

Microwave Spectrum, Structure, and Dipole Moment of Ethynyldifluoroborane, $\text{H-C}\equiv\text{CBF}_2$

By WALTER J. LAFFERTY* and J. J. RITTER

(National Bureau of Standards, Washington, D.C. 20234)

Summary The structure and dipole moment of ethynyldifluoroborane have been determined from a study of its microwave spectrum.

A SYNTHESIS and characterization of the ethynyldifluoroborane molecule is reported above.¹ Only small amounts of sample have been produced to date. Because of this, only a limited number of physical measurements was possible. This work was undertaken with the objective of obtaining as much structural information from the microwave spectrum as possible.

The sample used in this study was prepared by Ritter *et al.*¹ A conventional Stark modulated spectrometer was used, and the spectra were all obtained at dry-ice temperature. Despite the fact that the waveguide was pre-conditioned with BF_3 for 16 hr. prior to use, the sample of ethynyldifluoroborane decomposed rapidly in the brass waveguide; the half-life of the sample in the guide was about 1 min. This fact imposed a serious limitation on the study since only 1.5 cm.³ of gas at S.T.P. of the sample was available.

Because of the sample limitations only the strong lines in the 18,000–33,000 MHz. region were recorded. A

typical *A*-type spectrum of a near prolate rotor was observed and this spectrum was easily assigned on the basis of the Stark effect of the individual lines. About 15 lines were assigned for the ground state of the ^{11}B species and about 10 for the less abundant ^{10}B species. In addition, six satellite lines from the first excited vibrational state of the ^{11}B species were assigned. Both boron nuclei have quadrupole moments, but no quadrupole hyperfine structure was resolved, although most of the lines broadened.

distance is the same as in HBF_2 ,³ one calculates $\angle\text{FBF} = 118.2^\circ$ and $r_{\text{B-C}} = 1.53 \text{ \AA}$. Errors in these parameters are difficult to estimate. The bond distance, however, is probably accurate to within $\pm 0.02 \text{ \AA}$ and the angle to within $\pm 1^\circ$. The boron-carbon bond length then is not significantly different from that found⁴ for BH_3CO ($r_{\text{B-C}} = 1.540 \text{ \AA}$); the angle is virtually identical to that found for HBF_2 .

Measurements of the Stark effect displacements of the

Rotational constants (MHz.) and moments of inertia (Amu \AA^2) of $\text{H-C}\equiv\text{C-BF}_2$

	$\text{H-}^{12}\text{C}\equiv\text{}^{12}\text{C-}^{10}\text{B}^{19}\text{F}_2$ (ground state)	$\text{H-}^{12}\text{C}\equiv\text{}^{12}\text{C-}^{11}\text{B}^{19}\text{F}_2$ (ground state)	$\text{H-}^{12}\text{C}\equiv\text{}^{12}\text{C-}^{11}\text{B}^{19}\text{F}_2$ (ν_9)
<i>A</i>	10507.4 ± 2.8^a	10509.2 ± 2.7	10397.4 ± 5.9
<i>B</i>	3670.56 ± 0.06	3666.65 ± 0.06	3684.45 ± 0.20
<i>C</i>	2715.52 ± 0.04	2713.50 ± 0.06	2717.26 ± 0.15
I_a	48.112 ± 0.014	48.104 ± 0.014	48.622 ± 0.030
I_b	137.726 ± 0.002	137.873 ± 0.002	137.209 ± 0.014
I_c	186.164 ± 0.004	186.302 ± 0.004	186.047 ± 0.010
Δ	0.323 ± 0.015^b	0.326 ± 0.015	0.216 ± 0.035

^a Uncertainties cited are twice standard deviations.

^b $\Delta = I_c - I_a - I_b$.

The Table gives the rotational and inertial constants obtained for the ground state of both isotopic boron species as well as the constants obtained for the lowest vibrational state of the ^{11}B species. The following structural information can be deduced from the microwave spectrum: (1) The molecule studied apparently contains but one boron atom, since only two sets of lines originating from the ground state were observed. (2) The boron atom must be located on the *A* axis of the molecule since I_a is not significantly different for the two isotopic species. (3) A distinct intensity alternation is observed—transitions between states symmetric to a rotation about the *A* axis are roughly one-third of the intensity expected for them when compared with transitions between states asymmetric to rotation about the *A* axis. Therefore, an off-axis pair of equivalent nuclei with spin $\frac{1}{2}$ must be present in the molecule. (4) The small positive inertial defect ($\Delta = I_c - I_a - I_b$) reported in the Table indicates that the molecule is planar. (5) The moment of inertia of HBF_2 about the molecular symmetry axis² ($48.1608 \text{ Amu \AA}^2$) is almost identical to I_a in $\text{BF}_2\text{C}_2\text{H}$. This is strong evidence that the off-axis nuclei are fluorine atoms and that the BF_2 group has nearly equivalent geometry in both molecules.

This evidence indicates that the molecule has C_{2v} symmetry, *i.e.* that the boron is co-linear with the ethynyl group and that the two off-axis fluorines are symmetrically placed.

The two isotopic species studied are insufficient to determine the structure of the molecule completely. If, however, one assumes that the $\text{C}\equiv\text{C}$ and C-H bond lengths are unchanged from those in C_2H_2 ² and that the B-F bond

$4_{22} \leftarrow 3_{21}$ line of the ^{11}B isotopic species were made in the strong field limit. The waveguide spacing was calibrated using OCS as a standard.⁵ The dipole moment (and 2σ uncertainty) obtained for HC_2BF_2 , $1.93 \pm 0.06 \text{ D}$, can be compared with 0.971 D for HBF_2 ² and 1.67 D for CH_3BF_2 .⁶

An estimate of the lowest vibrational frequency of the molecule can be made by measuring the relative intensities of the vibrational satellite lines compared with the lines arising from the ground state. The lowest vibration in HC_2BF_2 is an in-plane skeletal bending mode of symmetry B_1 and the nuclear spin weighting is reversed from that of the ground state. The ratio of the relative intensities of the ground state to the intensity of the vibrational satellite was measured for the $5_{05} \leftarrow 4_{04}$ transition. For this transition the ground state has a nuclear spin weighting of one; the vibrational satellite line has a weighting of 3. The measured ratio of the intensity of the satellite line to that of the ground state was 1.03 ± 0.20 which leads to a value of $150 \pm 80 \text{ cm.}^{-1}$ for the in-plane bend. The large uncertainty in the frequency results from difficulty in the intensity comparisons because of the rapid sample decomposition.

When more sample becomes available we intend to extend our study to lower *J* values in order to obtain the boron nuclear quadrupole coupling constants. We hope, also, to study additional isotopic species in order to obtain an improved structure.

This work was supported in part by the Division of Research, U.S. Atomic Energy Commission.

(Received, June 18th, 1969; Com. 872.)

¹ J. J. Ritter, T. D. Coyle, and J. M. Bellama, preceding communication.

² W. J. Lafferty and R. J. Thibault, *J. Mol. Spectroscopy*, 1964, **14**, 79.

³ T. Kasuya, W. J. Lafferty, and D. R. Lide, *J. Chem. Phys.*, 1968, **48**, 1.

⁴ W. Gordy, H. Ring and A. B. Burg *Phys. Rev.* 1950, **78**, 512.

⁵ J. S. Muentzer, *J. Chem. Phys.*, 1968, **48**, 4544.

⁶ R. E. Naylor, jun., and E. B. Wilson, jun., *J. Chem. Phys.*, 1957, **26**, 1057.