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High-resolution spectroscopy near the continuum limit: the microwave spectrum of *trans*-3-bromo-1,1,1,2,2-pentafluoropropane

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ABSTRACT

The microwave spectrum of 3-bromo-1,1,1,2,2-pentafluoropropane has been observed using CP-FTMW spectroscopy. Potential energy scans have been performed and confirm the existence of two conformers – *trans* and *gauche* – for which further structural optimisations and electric field gradient calculations have been performed in order to get highly accurate nuclear quadrupole coupling constants for assignment purposes. The combination of multiple conformers and large nuclear quadrupole coupling constants produce a very dense spectrum at an estimated 1 transition/MHz, near the continuum limit. This spectral density makes it necessary to have very sophisticated computational approaches in order to get geometric and electronic structures that are very close to experimental observation. Analysis of the spectrum allowed for the assignment of the *trans* conformer, but the *gauche* proved to be prohibitive, although it is believed to be present in the current spectrum. Full analysis of the rotational spectroscopic parameters of two isotopologues – the [79]Br and [81]Br – have been observed and are reported. Geometric analysis of the experimentally observed conformer is also reported using Kraitchman coordinate and second moments arguments. Further analysis of the spectrum reveals the occurrence of dipole-forbidden, nuclear quadrupole allowed transitions with one forbidden transition possessing the first known *x*-type forbidden transition linkage pathway.
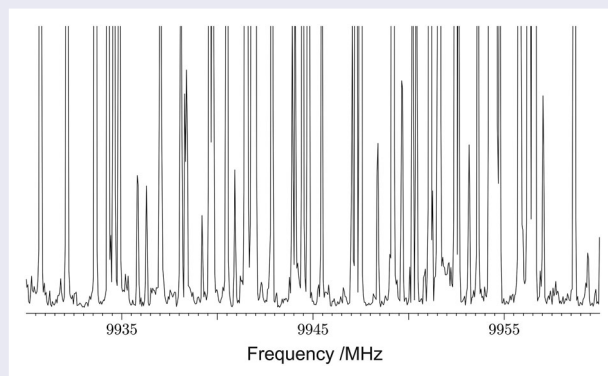
1. Introduction

Since the work of Javan [1] on the three-state maser and their discovery by Oka [2], there has been much work on electric dipole-forbidden, perturbation-allowed rotational transitions by multiple groups [3–6]. In many of these instances, the spectra observed and reported leverage some simple spectral caveat or anomaly that provides the necessary framework for such a transition to occur. Since 2009, however, the work of Grubbs and Cooke have built upon these principles by leveraging heavier molecules with large quadrupole coupling nuclei (like Br and I) [7–12]. The combination of large quadrupole coupling constants and small rotational constants mix states of dipole-allowed transitions via off-diagonal quadrupole

coupling tensor components and can amass multiple types of dipole-forbidden, quadrupole-facilitated transitions. Their work has been focused on investigating these transition pathways and understanding the breakdown of traditional selection rules. The transitions studied are typically $\Delta J = 2$- or $\Delta J = 3$-types with significant (i.e. S:N = 50:1) intensity. In 2016, experiments performed on bromoperfluoroacetone [13] showed that, given the proper geometry and size of the molecule, a large quadrupole coupling nucleus could supply large values to all off-diagonal nuclear quadrupole coupling tensor components giving rise to the extremely rare x-type transition, providing evidence for the complete breakdown of K-labelling in asymmetric top systems.

A second consequence of increasing both the mass of the molecule in question and the values associated with the nuclear quadrupole coupling tensor, though, is that spectra also start to become very dense. This spectral density is quite interesting because microwave rotational spectra are already highly resolved (< 500 kHz linewidths) which provide for the observation of very small energetic differences or effects (tunnelling, various spin couplings, and isotopically resolved spectra). In order to still acquire these types of information from these spectra, then, it remains of the utmost importance to be able to fully assign spectra using Hamiltonian creation software that utilises complete diagonalisation routines in conjunction with rigorous computational methodologies that quickly and accurately predict geometric and electronic structure for many-electron systems. A few MHz disagreement between theory and experiment can mean disaster in trying to arrive at a correct assignment.

However, the atoms typically responsible for these effects, Br or I, are usually quite difficult to calculate accurately and efficiently, needing large basis sets and proper DFT treatments in order to accurately encapsulate the geometric and electronic structure of the molecules containing them. In this work we present a combined theoretical and experimental approach, analysing the microwave rotational spectra for the previously unstudied system, *trans*-3-bromo-1,1,1,2,2-pentafluoropropane. Due to its bromine nucleus, mass, and structure, it possesses a rich, dense spectrum which provides the framework necessary for handling such difficult systems as one approaches the microwave spectrum continuum limit.

2. Experimental

3-Bromo-1, 1,1,2,2-pentafluoropropane was purchased from Synquest Laboratories® and used without further purification. Spectra were observed using a chirped
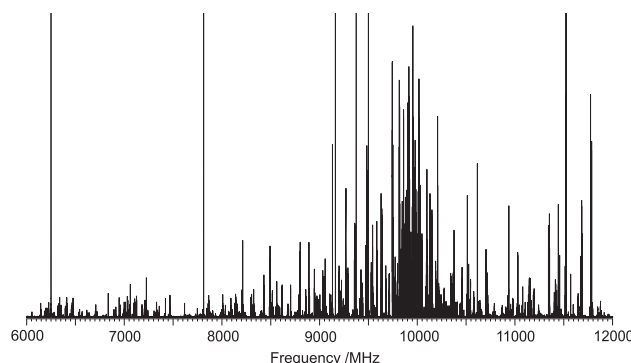
Figure 1. The resultant spectrum of the 6–12 GHz experiment of 3-bromo-1,1,1,2,2-pentafluoropropane averaged for 170k FIDs. Details of the experiment can be found in the text.

pulse-Fourier transform microwave (CP-FTMW) spectrometer located at Missouri S&T. This spectrometer has been detailed elsewhere in the literature [13,14]. Samples of the liquid were inserted into a 'U'-shaped tube approximately 40 cm upstream of the solenoid valve and covered with aluminium foil to avoid exposure to light. Six psig of Ar was bubbled through the sample carrying vapour to the spectrometer. Separate experiments were performed utilising the 6–12 and 12–18 GHz frequency ranges of the spectrometer's bandwidth. Four microsecond chirps were utilised and the experiment was performed at 1 Hz nozzle pulsing with 1, 20 μs free induction decay (FID) being collected per gas pulse. Separate experiments of 10,000 FID averages were coadded externally and Fourier transformed using Kisiel's FFTS programme using a Hanning or Bartlett windowing type [15]. 170,000 FIDs were collected for each experiment and an example of the observed spectrum in the 6–12 GHz region is located in Figure 1. Spectral linewidths ranged from 60–300 kHz FWHM with the 250 kHz arising from multiple transitions. Ten kHz uncertainty has been attributed to most line centres except for those with exceptionally large linewidths and/or blended transitions.

3. Quantum chemical calculations

With such high density, high-resolution spectra, it is imperative that quality quantum chemical calculations are performed at multiple starting configurations in order to achieve a successful assignment. To isolate possible monomer species in the sample, which are the most intense in molecular beam microwave spectra, the approach here was to first isolate and optimise the geometries of the lowest energy conformers of 3-bromo-1,1,1,2,2-pentafluoropropane. The results of all following methodologies are presented in Table 1.

Table 1. Quantum chemical parameters for 3-bromo-1,1,1,2,2-pentafluoropropane for[79]Br.

Parameter	*trans* Conformer	*gauche* Conformer
A (MHz)	2541.0	1919.8
B (MHz)	566.1	732.6
C (MHz)	556.0	659.3
χ_{aa} (MHz)	515.42	230.65
χ_{bb} (MHz)	−195.26	−58.13
χ_{cc} (MHz)	−320.16	−172.52
χ_{ab} (MHz)	297.3	371.99
χ_{bc} (MHz)	0.00	189.96
χ_{ac} (MHz)	0.00	268.63
μ_a (D)	−0.16	−0.86
μ_b (D)	1.76	0.78
μ_c (D)	0.00	1.32
ΔE (cm^{-1})	0	416.8

Figure 2. Potential energy scan of the FCCBr dihedral angle from 0–180° in 4° steps. The computational details of the scan are given in the text. The *gauche* conformer is found to be 416.8 cm^{-1} above the *trans* conformer.

All calculations were performed using the Gaussian09® programme suite [16]. To find the lowest energy conformer starting points, energy scans at the B3LYP/aug-cc-pVQZ level of theory were used. A graphical depiction of this scan is shown in Figure 2. A geometric starting structure for the scan was built using typical bond lengths and bond angles as found in the CRC handbook [17]. Because the –CF$_3$ group should not have a change in conformation upon rotation about the FCCF dihedral angle, the FCCBr dihedral angle was the only variable tested. Because a calculation like this is very computationally expensive, the geometry of the molecule was leveraged by having the FCCBr angle vary in 4° units starting at the *trans* configuration and ending the calculation at the 180° point. This resulted in

two stable conformers, *trans* – and *gauche* – 3-bromo-1,1,1,2,2-pentafluoropropane separated by 416.8 cm^{-1} (1.19 kcal/mol) (Figure 3).

Once the possible conformers were identified, the energy scan structures provided the starting points for optimisations performed at the MP2/6-311+G(3df,3pd) level of theory for more reliable geometrical structures. This was needed because the rotational constants for the species are relatively low – ≈ 2500 MHz for A and < 1000 MHz for B and C – resulting in the observed spectra having transitions moderately high in J even for an experiment starting at 6 GHz, so the better starting geometries result in predicted spectra closer to the experimental result.

The second calculation that was made and was crucial to assigning these spectra was the nuclear electric quadrupole coupling due to the bromine nucleus made on the optimised structure. Having a relatively large quadrupole moment for bromine – reported as 313 mb for[79]Br [18] – can mean exceptionally large nuclear quadrupole coupling constants (NQCCs) that will result in large splitting of rotational states (many MHz) and various amounts of shifting in transitions. The purpose of the calculations made here, then, is to predict[79]Br and[81]Br nuclear quadrupole coupling constants (NQCCs) of sufficient accuracy to assist with the assignment of the hyperfine structure in the microwave spectrum of 3-bromo-1,1,1,2,2-pentafluoropropane.

Components of the NQCC tensor, χ_{ij}, are related to those of the electric field gradient tensor, q_{ij}, by

$$\chi_{ij} \text{ (MHz)} = (eQ/h) \times q_{ij} \text{ (a.u.)} \qquad (1)$$

where e is the fundamental electric charge, Q is the electric quadrupole moment of the nucleus in question, and h is Planck's constant. The coefficient eQ/h is taken as a best-fit parameter determined by linear regression analysis of calculated q_{ij} on the experimental structures of a number of molecules versus experimental χ_{ij}. The premise that underlies this procedure is that errors inherent in the computational model – as well as zero-point vibrations and relativistic effects – are systematic and can be corrected, at least partially, by the best-fit coefficient eQ/h.

For bromine, the recommended model for calculation of the q_{ij} is B1LYP/TZV(3df,3p) [19]. Here, B1LYP is Becke's one-parameter method with Lee–Yang–Parr correlation as implemented by Adamo and Barone [20,21]. TZV are Ahlrichs bases [22] augmented here with three sets of d and one set of f polarisation functions on heavy atoms with three sets of p functions on hydrogens. These polarisation functions are those recommended for use with Pople 6-311G bases, and were obtained online from the EMSL basis set library [23,24]. Thus, for conversion

of q_{ij} to χ_{ij}, $eQ/h\,(^{79}\text{Br}) = 77.628(43)$ MHz/a.u. and eQ/h $(^{81}\text{Br}) = 64.853(40)$ MHz/a.u. was used [19,25].

4. Results and analysis

The quantum chemical calculations were used as a starting point for quantum number assignment. As the quantum chemical calculations predict, *trans*-3-bromo-1,1,1,2,2-pentafluoropropane is the most stable conformer and generally corresponded to the most intense transitions. Two isotopologues, ^{79}Br and ^{81}Br, were observed for the *trans* conformer and are reported in Table 2. Spectra were assigned using Pickett's SPFIT/SPCAT programme suite [26] with Kisiel's AABS package [27], available from the PROSPE website [28,29], used as a front-end in order to visually observe predicted transition patterns and expedite transition assignment. In total, over 3100 transitions were assigned with obs-calc residuals less than or equal to 3σ of the line centre uncertainty. These transitions primarily consisted of strong P-, Q-, and R-branch, *b*-type transitions and much weaker R-branch, *a*-type transitions, in accordance with the predicted dipole moment values reported in Table 1. The spectra were fit using a Watson S-reduced Hamiltonian [30] in the I^r representation. All quartic centrifugal distortion constants arising from this reduction Hamiltonian were determined. All diagonal components and one off-diagonal component, χ_{ab}, of the nuclear quadrupole coupling tensor arising from the bromine nucleus were also determined. A complete list

Table 2. Spectroscopic parameters for *trans*-3-bromo-1,1,1,2,2-pentafluoropropane.

Parameter	$C_3H_2^{79}BrF_5$	$C_3H_2^{81}BrF_5$
A (MHz)	2536.1957(1)[a]	2535.9158(1)
B (MHz)	561.65607(3)	555.39358(3)
C (MHz)	551.65213(3)	545.59653(3)
D_J (kHz)	0.01710(3)	0.01691(3)
D_{JK} (kHz)	0.2190(2)	0.2166(2)
D_K (kHz)	0.1042(4)	0.1064(4)
d_1 (Hz)	−0.121(7)	−0.137(8)
d_2 (Hz)	0.028(2)	0.030(2)
χ_{aa} (MHz)	510.051(4)	425.762(5)
χ_{bb} (MHz)	−191.851(6)	−159.932(6)
χ_{cc} (MHz)	−318.199(6)	−265.830(6)
χ_{ab} (MHz)	300.06(1)	251.10(1)
χ_{zz} (MHz)	620.839(7)	518.675(8)
χ_{xx} (MHz)	−302.639(8)	−252.844(8)
χ_{yy} (MHz)	−318.199(6)	−265.830(6)
η^{b} (MHz)	0.02506(2)	0.02504(2)
θ_{za} (°)	20.2651(5)	20.3056(6)
MW σ_{rms}^{c} (kHz)	12.4	12.4
σ_{rms}^{d}	1.22	1.23
N^{e}	1676	1468

[a]Numbers in parentheses represent 1σ uncertainty (67% confidence level) and are given in units of the least significant digit.
[b]Asymmetry of the diagonalised χ tensor: $\eta = \frac{\chi_{xx} - \chi_{yy}}{\chi_{zz}}$.
[c]MW RMS is defined as $\sqrt{(\sum[(obs - calc)^2]/N)}$.
[d]RMS is defined as $\frac{\sqrt{(\sum[(obs - calc)^2]/N)}}{\text{Average of Attributed Uncertainty}}$.
[e]Number of transitions assigned.

of all assigned transitions and fits can be found in the Supplemental Information.

After this assignment was made, the *gauche* conformer was tried for by subtracting out the assigned transitions of the *trans* conformer utilising the 'blank lines' function of the SVIEW programme in the AABS
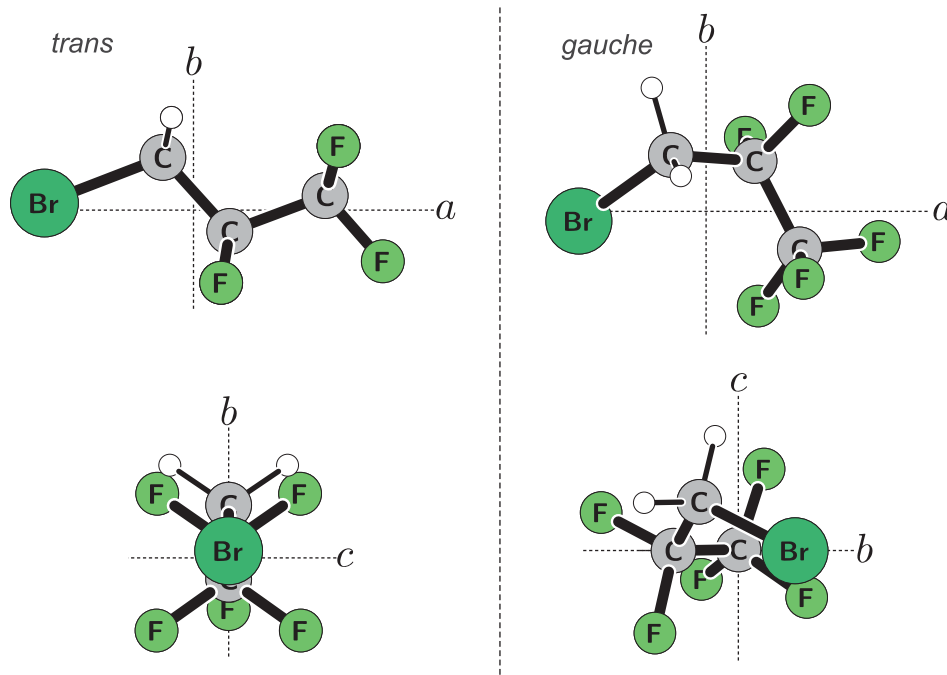
Figure 3. The calculated structures of the *trans* and *gauche* conformers in the principal axis *ab*- and *bc*-planes. The *trans* conformer has the FCCCBr backbone laying along the *a*-axis, while the *gauche* has the FCCCBr backbone wrapping around it.
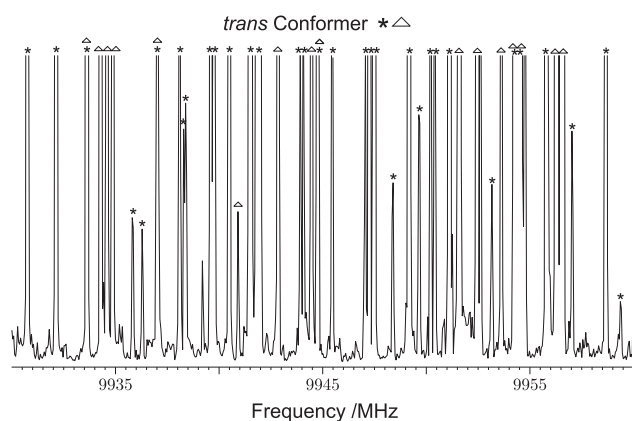
Figure 4. A portion of the observed 3-bromo-1,1,1,2,2-pentafluoropropane spectrum in the range of 9930–9960 MHz. The zoom-in portion illustrates the spectral density observed in many ranges of the spectrum. The [79]Br and [81]Br of the *trans* conformer have been marked with red and green lines, respectively.

package and using the calculated spectroscopic constants of Table 1 as a starting point, but an adequate fit to spectroscopic parameters could not be reached. Reasons for this impasse can be found the *Discussion* section. In addition, no ^{13}C isotopologue spectra in natural abundance were assigned as the spectral density along with the weakness of these species caused considerable problems with transition observation and assignment.

4.1. Near-continuum limit

As shown in Figure 4, the resulting spectrum of 3-bromo-1,1,1,2,2-pentafluoropropane is very dense. The density of the observed species is 1 transition/4 MHz, but there are many remaining unassigned transitions. Overall, the spectral density arising from all transitions is estimated to be on the order of 1 transition/MHz, putting it near the continuum limit, even for such high resolution. The way the authors dealt with this assignment problem is discussed in the next section.

5. Discussion

5.1. Assigning near-continuum spectra

CP-FTMW spectroscopy has changed the paradigm with respect to how rotational spectra are approached. Instead of identifying a system, using sophisticated computational methods, and searching for a particular spectrum, now one will introduce a sample into the spectrometer and identify systems within the resultant broadband spectrum using known spectral catalogues, quantum chemical methodologies, and assignment routines or personal prowess. This is because fast acquisitioning and deep averaging capabilities of the oscilloscopes allow for

many averages of the FIDs produced from each molecular excitation. Since problems of cavity drift and narrowband power regions are eliminated, the deep averaging limit, sample consumption, and time become the only absolute obstacles of the experiment apart from the required possession of a dipole moment and the species be in the gas phase. This is a huge advantage and has led to new methodologies including, but not limited to custom sourcing techniques [31,32], chiral tagging experiments [33], and coherent light experiments with chiral molecules [34,35].

However, these new possibilities also come with some inherent problems. One problem is that of spectral density. CP-FTMW spectroscopy, being a pure rotational spectroscopy technique, produces spectra that are various combinations of rotational constants based on the dipole moments of the molecular system of study. These rotational constants are inversely proportional to the moments of inertia about each principal axis. Furthermore, the intensities of the resultant spectra are governed by the system's statistical mechanics and dipole moment vector components in the principal axis system. As systems become large, rotational constants become small, creating dense spectra that are generally weaker in intensity, making assignment a challenging process. This is particularly true with chiral tagging experiments where the systems are governed by complexation chemistry, size, and number of produced diastereomers. Furthermore, additional angular momenta (like quadrupole coupling nuclei) can further split and spread spectra out making assignment, even with automated routines, a very difficult task.

This is where truly powerful computational methodologies and assignment tools can be of significant use in CP-FTMW spectroscopic techniques. Grimme has done work in this area using DFT methodologies in order to get very accurate rotational constants [36] which has proven useful for large biomolecules like verbenone [37]. 3-bromo-1,1,1,2,2-pentafluoropropane poses a different challenge, though, because it is a large system (possesses 100 electrons and has an atomic mass of 212 amu for the [79]Br isotope) that has two conformers – *trans* and *gauche* – with very different electronic and geometric structures, producing very different sets of rotational constants, NQCC tensors, and dipole moments. These different values produce very different microwave spectra, but a small change in any single parameter is detrimental to achieving a correct assignment. This proved to be problematic when trying to assign the *gauche* conformer because there was no discernable pattern that manifested itself from the predicted spectroscopic constants, even when using iterative values of the rotational and NQCC parameters near (within 200 MHz

above and below) the predicted result. Considering that there are many more variables in assigning the *gauche* conformer, particularly the additional χ_{ac} and χ_{bc} parameters, and the significant predicted dipole moments along each principal axis giving *a*-type, *b*-type, and *c*-type spectra, every change in parameters significantly changed multiple patterns at the same time and this proved to be significantly difficult to make a proper assignment at the near-continuum limit. As the authors know of no automated fit routines that include nuclear quadrupole coupling parameters in their programming, this led to an impasse for moving forward with the *gauche* conformer, but the *gauche* conformer is believed to be present in the spectrum along with other possible systems (complexes, degradation species).

An example of the need for these computational methods is shown in Figure 5 for the[79]Br isotopologue of the *trans* conformer. As pattern recognition schemes are common and have been formulated in the literature for uncoupled rotational spectra, coupled angular momenta pattern schemes are not nearly as obvious or prevalent, making accurate calculations a dire need for the accurate spectral assignment. For the *trans*/[79]Br isotopologue of 3-bromo-1,1,1,2,2-pentafluoropropane, the theoretically predicted spectrum has transitions around 9700 MHz with splitting due to the quadrupole coupling of the bromine nucleus. The corresponding experimental transitions are located about 9630–9640 MHz. Although isolating this pattern in the presence of the other spectra not belonging to the *trans*/[79]Br isotopologue is already challenging, the problem is made much easier because the intensity of the predicted transitions and the spread are nearly identical. Figure 5 also shows what the predicted spectra would be if the calculated χ_{aa} value was 100 MHz less. This spectrum is much more difficult to identify in the experimental spectrum showing that if NQCC values are not accurate, which can be a common problem when calculating bromine and iodine quadrupole coupling constants, they can greatly affect the success of achieving a successful assignment, particularly in situations near the continuum limit.

After the first few assignments, a new prediction can be made by determining intermediate spectroscopic constants through SPFIT and predicting new transition patterns with SPCAT. This new prediction can then be used to add in more transitions and the cycle can be repeated adding in more transitions and appropriate spectroscopic constants until a suitable fit is reached containing as many transitions as observed. Caution must be used here, though, because any small change can, as already discussed, drastically change the predicted spectrum and get the user off track. It is suggested that when dealing with dense spectra, the user try and assign more isolated
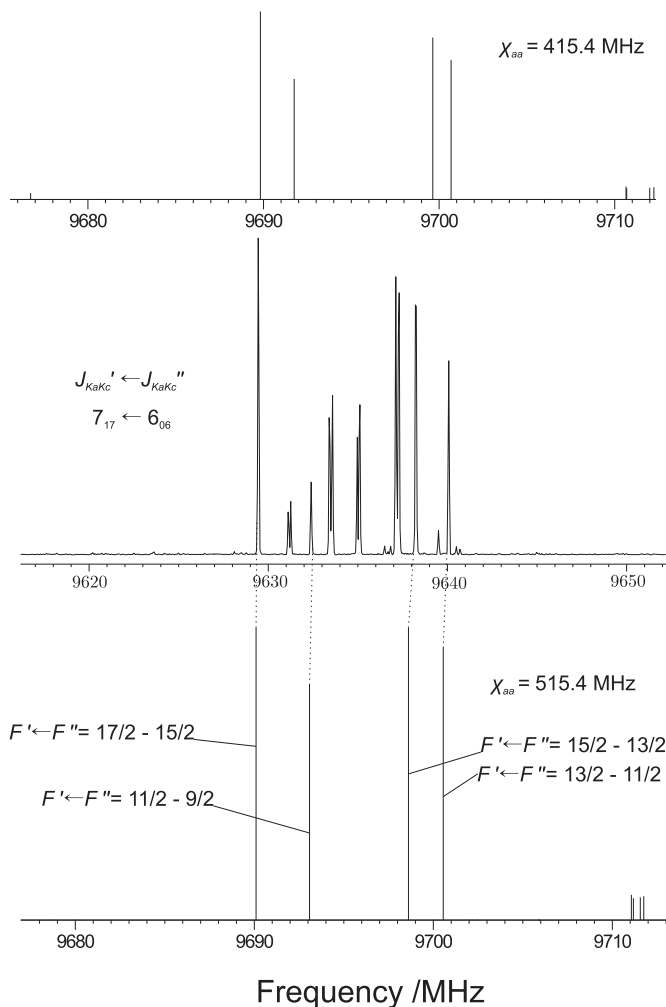
Figure 5. Bottom: Comparison of the predicted spectrum to observed spectrum using the quantum chemically calculated parameters. The pattern is easily picked out and assigned. Top: Reducing only the calculated χ_{aa} value by 100 MHz begins to make assignment problematic.

spectra first as the prediction and experiment will more obviously 'fit' or not 'fit' one another. For *trans*-3-bromo-1,1,1,2,2-pentafluoropropane, the transitions found in Figure 5 were made first and, as more and more transitions were added to a working fit, it was recognised that there existed typical *b*-type, *Q*-branch patterns at approximately 10 GHz which then greatly increased the speed of assignment and ultimately led to the successful fit presented in Table 2.

5.2. Structural parameters for *trans*-3-bromo-1,1,1,2,2-pentafluoropropane

As mentioned in the *Results and Analysis*, no[13]C isotopologue spectra in natural abundance were assigned. However, some structural insights into the molecule can still be made using the spectra that were collected and the predicted structure.

Table 3. Calculated and experimental structural parameters for *trans*-3-bromo-1,1,1,2,2-pentafluoropropane[a]

| | Kraitchman coordinates [38] | | | | | |
| | Theory | | | Experiment | | |
Atom	a	b	c	a	b	c
Carbon (Å)	1.992	0.220	0.000	—	—	—
Carbon (Å)	0.549	−0.322	0.000	—	—	—
Carbon (Å)	−0.464	0.798	0.000	—	—	—
Fluorine (Å)	0.419	−1.100	1.092	—	—	—
Fluorine (Å)	0.419	−1.100	−1.092	—	—	—
Fluorine (Å)	2.865	−0.775	0.000	—	—	—
Fluorine (Å)	2.195	0.971	1.081	—	—	—
Fluorine (Å)	2.195	0.971	−1.081	—	—	—
Hydrogen (Å)	−0.334	1.403	−0.891	—	—	—
Hydrogen (Å)	−0.334	1.403	0.891	—	—	—
Bromine (Å)	−2.256	0.107	0.000	−2.26405(66)[b,c]	0.106(14)	0.00(30)[d]

| | Second moments[e] | |
Parameter	Theory	Experiment
P_{aa} (uÅ^2)	801.4	808.32700(3)[f]
P_{bb} (uÅ^2)	107.6	107.79201(3)
P_{cc} (uÅ^2)	91.3	91.47455(3)

[a]Values presented are for the[79]Br isotopologue.
[b]Numbers in parentheses represent 1σ uncertainty (67% confidence level) and are given in units of the least significant digit.
[c]Kraitchman coordinates do not give sign values, but sign given is from the calculation.
[d]Determined value is imaginary.
[e]Measure of mass distribution about each axis. $P_{ii} = 0.5(I_j + I_k - I_i)$ where each I is a given moment of inertia corresponding to an axis.
[f]Numbers in parentheses are the Costain errors [40].

Table 3 shows a comparison of the calculated coordinates in the principal axis system and second moments to the experimentally determined values. The first piece of evidence showing the calculated structure is close to the experimental one is the fantastic agreement between the calculated coordinates and the experimentally derived Kraitchman substitution coordinates [38]. The values are virtually identical when the sign given by the calculation is assigned to the substitution coordinates and the imaginary value is considered to correspond with a value of 0. Because the bromine is the only atom that we can determine the coordinates of, we can then move to a second moment discussion keeping the placement of the bromine in the principal axis system in mind.

Second moments are a measure of the mass distribution about each axis. They are also referred to as planar moments because they are effectively a measure of the out-of-plane contribution to the mass. This means the out-of-ab-plane mass can be measured by P_{cc}. This is determined to be 91.47455(3) uÅ^2 for the[79]Br isotopologue. Using the second-moment arguments of Bohn [39], the average value for P_{cc} for CF$_2$/CF$_3$ groups is approximately 45 uÅ^2. For CH$_2$/CH$_3$, the average value is 1.6 uÅ^2. Because the molecule has a CF$_2$, a CF$_3$, and a CH$_2$ group (ignoring the bromine which is in the plane), this gives a predicted value based on average second moments of 91.6 uÅ^2, which is closer to the determined P_{cc} value, but overestimates it, than the quantum chemical calculations, which underestimates the value slightly and produced rotational constants to

Table 4. Comparison of bromine-centred χ_{zz} values and electric field gradients of similar molecules.

Molecule	[79]Br χ_{zz} (MHz)	V_{zz} (atomic units)[a,b]	Reference
CH$_3$Br	573[d]	7.79	[41]
	578.847(48)[c,d]	7.87	[42]
CH$_3$CH$_2$Br	541	7.36	[43]
	537.5[e]	7.31	[44]
(CH$_3$)$_2$CHBr	514.2(5)	6.99	[45]
gauche-CH$_3$CH$_2$CH$_2$Br	526.4	7.16	[46]
anti-anti-CH$_3$(CH$_2$)$_2$CH$_2$Br	543.45(32)	7.39	[47]
CH$_2$FBr	554.52(38)	7.54	[48]
CHF$_2$Br	564.14(12)	7.67	[49]
CF$_3$Br	618.2(3)[d]	8.41	[50]
CF$_3$CF$_2$Br	611.459(96)	8.31	[12]
CF$_3$COCF$_2$Br	595.4(5)	8.10	[13]
trans-CF$_3$CF$_2$CH$_2$Br	620.839(7)	8.44	This work

[a]Electric field gradient atomic unit is E_h/ea_0^2 where E_h is the hartree, e is the charge on the electron, and a_0 is the Bohr.
[b]$V_{zz} = \chi_{zz}/(234.9647Q)$, where χ_{zz} is in MHz and Q is 0.313 barn (10^{-28}m^2) as reported in reference [18].
[c]Numbers in parentheses represent reported uncertainties and are given in units of the least significant digit. Reported numbers without parentheses were not reported with error.
[d]Reported as eQq in the literature.
[e]Reported as eQq_{bond} in the literature.

within 1% of experimentally determined values. This is further evidence that the presented calculated structure is close enough to the experimental structure to be considered as a very suitable substitute.

5.3. Dipole-forbidden/nuclear electric quadrupole coupling allowed transitions

The spectra contain multiple dipole-forbidden transitions. These are transitions which have $\Delta J > 1$ or

Dipole Forbidden Transition

$J_{K_aK_c} F' \leftarrow J_{K_aK_c} F''$

8_{18} 17/2 $\leftarrow$ 6_{25} 15/2
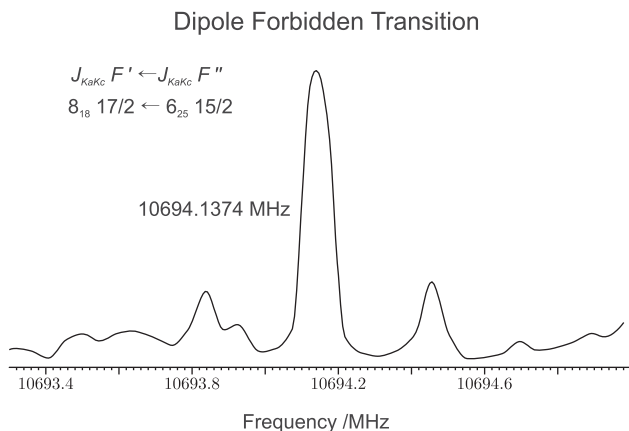
10694.1374 MHz

Figure 6. Example of an observed dipole-forbidden transition at 10,694.1374 MHz.

transitions where neither K_a nor K_c have a change in parity. An example of an observed transition is given in Figure 6. As mentioned in previous literature, these transitions arise from 'large' off-diagonal nuclear quadrupole coupling tensor components when compared to rotational constants. The facilitator of the observed *trans* forbidden transitions is completely due to χ_{ab}. That is, the value of χ_{ab} is large enough in comparison to the rotational constants in the *trans* conformer in order to create a mixing of allowed transition states to bring about a dipole-forbidden transition.

This was investigated for the case of the transition observed in Figure 6, $J'_{K_aK_c} \leftarrow J''_{K_aK_c}, F' \leftarrow F'' = 8_{18} \leftarrow 6_{25}, \frac{17}{2} \leftarrow \frac{15}{2}$ which occurs at 10,694.1374 MHz. A flag can be enacted in SPFIT/SPCAT that will create a file with the extension .egy. Within the .egy file, the quantum states with their calculated energy levels are presented along with a mixing coefficient that can be associated with the 'purity' of the state. The further this value is from unity, the more the state is mixed. It is found that the $6_{25}, \frac{15}{2}$ level has a mixing coefficient of 0.897 while the $8_{18}, \frac{17}{2}$ level is near unity, indicating the $6_{25}, \frac{15}{2}$ level is the one that is mixing. Upon inspection of the file, there is a state within 30 MHz of the $6_{25}, \frac{15}{2}$ level with the quantum numbers $7_{07}, \frac{15}{2}$ also with a mixing coefficient of 0.897. When the assigned transitions are looked at, there is an allowed, observed transition with $J'_{K_aK_c} \leftarrow J''_{K_aK_c}, F' \leftarrow F'' = 8_{18} \leftarrow 7_{07}, \frac{17}{2} \leftarrow \frac{15}{2}$ at 10717.7769 MHz, approximately 23 MHz higher in energy, indicating this is the forbidden transition pathway. This is unique because this would mean that this forbidden transition is brought about by a *x*-type change in parity which, to the author's knowledge, has never been indicated as a mechanistic pathway in the literature. However, there is no evidence suggesting there is another pathway for the transition to be brought about as the $7_{07}, \frac{15}{2}$ energy level is the only

state near the energy of the $6_{25}, \frac{15}{2}$ with a coefficient indicating mixing, so this must be the formal pathway and the two states must be so close in energy that they are essentially degenerate. This *x*-type linkage could prove to be a powerful tool in understanding the necessity of the dipole moment in creating and tuning forbidden transitions in the future, but this area is unexplored and would need more investigation.

6. Conclusions

The microwave spectrum of *trans*-3-bromo-1,1,1,2,2-pentafluoropropane has been observed and analysed for the first time using CP-FTMW spectroscopy. Two isotopologues,[79]Br and [81]Br have been observed, assigned, and reported. The spectrum is quite dense and near the continuum limit with an estimated density of approximately 1 transition/MHz with 1 transition/4 MHz representing the *trans* conformer alone. The spectra are predominantly *b*-type due to the large predicted *b* dipole moment vector component. The spectra were assigned using a combination of sophisticated theoretical and assignment approaches which are greatly needed in order to find any patterns in the spectra and small differences can lead to an unsuccessful assignment like what is found with the current state of the *gauche* conformer.

Analysis of the spectrum indicates that the experimental structure is very close to that of the calculated structure as expected since so much care was taken to ensure a suitable starting geometry for assignment, but that this conclusion can be aided with the spectroscopic constants determined even though a full substitution structure is not present. Furthermore, the large determined χ_{ab} component for the *trans* conformer does generate forbidden transitions but, uniquely, it has produced the first such transition known to the authors of a *x*-type linkage in the forbidden transition pathway due to a very near-degeneracy which could lead to the future study of the necessity of the electric dipole moment with respect to the energy differences.

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