ASSIGNMENT AND ANALYSIS OF THE ROTATIONAL SPECTRUM OF BROMOFORM ENABLED BY BROADBAND FTMW SPECTROSCOPY

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The rotational spectrum of the bromoform molecule, $HCBr_3$, was first studied well over half a century ago in two different laboratories.[a,b] Their results led to two different sets of rotational constants, which were difficult to reconcile[c] and no further studies have been reported since then. This is not surprising, in view of the difficulties in the analysis arising from the presence of four isotopic species of comparable abundance and of complex nuclear hyperfine structure due to the three bromine nuclei. Furthermore, in the lowest J transitions the hyperfine structure of the four different bromine isotopologues of $HCBr_3$ is completely overlapped.

These difficulties were overcome by recording the rotational spectrum at conditions of supersonic expansion with the new version of the broadband FTMW spectrometer developed in Virginia. The spectrometer operates in a simple configuration with direct chirped pulse generation and direct FID digitization, and allows acquisition of complete 2-8.5 GHz spectra. The spectrum of bromoform was averaged over 200k pulses and was assigned and fitted to experimental accuracy using the AABS package[d] for *Assignment and Analysis of Broadband Spectra* and the SPFIT program.[e] Additional measurements were made with the Balle-Flygare type FTMW spectrometer, and in the millimeter-wave region, and the detailed results obtained for four isotopic species of $HCBr_3$ and four isotopic species of $DCBr_3$ bromoform are presented.

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[a] S. Kojima et.al., *J. Chem. Phys.*, **20**, 804-808 (1952).

[b] Q. Williams, J. T. Cox, W. Gordy, *J. Chem. Phys.*, **20**, 1524-1525 (1952).

[c] G. Herrmann, *J. Chem. Phys.*, **22**, 2093L (1954); S. Kojima, K. Tsukada, *ibid.*, 2093-2094L.

[d] Z. Kisiel, AABS package, *available at* http://info.ifpan.edu.pl/~kisiel/prospe.htm.

[e] H. M. Pickett, SPFIT/SPCAT package, *available at* http://spec.jpl.nasa.gov.