The Rotational Spectra of Dibromodifluoromethane

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Abstract Dibromodifluoromethane (CBr2F2), a molecule with a potential four-fold internal rotor, has been studied by the Novick group using high resolution Fourier-transform microwave (FTMW) spectroscopy. This project is a continuation of existing research of other molecules involving hydrogen and halogen sources, including H_2 MOF and CF_3I. The research was designed to prove that Dibromodifluoromethane could serve as the bromine source for Silver bromide (AgBr) and Dihydrogen silver bromide (H2AgBr) but examining the rotational transitions of its Carbon-12 parent isotopes and Carbon-13 isotopes has produced an interesting study of the Fluorine monomer.

Introduction This project was created to address a need for a reliable Bromine source for studies of Ar-AgBr and H_2 AgBr. Earlier studies of H_2 in H_2 MOF and Cl_2 as the chlorine source in several experiments demonstrated deficiencies in H_2 and Cl_2. However, success using CF_3I to generate AgI prompted us to consider using Dibromo - difluoromethane (CBr_2F_2) as our bromine source. (**Fig. 1**)

Experimental Samples were prepared of <1% CBr_2F_2 in tanks of high purity, dry Argon, which was used as a backing gas in supersonic expansion into the vacuum chambers of our spectrometer, a Balle-Flygare cavity Fourier transform microwave (FTMW) spectrometer. (**Fig. 2**) 0.2 ml of CBr_2F_2 was placed in the gas line behind the nozzle and over 300 transition frequencies of the parent isotopes (Carbon-12 isotopes: 79_79, 79_81, 81_81) were observed using this setup. We analyzed the recorded frequencies using programs such as **ascp_l**, **SPFIT**, and **SPCAT** to fit the rotational spectra and assign the torsional state rotational transitions. (**Fig. 3**)

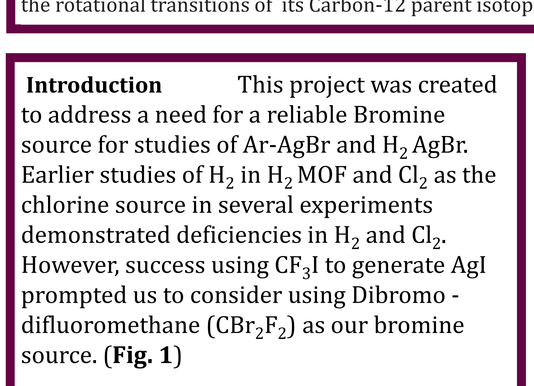
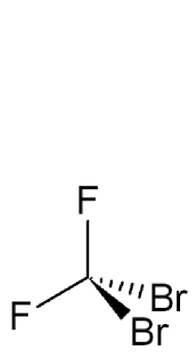


Figure 2. Balle-Flygare cavity Fourier transform microwave spectrometer (Enrico)



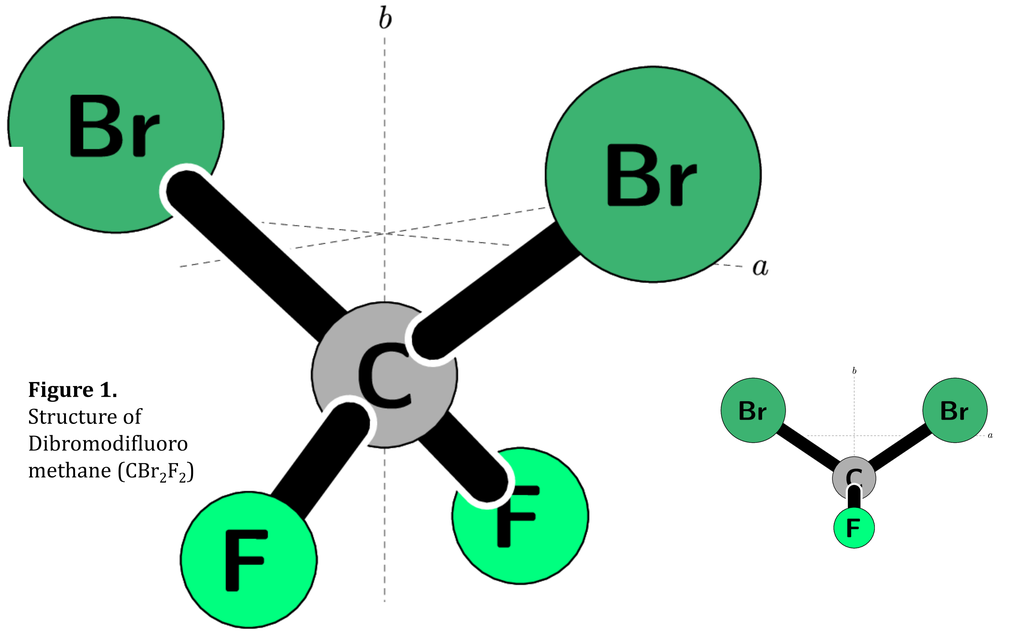
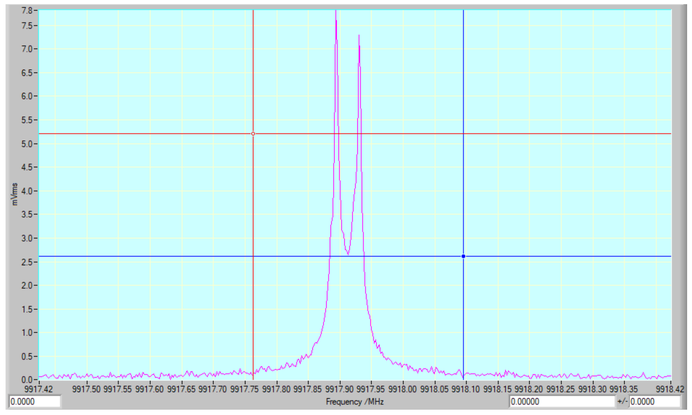


Figure 1. Structure of Dibromodifluoro methane (CBr_2F_2)

Figure 4. Sample Transition of the $^{12}C^{79}Br_2F_2$ Parent Isotopomer



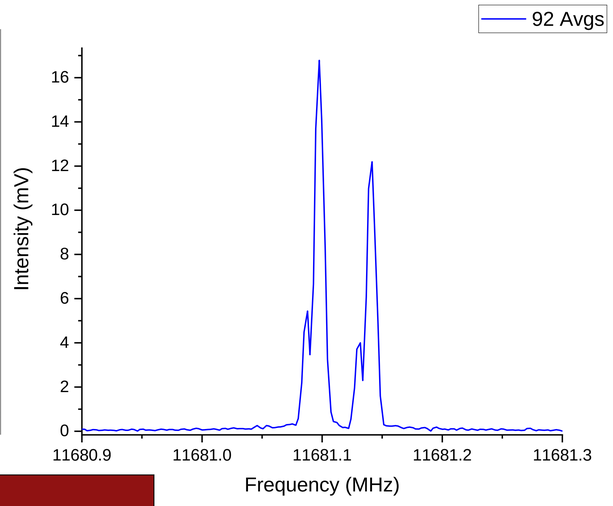


Figure 5. Sample Transition of the $^{12}C^{79}Br_2F_2$ Parent Isotopomer Reduced Signal to Noise

	^{79}Br-^{79}Br	^{19}F-^{19}F	^{79}Br-^{19}F
D_{aa} (kHz)	-0.41	11.47	-0.10
D_{bb} (kHz)	0.21	11.47	-0.62
D_{cc} (kHz)	0.21	-22.95	0.72

Figure 6. Predicted form DFT optimized structure and reported g-factors

Discussion In keeping with theory used in earlier studies involving Halogen sources, we approached CBr_2F_2 as a potential source of AgBr in ablative expansion. By using this molecule, the Novick Group hoped to avoid corrosive reactions in the lab's flow controllers produced by the mixing of gases during the experiment. *Ab initio* calculations were carried out to determine the bond angles of CBr_2F_2 and estimate the barrier to internal rotation. We have fits of the $^{12}C^{79}Br_2F_2$, $^{12}C^{81}Br_2F_2$, and $^{12}C^{79}Br^{81}BrF_2$, with over 100 lines in each fit to better than 7 kHz rms. (**Fig. 4, Fig. 5**) The structure of dibromo -difluoromethane is such that only the four bond lengths and bond angles of the bromine carbon bonds and isotopic information of ^{12}C and ^{13}C give more data than is usually necessary to evaluate the molecule. However, Fluorine is still present in additional splitting in some of the higher-intensity Carbon isotope transitions.

Conclusion While our initial experiment determined that CBr_2F_2 was not a good alternate source of bromine to make AgBr, our work has produced rather interesting results about the monomer. Via examination of the () we confirmed that, out of all the predicted spin-spin and spin-rotation interactions, only spin-spin of ^{19}F-^{19}F has the correct magnitude to cause this splitting. (**Fig. 6**) The Novick Lab does not usually work with large enough magnetic fields to observe such behavior and will continue to measure the Carbon-13 isotopologues to expand our results.

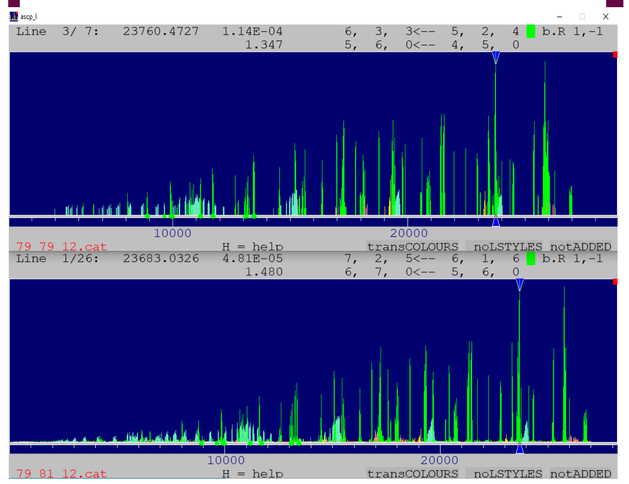


Figure 3. Carbon-12 transitions for the 79_79 (above) and 79_81 (below) isotopes of CBr2F2 in **ascp_l**, a fitting program (colors assigned to each isotope).

References

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