



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 HCBBr_3 and four DCBr_3 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 HCBBr_3 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 CH_2I_2 was only assigned in 1996 [1], and the hyperfine structure of CHCl_3 was assigned even more recently, in 2006 [2]. The rotational spectrum of the bromoform molecule, HCBBr_3 (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 ^{79}Br and ^{81}Br isotopes have comparable natural abundance, so that this compound will consist of a mixture of four equally abundant isotopic species. Two of those, $\text{HC}^{79}\text{Br}_3$ and $\text{HC}^{81}\text{Br}_3$, are oblate symmetric top species of C_{3v} symmetry, whereas the remaining two species, $\text{HC}^{79}\text{Br}_2^{81}\text{Br}$ and $\text{HC}^{79}\text{Br}^{81}\text{Br}_2$, are oblate asymmetric tops of C_s symmetry, in

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 ($\mu_c \approx 1\text{D}$, [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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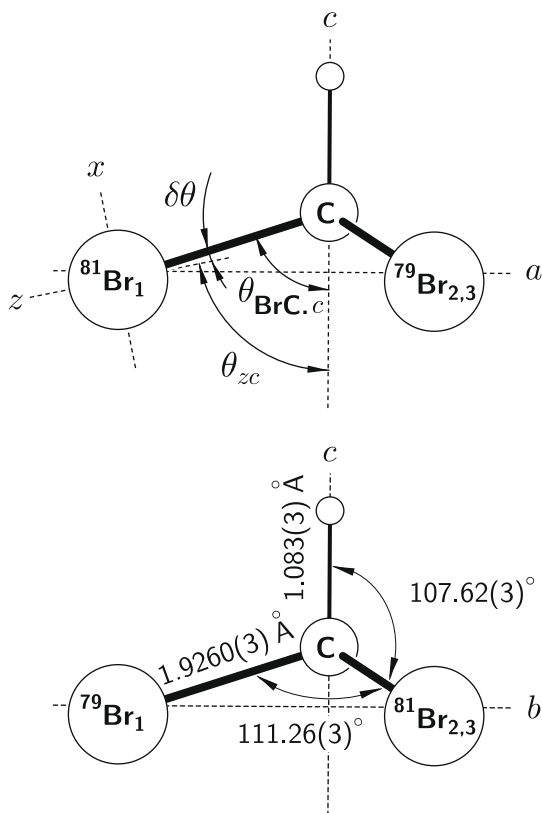


Fig. 1. The orientation of the bromoform molecule in the inertial axes. In the symmetric top and the $^{79}\text{Br}_2^{81}\text{Br}$ species there is a bromine atom in the ac inertial plane (top), while in the $^{79}\text{Br}^{81}\text{Br}_2$ species the unique bromine atom is positioned in the bc inertial 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 CBr_1 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 μs . 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

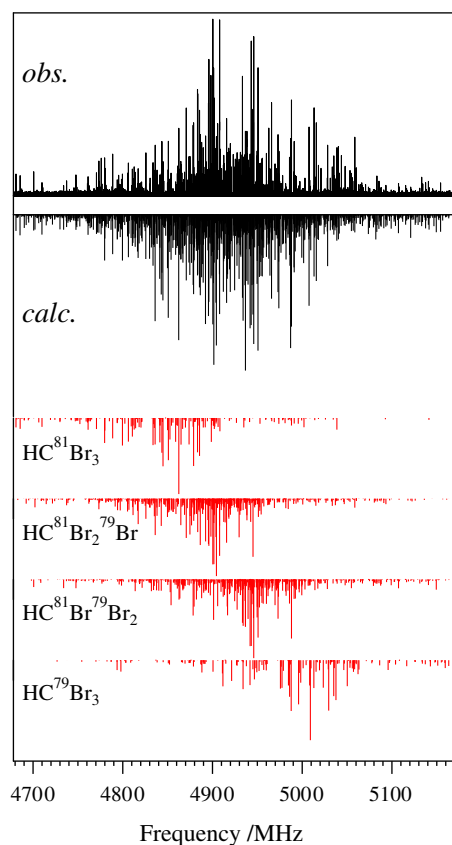


Fig. 2. Comparison of the chirped-pulse Fourier transform microwave spectrum of the complete $J=2 \leftarrow 1$ transition of HCB_r3 with calculation based on final fitted constants. The nuclear quadrupole hyperfine splitting patterns of the different bromine isotopic species overlap to such an extent 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 HCB_r3 and DCB_r3 were obtained by FFT of time-domain signals averaged over 2×10^5 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 HCB_r3 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 HCB_r3 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 $\text{S}(\text{CN})_2$ [19] and ClONO_2 [20].

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