation constants

The values of spin–rotation constants for heavier molecules are normally at the threshold of determinability from rotational spectroscopy, even with supersonic expansion data. The use of such constants usually lowers deviation of fit, but the physical significance of the derived values has not been easy to assess. Fortunately, it has been demonstrated for molecules of varied symmetry, including HCN [49], CH₃F [50], O₃ [51] that *ab initio* calculation can deliver sufficiently reliable estimates for assessing the experimental values. In deriving the values of the spin–rotation constants for bromoform we used the symmetry equivalence of the bromine nuclei in the same way that was applied for the hyperfine coupling tensor. If the spin–rotation tensor for nucleus Br₁ is set up with only the diagonal elements, M_{aa} , M_{bb} , and M_{cc} and is subjected to ±120° rotation then we obtain for the remaining two nuclei

$$M_{aa}(Br_{2,3}) = (M_{aa} + 3M_{bb})/4$$

$$M_{bb}(Br_{2,3}) = (3M_{aa} + M_{bb})/4$$

$$M_{cc}(Br_{2,3}) = M_{cc}.$$
(8)

Table 7

Comparison of the values of the nuclear quadrupole splitting constants χ_{zz} (MHz) for the halogeno substituted methane derivatives.

х	CH ₃ X	Ref.	CH_2X_2	Ref.	CHX ₃	Ref.
³⁵ Cl ⁷⁹ Br ¹²⁷ I	-74.7514(11) 577.1088(57) -1934.1395(23)	[46] [25] [47]	-75.35(21) 595.74(31) ^a -2030.11(49)	[12] [26] [1]	-78.688(18) 622.1083(87)	[2] This work

^a The value for the ⁷⁹Br nucleus in $CH_2^{79}Br^{81}Br$.

Table 8

Comparison of fitted and calculated values of spin-rotation constants (kHz) for chloroform and bromoform.

	HC ³⁵ Cl ₃		HC ⁷⁹ Br ₃		
	Exp. ^a	Calc. ^b	Exp.	Calc. ^b	
M _{aa} c		0.36		0.68	
M_{bb}	1.62(7)	1.09	4.18(26)	2.83	
M _{cc}	0.84(18)	0.78	1.57(7)	2.00	

^a Ref.[2].

^b Calculated at the MP2/aug-cc-pVDZ level with ACES II [52].

^c The **M** tensor components are consistent with the definition $H_{sr} = + \mathbf{I} \cdot \mathbf{M} \cdot \mathbf{J}$, and are applicable to the halogen nucleus positioned in the *ac* inertial plane.

The required linear combinations of spin-rotation elements were declared in the input data for the SPFIT program, as documented in Tables S1–S8. It was found for bromoform, as previously for chloroform [2], that M_{aa} is probably too small to be determinable. Only the values of M_{bb} and M_{cc} could be fitted, as listed in Tables 1 and 2. The sensitivity of the experimental frequencies to spin-rotation contributions also did not warrant fitting separate sets of values for the in-plane and out-of-plane nuclei in the asymmetric species so that values averaged by the assumption implicit in Eq. (8) are reported. The experimentally derived values for the spin-rotation constants are compared in Table 8 with ab initio values calculated at the MP2/aug-cc-pVDZ level with program ACES II [52]. Even though the calculated values could be refined further their agreement with experiment is quite satisfactory, the indeterminability of M_{aa} is rationalised, and the comparison of values calculated for the three coupling nuclei confirms the model in Eq. (8).

8. Molecular geometry

Reliable structural analysis for bromoform proved unexpectedly difficult. The availability of rotational constants for eight isotopic species should normally constitute plentiful information for determination of molecular geometry. It was an unpleasant surprise, therefore, when it was found that determination of the currently preferred, $r_m^{(1)}$ geometry [53], was not possible. The main reasons for this are the lack of data for the ¹³C isotopologs and the very small *c* coordinates of the bromine nuclei, which are close to 0.03 Å. In addition, the ground state vibration–rotation contributions that are encompassed by the c_{α} constants of the $r_m^{(1)}$ fit are expected to be smaller than usual in relation to the moments of

Table 9

Comparison of experimental and calculated geometries for bromine substitued methane derivatives.

	CH ₃ Br	CH ₂ Br ₂	CHBr ₃
Experimental	r _e , Ref. [54]	r_z^{a}	r_z^{b}
r(CH)/Å r(CBr)/Å ∠(HCBr)/deg ∠(BrCBr)/deg	1.0823(3) 1.9340(3) 107.73(10)	1.0809(4) 1.9304(1) 107.760 112.527(9)	1.0831(32) 1.9260(3) 107.622(27) 111.255(25)
Calculated, MP2/	6-31G(d,p)		
r(CH)/Å r(CBr)/Å ∠(HCBr)/deg ∠(BrCBr)/deg	1.0833 1.9385 108.09	1.0824 1.9305 108.00 112.90	1.0825 1.9312 107.65 111.23

^a Refitted in this work using the data for five isotopic species from [26,55].

^b Determined in this work from 18 rotational constants for 8 isotopic species, fitted to a standard deviation of 0.013 u Å². The two least precisely determined constans, i.e. the *C* constants for the symmetric CDBr₃ species were not used in the fit.

Table 10

Comparison of values of the rotational constant B (MHz) determined for the ground states of the symmetric top isotopic species of bromoform.

	Ref.[3]	Ref.[4]	This work
HC ⁷⁹ Br ₃	1281.	1247.61(3)	1247.71512(5)
HC ⁸¹ Br ₃	1238.5	1217.30(3)	1217.38312(10)
DC ⁷⁹ Br ₃		1239.45(3)	1239.55580(13)
DC ⁸¹ Br ₃		1209.51(3)	1209.60495(13)

inertia, in a ratio of less than 0.5 u Å² to 405 or 798 u Å² for I_b and I_c , respectively. The least-squares r_0 geometry could be determined at a satisfactory deviation of fit, but when the resulting r(CH) = 1.105(3) Å and r(CBr) = 1.9187(3) Å are compared with geometries of similar molecules, r(CH) turns out to be unexpectedly long, while r(CBr) seems unusually short. Similar problems were encountered for CH₂Br₂ [55] where the solution has been to fit the average, r_z , geometry. We applied the same procedure for bromoform. The ground state rotational constants were corrected to the average constants by means of contributions evaluated from the harmonic force field, and small isotopic shifts in r_z distances were evaluated from vibrational amplitudes, as described in [55] and references cited therein. The analysis was based on the same ab initio harmonic force field that was used above for centrifugal distortion constants. A modified version of program VIBCA [18] was used to calculate vibrational amplitudes, and the geometry was fitted using the program STRFIT [56,18].

The structural results obtained for bromoform are compared in Table 9 with those for CH₃Br and CH₂Br₂. For the latter the use of an *ab initio* force field was found to give results which were practically identical to those in [55]. For CH₃Br the experimental equilibrium geometry is available [54] and is seen to be fortuitously close to the geometry evaluated at the diagnostic MP2/6-31G(d,p) level. The differences between r_z and equilibrium bond distance have been estimated for CH₂Br₂ to be at the level of 0.005 Å, and are expected to be comparable or smaller for bromoform. Comparison of the major trends in experimental and calculated values shows good general agreement, such as the relative invariance of r(CH) and $\angle(HCBr)$ in the three molecules, and the appreciable decrease in $\angle(BrCBr)$ from CH₂Br₂ to CHBr₃.

9. Summary

The present work finally resolves the uncertainty concerning the spectroscopic constants of bromoform. Comparison with previous results in Table 10 shows that the determination of Ref. [4] was essentially correct. The small systematic difference in rotational constants of around 0.1 MHz can be attributed to a distortion arising from measurement in Ref. [4] of unresolved centrifugal and hyperfine structure made under Stark modulation. Even though we only obtained partial coverage of the $J = 1 \leftarrow 0$ transition, our spectrum and predictions show minimal correlation with results of Ref. [3]. Their measurements were rather ambitious in that video mode was used and the authors attempted to derive difference spectra by using rather high sample pressure of 3 Torr. Regrettably it appears that those results must have still been dominated by spurious microwave reflection effects.

Application of different types of rotational spectrometers in the present work allowed a comprehensive investigation of the rotational spectrum of bromoform. Many types of spectroscopic constants could be determined precisely leading to detailed insight into various molecular properties of bromoform. Useful comparisons with properties of similar molecules and with results of quantum chemistry computations were also made. The underlying reason for the success of the present investigation was, however, the recording and making available for off-line analysis of the broadband supersonic expansion spectrum containing complete hyperfine patterns of several lowest-J rotational transitions. The CP-FTMW technique used for this purpose holds considerable promise for solving complex spectroscopic problems where confident assignment can be made efficiently only on the basis of extensive coverage of the relevant spectrum.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jms.2009.08.006 and as part of the Ohio State University Molecular Spectroscopy Archives (http:// msa.lib.ohio-state.edu/jmsa_hp.htm).

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