

# Avoided-crossing molecular-beam experiments on fluoroform (CF<sub>3</sub>H) and fluoroform-*d* (CF<sub>3</sub>D)

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The avoided-crossing molecular-beam method for studying normally forbidden ( $\Delta K \neq 0$ ) transitions in symmetric tops has been applied to fluoroform (CF<sub>3</sub>H) and fluoroform-*d* (CF<sub>3</sub>D), thus marking the extension of the method to systems which are *not* near spherical rotors. In order to reach the high electric fields required while still retaining the necessarily narrow linewidth, the electric resonance spectrometer has been equipped with a new pair of Stark plates capable of providing electric fields up to about 20 kV/cm with a homogeneity of 1 part in 10<sup>5</sup> over a length of 3 cm. The anticrossing ( $J, K$ ) = (1, 0) ↔ (1, ±1) has been studied for both CF<sub>3</sub>H and CF<sub>3</sub>D. In each case, the rotational constant  $C_0$  along the symmetry axis has been obtained to 0.002%. From anticrossing spectra observed in combined electric and magnetic fields, the signs of the rotational  $g$  factors  $g_{\parallel}$  and  $g_{\perp}$  have been shown to be negative. From a conventional molecular beam study for each isotopic species, a value of the permanent electric dipole moment accurate to 60 ppm was determined and improved values of  $g_{\parallel}$  and  $g_{\perp}$  were obtained. The direction of the electric dipole moment is shown by two methods to be +HCF<sub>3</sub>-. A brief discussion of the difficulties in these methods is given.

## I. INTRODUCTION

A simple avoided-crossing technique has recently been developed<sup>1-3</sup> that allows for a direct measurement of the rotational constant along the symmetry axis in a symmetric top molecule. The normal selection rule ( $\Delta K = 0$ ) for pure rotational transitions in symmetric rotors in the ground vibronic state is broken by applying an appropriate electric field  $\epsilon$ . If this field is chosen such that the difference in Stark energies between the two levels under study exactly cancels the rotational splitting to be measured, then the separation between the two levels will be a minimum. This particular value of  $\epsilon$  is called the crossing field  $\epsilon_c$ . If the two levels have a coupling matrix element, the minimum separation is nonzero and the two levels undergo an avoided crossing. Under certain conditions,<sup>3</sup> this anticrossing can be detected with a molecular-beam electric-resonance (MBER) spectrometer. From measurements of  $\epsilon_c$  and the electric dipole moment  $\mu$ , the rotational splitting can be obtained.

This method has been successfully applied in the past to OPF<sub>3</sub><sup>1,3</sup> and to CH<sub>3</sub>CF<sub>3</sub>.<sup>2</sup> However, both of these molecules are virtually ideally suited to the anticrossing technique. Each is a near spherical top so that the rotational splitting  $\Delta_{\text{ROT}}$  is small. Furthermore, each has a large value for  $\mu$ . Since  $\epsilon_c \propto \Delta_{\text{ROT}}/\mu$ , only moderately high electric fields of up to 3 kV/cm were required.

For a more general symmetric rotor which still has  $\mu \sim 1$  D but in which  $\Delta_{\text{ROT}}$  is typically several GHz, the smallest electric field required to observe an avoided crossing is  $\geq 10$  kV/cm. There are no serious technical problems in obtaining fields even as large as 200 kV/cm at the low pressures in a MBER spectrometer. However, in order to observe the anticrossings, the homogeneity over a region a few centimeters long must typically be better<sup>3</sup> than 1 part in 10<sup>4</sup>. An increase in

the homogeneity by as much as a factor of 10 will usually improve considerably the accuracy of the rotational constant obtained. A parallel plate system has been constructed which meets the field strength and homogeneity requirements for a broad range of symmetric rotors. A method was developed to stabilize and calibrate the electric field strength to sufficient accuracy.

With the improved spectrometer, a study was carried out of the avoided crossing ( $J, K$ ) = (1, 0) ↔ (1, ±1) in fluoroform (CF<sub>3</sub>H) and fluoroform-*d* (CF<sub>3</sub>D). The  $C_0$  rotational constants in each molecule were determined to an accuracy of 0.1 MHz out of 5.67 GHz. From anticrossing spectra observed in combined electric and magnetic fields, it was established *experimentally* that the two molecular  $g$  factors ( $g_{\parallel}$  and  $g_{\perp}$ ) are negative. From conventional MBER measurements, the electric dipole moment for each isotopic species was measured to 6 parts in 10<sup>5</sup>.

The direction of the dipole moment was determined experimentally by two methods. The first is based on the sign of the change in  $|\mu|$  upon deuteration. The second is based on the change in ( $g_{\perp}/B_0$ ) upon deuteration. Both methods yield the same direction for  $\mu$ , namely, +HCF<sub>3</sub>-, and this direction agrees with what one would expect on the basis of general chemical arguments. In spite of this, both methods must be treated with care; a brief discussion is given of some of the difficulties.

In order to apply the ( $g_{\perp}/B_0$ ) method of determining the sign of  $\mu$ , more accurate values for the molecular  $g$  factors in CF<sub>3</sub>H and CF<sub>3</sub>D were required than are presently available in the literature. Improved values for  $g_{\parallel}$  and  $g_{\perp}$  were obtained for both CF<sub>3</sub>H and CF<sub>3</sub>D from a study of the normal MBER Zeeman spectrum. The molecular quadrupole moment  $\theta_{\parallel}$  was recalculated for CF<sub>3</sub>H.

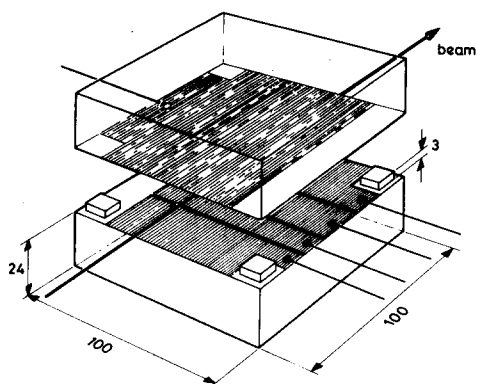


FIG. 1. The Pyrex C field used to observe the anticrossing transitions in fluoroform. Only the shaded surfaces are coated with the aluminium gold layer. The dimensions are in mm.

## II. EXPERIMENTAL

The experimental methods and conditions were very similar to those used in our earlier studies of  $\text{OPF}_3$ .<sup>3,4</sup> The seeded beam technique was used to concentrate the population in the lower rotational levels. A mixture of 4% fluoroform in argon was expanded through a  $40\ \mu\text{m}$  nozzle at a backing pressure of 1.0 bar with the source held at room temperature. The beam velocity was  $\sim 550\ \text{m/s}$  and the beam rotational temperature was  $\sim 5\ \text{K}$ . Commercial gases were used. The  $\text{CF}_3\text{H}$  and  $\text{CF}_3\text{D}$  beams were monitored at the ion peaks with mass-to-charge ratios of 51 and 52, respectively.

The basic MBER apparatus has been described in detail elsewhere.<sup>5</sup> In the remainder of this section, the discussion will be confined to the generation, stabilization, and calibration of an electric field with the required strength, homogeneity, and stability. In earlier avoided-crossing work,<sup>1-3</sup> the C field consisted of two 30 cm diameter optically flat quartz plates coated with a semitransparent layer of aluminium and gold and separated by 6 mm thick spacers. The maximum useful field was  $\sim 3\ \text{kV/cm}$ ; at higher field strengths, the coating deteriorated rapidly and irreversibly, giving unacceptably poor homogeneities.

To overcome this problem, the C field condenser shown in Fig. 1 was constructed. The quartz substrate was replaced by Pyrex because the aluminium gold film on such a surface is extremely stable, even at rather high electric fields. The two optically flat Pyrex plates were manufactured by the Van Keuren Company with one surface of each plate being ground to an accuracy of 100 nm concave. Each ground surface was coated with an aluminium gold film with an optical transmission of about 10%. The thickness of this film was between 10 and 20 nm. The coated surfaces were separated with four 3 mm thick optical flats.

After the plates were mounted together, the parallelism of the coated surfaces was checked with the aid of Haidinger fringes in reflected sodium light. The distance variation over the beam path through the entire condenser could be reduced to less than one quarter of a wavelength (150 nm) by applying small clamping forces to the plates. Considerable improvement in the line-

width could be obtained, however, by using only a small part of the surface to drive the transitions. For this reason, the coating on the lower plate was divided into four sections. The best results were obtained by applying the rf radiation to a section 30 mm long.

An anticrossing transition in  $\text{CF}_3\text{H}$  using this section is shown in Fig. 2. The observed full width at half-height of 48 kHz is dominated by the inhomogeneity, because the linewidth due to time of flight is 15 kHz and hyperfine broadening is  $\leq 20\ \text{kHz}$  (see Sec. IV). Since the Stark effect for this anticrossing has a magnitude of 4.7 GHz, the inhomogeneity is  $\leq 10\ \text{ppm}$ . In spite of the narrow linewidth, large regions can be searched rather quickly. In favorable cases, a search over an interval of a few hundred MHz is not prohibitive. It should be pointed out that a design based on two simple metal plates is not suitable for this application. The semitransparent property is essential for the optical adjustment of the plates.

In the earlier studies,<sup>1-3</sup> the voltage applied to the C field was taken from two power supplies, a Fluke #335A and a Fluke #332A, each having a long term stability of  $\sim 2$  in  $10^5$  and a short term stability of  $\sim 2$  in  $10^6$ . With the two in series, the maximum potential difference was 2100 V. To attain the high voltages required here, it was necessary to use a supply with poorer specifications; a Fluke #408B (0 to 6 kV) was selected. For this supply, the manufacturer guarantees the stability and absolute voltage to only 200 ppm (1 MHz for a 5 GHz Stark shift). Since this limit is much too high, the simple measuring and stabilization system shown in Fig. 3 was used. This, in effect, locks the voltage  $V_c$  across the C field to the voltage setting

$J=1\ K=0 \leftrightarrow \pm 1$   
anticrossing in  $\text{CF}_3\text{H}$

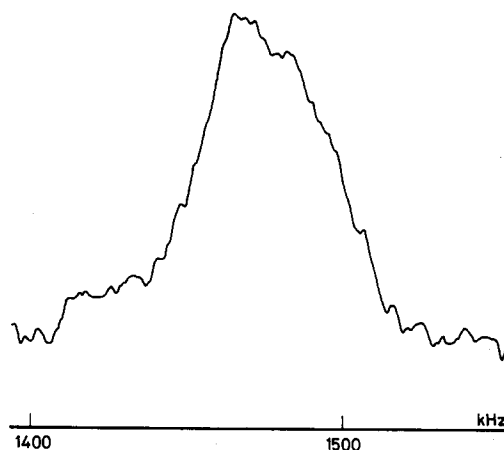


FIG. 2. Spectrum of the hyperfine anticrossing in  $\text{CF}_3\text{H}$ . Because it was observed in the Earth's magnetic field, this is a hybrid of  $(m_J = \pm 1 \leftrightarrow \mp 1)$  and  $(m_J = \pm 1 \leftrightarrow \pm 1)$ . The recorded trace was taken just below the crossing field at  $\epsilon = 11\ 058\ \text{V/cm}$  in a single sweep with a time constant of 2 s. The full width at half-height is 48 kHz.

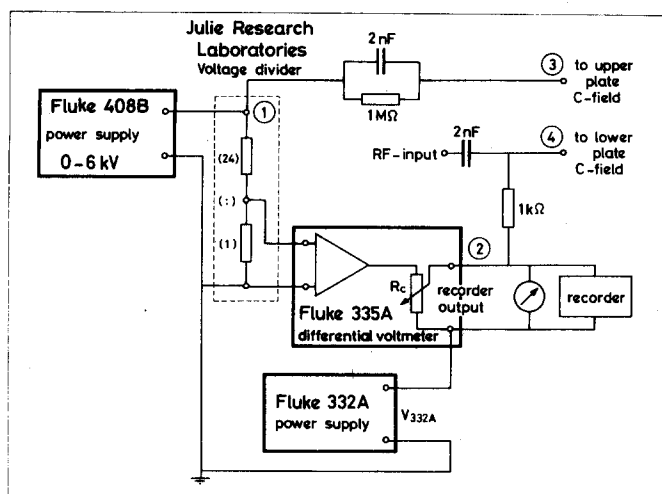


FIG. 3. Block diagram of the circuit used to generate, stabilize, and measure the dc voltage applied to the C field. The long term stability is  $\sim 2$  in  $10^5$  and the short term stability is  $\sim 2$  in  $10^6$ .

$V_{335A}$  of the Fluke #335A unit, now run as a differential voltmeter.

The operation of the system is most easily understood by initially assuming that the output of the Fluke #332A is fixed at zero, thereby grounding the one terminal of the recorder output of the #335A. The low voltage plate of the C field is then lifted off ground by an amount determined only by this recorder output. (The sole function of  $V_{332A}$  is to provide an additional offset in the "splitting method" described below.) The voltage  $V_{408B}$  applied to the upper plate of the C field by the #408B supply is measured using a Julie Research Laboratories precision voltage divider and the #335A differential voltmeter. The gain of the recorder output is adjusted with  $R_c$  so that any change  $\Delta V_1$  in  $V_{408B}$  results in an equal voltage change  $\Delta V$  being applied to the lower C-field plate. Thus, the voltage across the C field (i.e., between points 3 and 4 in Fig. 3) is held constant. The stabilization loop is capable of compensating up to  $\pm 500$  mV with a linearity better than 1% of  $\Delta V_1$ . Because  $V_{408B}$  typically drifted only 50 ppm in a 1 h period with no serious higher frequency variations, this simple loop was more than adequate. The specifications on the voltage divider are such that the stability of  $V_c$  is entirely determined by the differential voltmeter. Thus, this high voltage system is as good as the low voltage arrangement mentioned earlier.

The calibration of the C field here follows a procedure similar to that used for OPF<sub>3</sub>.<sup>3</sup> The electric field  $\epsilon = \kappa V_{335A}/d$ , where  $\kappa$  is the ratio of the voltage divider ( $\kappa \sim 25$ ) and  $d$  is the separation of the plates. The Stark shift  $\Delta_{ST}$  is a function of  $\mu\epsilon$  so that

$$\Delta_{ST} = f\left(\frac{\mu\kappa}{d} V_{335A}\right). \quad (1)$$

The purpose of the calibration procedure is to measure  $(\mu\kappa/d)$  directly, as this yields a much more accurate value of  $\Delta_{ST}$  than can be obtained from measurements of  $\mu$ ,  $\kappa$ , and  $d$  individually. Two steps are necessary.

First, a measurement of the  $(\Delta m_J = 0)$   $l$ -doubling spectrum for OCS in its first excited bending vibrational state ( $01^1_0$ ) was used to measure  $\mu_{OCS}^E \kappa/d$ , where  $\mu_{OCS}^E$  is the dipole moment<sup>6</sup> in the ( $01^1_0$ ) state. Second, the ratio to  $\mu_{OCS}^E$  of the fluoroform dipole moment  $\mu$  in its ground vibronic state was measured. Because this involved  $(\Delta m_J = \pm 1)$  transitions which cannot be observed with the configuration shown in Fig. 1, a recoated system was required.<sup>3</sup> For convenience, the large quartz C field was used. The combination of the two measurements yielded  $\mu\kappa/d$  to sufficient accuracy that the final error in  $\Delta_{ST}$  is determined by the long term stability and resetability of  $V_{335A}$ . Although the resulting absolute error is 20 ppm, previous experience<sup>3</sup> has shown that an uncertainty of 10 ppm can be used for comparing different crossing fields, when the measurements are made within a period of 1 to 2 weeks without disturbing the C field or the supplies.

It often arises that the difference in two nearly equal crossing fields must be determined. When the two values of  $\epsilon_c$  are measured independently by resetting  $V_{335A}$  and  $V_{408B}$ , then each value is limited in accuracy to this 10 ppm and the difference will have an uncertainty  $\sim 15$  ppm of the absolute Stark shift (e.g., 75 kHz for a 5 GHz Stark effect). This error can be reduced considerably by using the *splitting method* in which the lower plate of the C field is shifted (up or down) relative to ground by an additional small dc voltage  $V_{332A}$  with the #332A supply shown in Fig. 3. In measuring the two different  $\epsilon_c$ ,  $V_{335A}$  and  $V_{408B}$  are left fixed and only  $V_{332A}$  is changed. Now the total electric field strength  $\epsilon = (\kappa V_{335A}/d) + \Delta\epsilon$ , where  $\Delta\epsilon = -V_{332A}/d$ . The ratio  $V_{332A}/d$  can easily be calibrated to 60 ppm. For  $|\Delta\epsilon| \leq 0.02\epsilon$ , the uncertainty in  $\epsilon$  due to the calibration error in  $\Delta\epsilon$  is less than 1 ppm of  $\epsilon$  and is negligible compared to the short term stability of 2 ppm in  $V_{335A}$ . Thus, by adjusting only  $V_{332A}$ , splittings up to  $0.02\Delta_{ST}$  can be measured to an accuracy as high as  $2 \times 10^{-8}\Delta_{ST}$ . This is 10 kHz for  $\Delta_{ST} = 5$  GHz, and is almost an order of magnitude better than the accuracy obtained from two independent measurements.

### III. THE ELECTRIC DIPOLE MOMENT

Precision determinations were made of the electric dipole moments of CF<sub>3</sub>H and CF<sub>3</sub>D by a conventional MBER study of the  $(\Delta J = 0, \Delta m_J = \pm 1)$  spectrum. As discussed previously,<sup>4</sup> this spectrum is generally split in an asymmetric manner by the nuclear hyperfine interactions. Particularly in molecules with nuclear quadrupole interactions such as CF<sub>3</sub>D, the resulting shift in the center of the hyperfine multiplet away from the hyperfine-free frequency can be important. Fortunately, in the  $(J_K = 3_{\pm 2})$  state of a symmetric rotor, as does the energy contribution from the anisotropy ( $\alpha_{||} - \alpha_{\perp}$ ) in the polarizability.<sup>7</sup> For these reasons, the  $3_{\pm 2}$  state is particularly well suited to precision studies of the dipole moment.

For each isotopic species, both the  $(J_K = 3_{\pm 2}, m_J = \mp 1 \rightarrow 0)$  and the  $(3_{\pm 2}, \mp 2 \rightarrow \mp 1)$  spectra were observed. The measurements were taken in electric fields of approxi-

TABLE I. Molecular constants for CF<sub>3</sub>H and CF<sub>3</sub>D.

Quantity	CF <sub>3</sub> H			CF <sub>3</sub> D		
	Present results	Others	Reference	Present results	Others	Reference
$\mu/\mu$ (OCS) <sup>a</sup>	2.309 178(15)			2.311 970(15)		
$\mu$ (D) <sup>a</sup>	1.651 50(10) <sup>b</sup>	1.6523(10) <sup>c</sup>	9	1.653 50(10) <sup>b</sup>	1.6534(10) <sup>c</sup>	9
$B_0$ (MHz)		10 348.867(2)	15		9921.126(2) <sup>d</sup>	13, 14
$D_J$ (kHz)		11.33	15		9.87	16
$D_{JK}$ (kHz)		-18.10	15		-14.8 <sup>e</sup>	17
$D_K$ (kHz)		9.8 <sup>e</sup>	18		9.2 <sup>e</sup>	18
$C_0$ (MHz)	5673.46(10)			5673.21(10)		
$C_3$ (MHz)	5668.36(10) <sup>f</sup>					
$\alpha_6^C$ (MHz)		10.247(39)	19	10.8(4)	12(3)	20
$C_6$ (MHz)	5663.21(10)	5663.7(4)	12		5662.40(35)	12
$g_{\perp}$ (nm)	-0.036 27(2)	-0.036 27(9) <sup>g,h</sup>	22	-0.034 85(2)	-0.0345(8) <sup>g,h</sup>	23
$g_{\parallel}$ (nm)	-0.033 33(7)	-0.033 33(9) <sup>i,h</sup>	22	-0.032 5(8)		

<sup>a</sup>Here  $\mu$  represents  $\mu_{3,2}$  as obtained from the allowed transitions ( $J_K=3_{2,2}$ ,  $m_J=\mp 1 \rightarrow 0$ ) and ( $J_K=3_{2,2}$ ,  $m_J=\mp 2 \leftrightarrow \mp 1$ ).

<sup>b</sup>This was calculated using  $\mu$  (OCS)=0.715 19(3)D.<sup>6</sup>

<sup>c</sup>The number quoted here is the average for the measurements in Ref. 9 for the ( $J=1 \leftarrow 0$ ) and the ( $J=2 \leftarrow 1$ ) transitions, corrected to  $\mu$  (OCS)=0.715 19 D.

<sup>d</sup>This was calculated from the hyperfine free frequency ( $2B_0 - 4D_J$ ) of the ( $J=1 \leftarrow 0$ ) rotational transition.

<sup>e</sup>This was determined from the force field.

<sup>f</sup>This was calculated using  $\alpha_3^C=5.096(87)$  MHz.<sup>19</sup>

<sup>g</sup>Only the magnitude was determined experimentally.

<sup>h</sup>The sign of the  $g$  factor was taken from theoretical arguments given in Ref. 23.

<sup>i</sup>The magnitude was obtained by assuming that  $g_{\parallel} > g_{\perp}$  and that both  $g$  factors have the same sign.

mately 865 and 1730 V/cm, resulting in Stark splittings of 120 and 240 MHz, respectively. The large quartz  $C$  field was used. The electric field strength was calibrated using Stark transitions in OCS in the ground vibronic state. The electric dipole moments in CF<sub>3</sub>H and CF<sub>3</sub>D were calculated by diagonalizing the Stark rotation matrices after truncation at  $\Delta J=3$ . The rotational constants were taken from the literature as summarized in Table I; the fundamental constants were taken from Cohen and Taylor.<sup>8</sup>

For each isotopic species of fluoroform, Table I lists the dipole moment  $\mu_{3,2}$  for the  $3_{2,2}$  state relative to the ground state dipole moment  $\mu$  (OCS), as well as the absolute value of  $\mu_{3,2}$  obtained using  $\mu$  (OCS)=0.715 19(3) D.<sup>6</sup> The isotopic shift in the fluoroform dipole moment is

$$[\mu_{3,2}(\text{CF}_3\text{D}) - \mu_{3,2}(\text{CF}_3\text{H})]/\mu_{3,2}(\text{CF}_3\text{H}) = 1.209(9) \times 10^{-3}. \quad (2)$$

The error in this shift is limited only by the internal consistency among the fluoroform data, which was  $\sim 3$  ppm. This limit was dominated by uncertainty in the frequency measurements. As indicated in Table I, the electric dipole moments obtained here for fluoroform agree very well with the earlier, less accurate measurements made using microwave absorption spectroscopy.<sup>9</sup>

For the avoided crossings studied here (see Sec. IV), there is required a precision value of  $\mu_{1,1}$  for the ( $J_K=1_{\pm 1}$ ) state. Because of centrifugal distortion effects,  $\mu_{1,1} = (\mu_{3,2} - 3\mu_K - 10\mu_J)$ , where  $\mu_K$  and  $\mu_J$  are distortion dipole constants.<sup>3,10</sup> Although  $\mu_J$  and  $\mu_K$  are generally small, their contribution can be large enough to increase the error in  $\mu_{1,1}$  significantly and hence affect the errors in the rotational splittings obtained in

the anticrossing experiments. To eliminate this possibility, the normal MBER spectrum of CF<sub>3</sub>H for the  $1_{\pm 1}$  state was measured relative to that for the  $3_{2,2}$  state. A field of about 2400 V/cm was used, producing frequencies of approximately 1000 and 330 MHz, respectively. It was determined that  $\mu_{1,1}(\text{CF}_3\text{H}) - \mu_{3,2}(\text{CF}_3\text{H}) = 1.2(6) \times 10^{-5}$  D.

Two systematic effects on the  $1_{\pm 1}$  frequencies had to be eliminated in arriving at this result. First, the contribution due to the anisotropy in the polarizability was calculated to be negligible using  $(\alpha_{\parallel} - \alpha_{\perp}) = -0.27 \times 10^{-24}$  cm<sup>3</sup>.<sup>11</sup> Second, the hyperfine asymmetry mentioned earlier was evaluated. In the  $1_{\pm 1}$  state of CF<sub>3</sub>H, this arises only from the hydrogen-fluorine spin-spin interaction. The coupling constants that enter<sup>3</sup> can be calculated from the structure<sup>12</sup> to be  $d^{\text{FH}} = 5.84$  kHz and  $\frac{1}{2}(d_{xx}^{\text{FH}} + d_{yy}^{\text{FH}}) = 8.28$  kHz. The resulting asymmetry shift is smaller than 2 kHz and is dominated by the uncertainty of 3 kHz in the frequency measurements.

In CF<sub>3</sub>D this same hyperfine asymmetry shift can be much larger due to the deuterium electric quadrupole interaction. It is therefore not possible to perform a similar measurement in CF<sub>3</sub>D with such small error limits. However, it can be safely assumed that  $[\mu_{1,1}(\text{CF}_3\text{D}) - \mu_{3,2}(\text{CF}_3\text{D})] = [\mu_{1,1}(\text{CF}_3\text{H}) - \mu_{3,2}(\text{CF}_3\text{H})]$  to within the present level of accuracy.

#### IV. THE $C_0$ ROTATIONAL CONSTANT

The rotational constant  $C_0$  about the symmetry axis was determined by measuring the crossing field  $\epsilon_c$  for the ( $J, K$ ) = (1, 0)  $\leftrightarrow$  (1,  $\pm 1$ ) anticrossing. This crossing field is the lowest one available for an oblate symmetric top; to lowest order,  $\epsilon_c$  for this case equals  $2h(B_0 - C_0)/$

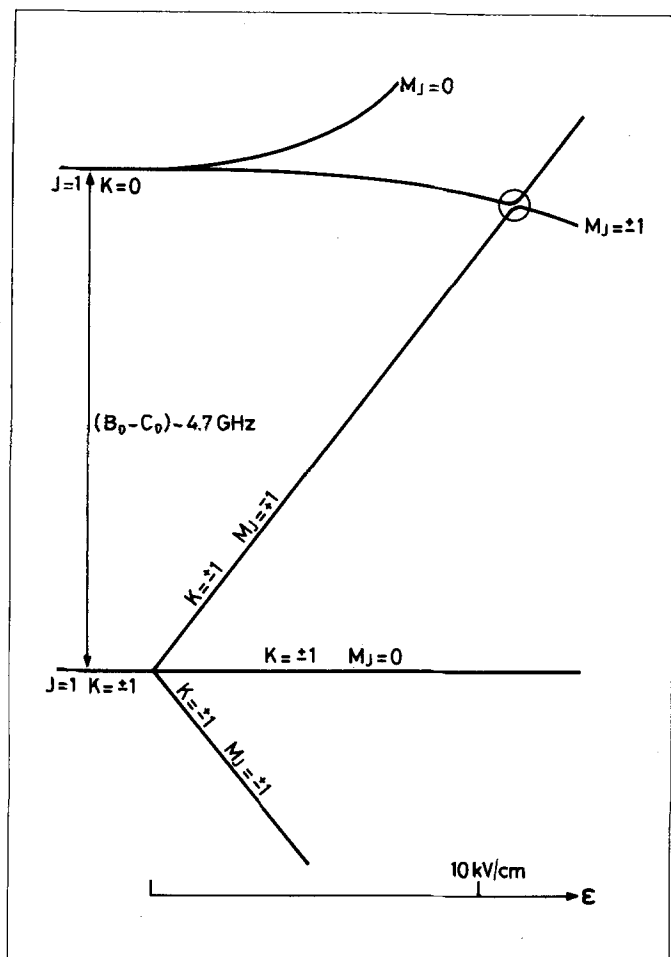


FIG. 4. Schematic plot against the electric field of the energy levels in the ( $J=1$ ) state of fluororoform. The nuclear magnetic quantum numbers and the hyperfine effects are not shown. The circle indicates the anticrossing region. For clarity, the curvature of the levels in this region and the quadratic Stark effect of the ( $K=0$ ) state have been greatly exaggerated.

$\mu$ . The energy level scheme for the ( $J=1$ ) states as a function of  $\epsilon$  is shown in Fig. 4. Because the upper state has  $K=0$  and hence a quadratic Stark effect, the lower state involved in the anticrossing must be that with ( $J=1, K=\pm 1, m_J=\mp 1$ ). Unless otherwise indicated, it can be assumed here that upper signs go only with upper signs and lower only with lower. There are then three possible anticrossing systems, all of which satisfy the focusing<sup>3</sup> requirements: ( $\beta$ ) = ( $J=1, K=\pm 1, m_J=\mp 1$ ) interacting with ( $\alpha$ ) = ( $1, 0, 0$ ), ( $1, 0, \mp 1$ ), or ( $1, 0, \pm 1$ ). The first of these is shifted to much higher field by the quadratic (and higher) terms and is of no further interest here. It is the last two which form the basis of the current study. They both have the same  $\epsilon_c$  if the external magnetic field  $B=0$  and hyperfine effects are neglected. By arguments similar to those used for OPF<sub>3</sub>,<sup>3</sup> these last two form a hybrid system for  $B=0$  that breaks up into two separate systems of two level problems for  $B \geq 2$  mT: ( $1, 0, \mp 1$ )  $\leftrightarrow$  ( $1, \pm 1, \mp 1$ ) and ( $1, 0, \pm 1$ )  $\leftrightarrow$  ( $1, \pm 1, \mp 1$ ).

The mechanisms coupling the two interacting levels in the anticrossing and the selection rules on the magnetic

quantum numbers in the coupling matrix elements can be determined using Ref. 3. For ( $J, K, m_J$ ) = ( $1, 0, \pm 1$ )  $\leftrightarrow$  ( $1, \pm 1, \mp 1$ ), the coupling is provided by the X-F spin-spin interaction  $\mathcal{H}_{IF}^{XF}$ ; the selection rules are ( $\Delta m_J = \pm 2$ ,  $\Delta m_X = \mp 1$ ,  $\Delta m_F = \mp 1$ ). Here X refers to H in CF<sub>3</sub>H or D in CF<sub>3</sub>D. For ( $J, K, m_J$ ) = ( $1, 0, \mp 1$ )  $\leftrightarrow$  ( $1, \pm 1, \mp 1$ ), the coupling arises from  $\mathcal{H}_{IF}^F$  and the fluorine spin-rotation interaction  $\mathcal{H}_{IF}^R$ ; the selection rules for both interactions are ( $\Delta m_J = 0$ ,  $\Delta m_X = \pm 1$ ,  $\Delta m_F = \mp 1$ ) and ( $\Delta m_J = 0 = \Delta m_X = \Delta m_F = 0$ ). Because the deuterium nucleus in CF<sub>3</sub>D is on the symmetry axis, there are no ( $\Delta K \neq 0$ ) matrix elements due to the deuterium quadrupole interaction. The total fluorine nuclear spin changes from  $3/2$  to  $1/2$  when  $K$  goes from  $0$  to  $\pm 1$ . This is clearly a *hyperfine* anticrossing, as distinguished from a *Stark* anticrossing.

The *normal* anticrossing spectrum of the hybrid system taken in zero magnetic field can, in general, be asymmetrically broadened or split by the hyperfine contribution  $\Delta_{\text{HYP}}$  to the zero-field splitting  $\Delta_0$ . In both CF<sub>3</sub>H and CF<sub>3</sub>D, an upper limit of 20 kHz can be placed on the splittings introduced from asymmetric and symmetric terms. This is the order of the time-of-flight width of 15 kHz, but is small compared to the observed width of 48 kHz (see Fig. 2). The anticrossing spectrum therefore appears as a single line.

The asymmetric shift in this line from the ( $\Delta_{\text{HYP}} = 0$ ) position can be of particular concern because this shift directly affects the value obtained for the rotational splitting  $\Delta_{\text{ROT}}$ . In CF<sub>3</sub>H, the asymmetry in  $\Delta_{\text{HYP}}$  is entirely due to the F-F spin-spin interaction. The associated coupling constant  $d^{FF}$  as defined in Ref. 4 has been calculated from the structure<sup>12</sup> to be 5.241 kHz. In CF<sub>3</sub>D, there are additional contributions from the deuterium quadrupole interaction, for which the coupling constant  $eQq_D = 170.5(20)$  kHz.<sup>13</sup> The resulting shift, however, is very small, being  $\leq 4$  kHz for both molecules. This limit is obtained by assigning equal weight to the matrix elements arising from the different selection rules given above on  $m_J$ ,  $m_F$ , and  $m_X$ . While this assumption is somewhat arbitrary, the resulting estimate should be good to at least a factor of 2. In any case, this shift is negligible compared to the absolute uncertainties (100 kHz) in  $\Delta_0$  arising from the calibration of  $\epsilon$ . This conclusion does not change if  $B$  is taken as the Earth's field.

For each isotopic species, the crossing field  $\epsilon_c$  of the ( $J, K, m_J$ ) = ( $1, 0, \pm 1$ )  $\leftrightarrow$  ( $1, \pm 1, \mp 1$ ) and ( $1, 0, \mp 1$ )  $\leftrightarrow$  ( $1, \mp 1, \pm 1$ ) hybrid anti-crossing system was measured in the Earth's magnetic field. Details of the type of procedure used are given in Ref. 3. For CF<sub>3</sub>H, two independent measurements of  $\epsilon_c$  were made separated by a period of 6 months. Between the two experiments, the C field had been dismantled, recoated, reassembled, and recalibrated. The results were  $\epsilon_c = 11\,062.40(24)$  and  $11\,062.45(24)$  V/cm, thus showing excellent reproducibility. For CF<sub>3</sub>D,  $\epsilon_c = 10\,044.46(24)$  V/cm.

The zero-field energy differences  $\Delta_0$  were calculated from the observed crossing fields using the values of  $\mu_{1,1}$ . As in Sec. III, the Stark-rotation matrix was diagonalized after truncation at  $\Delta J = 3$ . The contribu-

tion from  $(\alpha_{\parallel} - \alpha_{\perp})$  was again negligible. The resulting values of  $\Delta_0$  were 4675.38(10) MHz for CF<sub>3</sub>H and 4247.90(10) MHz for CF<sub>3</sub>D.

Because the hyperfine contribution is negligible,  $\Delta_0$  reduces directly to<sup>3</sup>

$$\Delta_{\text{ROT}} = (B_0 - C_0) + 2D_{JK} + D_K \quad (3)$$

For each isotopic species, values for  $B_0$ ,  $D_{JK}$ , and  $D_K$  are known<sup>13-18</sup> and are listed in Table I, although  $D_{JK}$  (CF<sub>3</sub>D) and  $D_K$  (CF<sub>3</sub>H and CF<sub>3</sub>D) are available only from the force field. Since these calculations reproduce the experimental values of  $D_J$  (CF<sub>3</sub>H and CF<sub>3</sub>D) and  $D_{JK}$  (CF<sub>3</sub>H) very well, it is safe to assume that the errors are less than 20%. The final results for  $C_0$  are listed in Table I.

The values for  $C_0$  show a slight isotopic effect

$$[C_0(\text{CF}_3\text{D}) - C_0(\text{CF}_3\text{H})]/C_0(\text{CF}_3\text{H}) = -44(12) \text{ ppm} \quad (4)$$

In calculating the error here, the long term stability of  $V_{335A}$  was taken as 10 ppm appropriate to internal comparison, rather than as 20 ppm which was used for the absolute value of  $\Delta_{\text{ROT}}$ . The change in  $C_0$  is expected to be small since the atom replaced is on the symmetry axis and moreover is bonded only to an on-axis atom. The result in Eq. (4) is probably due to changes in the zero-point motion.

The present value for  $C_0$  can be usefully combined with information in the literature on the vibrational dependence of  $C$ . The results are summarized in Table I. For CF<sub>3</sub>H, very accurate infrared values are available for  $\alpha_3^C$  and  $\alpha_8^C$ .<sup>19</sup> This has enabled us to calculate  $C_3$  and  $C_8$ . The latter agrees well with the microwave measurement of Ref. 12. For CF<sub>3</sub>D, the corresponding microwave value<sup>12</sup> for  $C_8$  has been used to calculate  $\alpha_8^C$ . This result agrees with the earlier, less accurate infrared determination.<sup>20</sup>

The structure determination carried out by Kawashima<sup>12</sup> is confirmed rather than improved by the work presented here. The MBER value of  $C_0$  is much more accurate than that used in Ref. 12. However, the limitations imposed by zero-point motion corrections prevent this increased accuracy from being used to improve the equilibrium rotational constants.

## V. THE ROTATIONAL $g$ FACTOR

The magnitudes and signs of the molecular  $g$  factor for both CF<sub>3</sub>H and CF<sub>3</sub>D were determined. The primary motivation behind this work was the determination of the sign of the electric dipole moment (see Sec. VII). In the usual notation,<sup>3,4</sup> the  $g$  factors are indicated by  $g_{\parallel}$  and  $g_{\perp}$ , where the subscripts refer, respectively, to rotation parallel and perpendicular to the symmetry axis.

The *first* step was to determine for each isotopic species the magnitude of  $g_{\perp}$  by studying the conventional MBER spectrum corresponding to selection rules  $\Delta m_J = \pm 1$ ,  $\Delta J = \Delta K = \Delta m_X = \Delta m_F = 0$  for the ( $J_K = 1_0$ ) state. A similar experiment on OPF<sub>3</sub> has been discussed previously in detail.<sup>4</sup> The magnetic field was 0.8 T, producing a Zeeman splitting for each isotopic species of

over 400 kHz. The large quartz  $C$  field was used to give an electric field of about 800 V/cm and a linewidth of less than 3 kHz. The hyperfine splitting was well resolved in CF<sub>3</sub>H and in CF<sub>3</sub>D. Although the hyperfine coupling constants can be determined from the spectrum, the accuracy of the existing beam maser values<sup>13,14</sup> was sufficiently high that no serious effort was made in this direction. Rather, the known values were used along with the analysis developed<sup>4</sup> for OPF<sub>3</sub> to identify the different hyperfine components and select a suitable single line for a Zeeman study. The value of  $g_{\perp}$  was then obtained using Eq. (9) of Ref. 4 for the Zeeman energy. The shielding anisotropies used were  $(\sigma_{\parallel}^F - \sigma_{\perp}^F) = -80.2$  ppm and  $(\sigma_{\parallel}^H - \sigma_{\perp}^H) = 9.8(5)$  ppm.<sup>21</sup>  $(\sigma_{\parallel}^D - \sigma_{\perp}^D)$  is negligible. The magnitudes obtained for  $g_{\perp}$  in CF<sub>3</sub>H and CF<sub>3</sub>D are given in Table I. They agree well with the best earlier, less accurate values obtained by beam maser methods<sup>22</sup> for CF<sub>3</sub>H and by microwave absorption<sup>23</sup> for CF<sub>3</sub>D. It should be emphasized that these two techniques as well as the beam experiment just described give no experimental information on the sign of the  $g$  factor measured.

The *second* step was to determine for each isotopic species the magnitude of  $g_{\parallel}$  and the relative sign of  $g_{\parallel}$  and  $g_{\perp}$ . CF<sub>3</sub>H will be considered first. From their beam maser studies on this molecule, Ellenbroek and Dymanus<sup>22</sup> found, in addition to the value for  $|g_{\perp}|$  given in Table I, that  $|g_{\parallel} - g_{\perp}| = 0.002936(60)$  nm; separate values for  $g_{\perp}$  and  $g_{\parallel}$  were obtained by assuming  $g_{\perp} < g_{\parallel} < 0$ . In the current work, the Zeeman splitting in the ( $J_K = 3_{\pm 2}$ ,  $m_J = \mp 1 - 0$ ) spectrum was measured; it was found that  $|\frac{2}{3}g_{\perp} + \frac{1}{3}g_{\parallel}| = 0.03516(27)$  nm. The lower accuracy arises from the fact that the hyperfine structure in this spectrum could not be resolved; only a single broadened line was observed. However, no systematic errors arise because, as was mentioned in Sec. III, the broadening in this state is symmetric. By combining the values for  $|\frac{2}{3}g_{\perp} + \frac{1}{3}g_{\parallel}|$ ,  $|g_{\parallel} - g_{\perp}|$ , and  $|g_{\perp}|$ , it was established experimentally that  $g_{\parallel}$  and  $g_{\perp}$  have the same sign. The present value for  $|g_{\perp}|$  was then combined with the beam maser value for  $|g_{\parallel} - g_{\perp}|$  to obtain an improved value for  $|g_{\parallel}|$ . As can be seen from Table I, the improvement is small, but now no sign assumptions were necessary to obtain  $|g_{\parallel}|$ .

The situation for CF<sub>3</sub>D is slightly different because only a measurement of  $|g_{\perp}|$  is available from earlier work.<sup>23</sup> The MBER study on the  $3_{\pm 2}$  state for CF<sub>3</sub>H was repeated for CF<sub>3</sub>D yielding  $|\frac{2}{3}g_{\perp} + \frac{1}{3}g_{\parallel}| = 0.03406(27)$  nm. This value was combined with our MBER value of  $|g_{\perp}|$  to yield  $|g_{\parallel}|$ . In doing this, the very reasonable assumption was made that  $(g_{\parallel}/g_{\perp})$  has the same sign as in CF<sub>3</sub>H. As can be seen from Table I, the value obtained for  $|g_{\parallel}|$  in CF<sub>3</sub>D is not significantly different from that in CF<sub>3</sub>H, although the error is somewhat larger; the more accurate beam maser measurement was not available.

The *final* step was to determine the absolute signs of the  $g$  factors by using the method described earlier<sup>3</sup> of studying hyperfine anticrossings in a magnetic field. In a large magnetic field, the hybrid system studied in Sec. III breaks up into two separate systems of two lev-

el problems as indicated above. The  $(J, K, m_J) = (1, 0, \pm 1) \rightarrow (1, \pm 1, \mp 1)$  anticrossing system is suitable for the sign determination. The spectrum consists of two magnetic components with  $g$  factors<sup>3</sup>

$$g_{\text{eff}} = \mp \left\{ (1 - \sigma_X) g_X + (1 - \sigma_F) g_F - \left[ 2g_{\parallel} + \frac{1}{2} (g_{\parallel} - g_{\perp}) \right] \right\}. \quad (5)$$

Here  $g_{\lambda}$  and  $\sigma_{\lambda}$  ( $\lambda = X, F$ ) are the nuclear  $g$  factor and average shielding, respectively. By measuring  $|g_{\text{eff}}|$ , the sign of the rotation contribution can be found.

In this measurement, the *splitting* method described in Sec. II was used. To obtain  $|g_{\text{eff}}|$ , the *difference* in the crossing fields for the two magnetic components (rather than their absolute values) must be determined as accurately as possible. Even in a moderate magnetic field of 0.2 T, the splitting between the two components is several tens of MHz, so that both cannot be measured at the same electric field. By using  $V_{332A}$  as described in Sec. II, this fact does not degrade the accuracy of the *difference* measurement: the Zeeman splitting of over 33 MHz for  $B = 0.2$  T can be measured to 15 kHz.

For CF<sub>3</sub>H, it was found that  $|g_{\text{eff}}| = 10.9118(50)$  nm. By using the values for the nuclear  $g$  factors<sup>24</sup> and the shielding constants<sup>25</sup> together with Eq. (5), it was determined that

$$g_R = g_{\parallel} + \frac{1}{4} (g_{\parallel} - g_{\perp}) = -0.0354(25) \text{ nm}. \quad (6)$$

From the determinations described above of  $|g_{\parallel}|$ ,  $|g_{\perp}|$ , and the sign of  $(g_{\parallel}/g_{\perp})$ , it follows that  $|g_R| = 0.0354(2)$  nm. The two magnitudes are in good agreement. The negative sign for  $g_R$  shows that both  $g_{\parallel}$  and  $g_{\perp}$  are negative. This conclusion was confirmed by a similar measurement of  $g_R$  in CF<sub>3</sub>D.

The current results provide the first experimental determination of the signs of the molecular  $g$  factors. It confirms the sign assumptions made in Ref. 23 and 22 to calculate the molecular quadrupole moment  $\theta_{\parallel}$ . With the experimental sign information and improved values for  $g_{\perp}$  and  $g_{\parallel}$ ,  $\theta_{\parallel}$  has been recalculated for CF<sub>3</sub>H; the result is  $\theta_{\parallel} = 1.253(16) \times 10^{-39}$  C m<sup>2</sup>. The pertinent equation is well known<sup>23,4</sup>; the value used for  $(\chi_{\parallel} - \chi_{\perp})$  was  $28.7(6) \times 10^{-30}$  J/T<sup>2</sup>.<sup>22,26</sup>

## VI. THE DIRECTION OF THE ELECTRIC DIPOLE MOMENT

Two different methods have been developed for measuring the direction of electric dipole moments in molecules. One of these is based on the sign of the change in  $|\mu|$  in deuteration. Muentzer and Laurie<sup>9</sup> put forward the hypothesis that an increase (decrease) in  $|\mu|$  on deuteration indicates that the substitution has been made at the positive (negative) end of the molecule. Their interpretation of the isotope shifts observed was certainly reasonable, but was admittedly tentative pending further experimental work.

In fluoroform, the situation was particularly difficult for Muentzer and Laurie. The magnitude of the isotopic change in  $|\mu|$  is unusually small. It was just at the limit of their technique, so that only the sign could be

determined. Their conclusion that  $|\mu(\text{CF}_3\text{D})| > |\mu(\text{CF}_3\text{H})|$  is confirmed by the result presented in Eq. (2). This would indicate the +HCF<sub>3</sub> - polarity, as is expected from general chemical arguments. With the current experiments, the magnitude of the shift is well determined. It is an interesting exercise now to apply Eq. (4) of Ref. 9 to obtain an estimate of the dipole derivative for the CH stretch:  $(\partial\mu/\partial r) \approx 0.67$  D/Å, which appears to be of the correct order of magnitude. However, as pointed out in Ref. 9, the isotopic shift here is so small that other effects such as the breakdown of the Born-Oppenheimer approximation might be important enough to call into question even the direction determination.

A second, completely independent method to determine this direction is based on the change in  $(g_{\perp}/B_0)$  upon isotopic substitution. The appropriate expression for the substitution of an atom on the symmetry axis of a symmetric rotor is<sup>27</sup>

$$\tilde{\mu}_N \left( \frac{g_{\perp}^{(2)}}{B_0^{(2)}} - \frac{g_{\perp}^{(1)}}{B_0^{(1)}} \right) = -2\tilde{\mu} \Delta b. \quad (7)$$

Here the superscripts (1) and (2) label the two different isotopic species;  $\Delta b$  represents the displacement of the center of mass of isotope (2) referred to the center of mass of isotope (1).  $\tilde{\mu}$  is the dipole moment itself, but the tilde has been added to show explicitly that the value has been derived from Eq. (7) rather than the Stark effect.

Because  $X = [(g_{\perp}^{(2)}/B_0^{(2)}) - (g_{\perp}^{(1)}/B_0^{(1)})]$  is generally much smaller in magnitude than the individual  $(g_{\perp}/B_0)$ , very accurate values of the  $g$  factors are usually required for this method. If the best previous values for  $|g_{\perp}|$  are used (see Table I) and it is assumed that  $g_{\perp} < 0$ , then, with (2) - CF<sub>3</sub>D and (1) - CF<sub>3</sub>H, Eq. (7) yields  $\tilde{\mu} = +(1.6 \pm 4.7)$  D, so that no conclusion could be drawn. With improved values for  $|g_{\perp}|$  in both isotopic species and an *experimental* value for the sign of  $g_{\perp}$  (see Table I and Sec. V), it has been found that  $X = -0.82(26) \times 10^{-14}$  Hz<sup>-1</sup> and that  $\tilde{\mu} = +0.48(15)$  D. All three uncertainties indicated above represent only the experimental errors in the  $g$  factors. The positive sign on  $\tilde{\mu}$  has more meaning now, indicating that the hydrogen end of the molecule is positive.

Before this conclusion is accepted, however, it should be noted that  $\tilde{\mu}$  differs very markedly from the Stark effect value for  $\mu$ . This disagreement clearly indicates the presence of errors in the model used to derive Eq. (7). Similar effects have been discussed previously for simple diatomic molecules (e.g., Ref. 28) and more complex asymmetric rotors (e.g., Ref. 29). The difficulty lies in several vibrational effects that are ignored in Eq. (7) including the change in the zero-point motion upon deuteration. These effects are most important for D - H isotopic substitution and for cases where  $|X|$  is small. Unfortunately, the proper treatment of these effects is impractical for most nonlinear molecules, so that the method becomes questionable when the vibrational corrections to  $\tilde{\mu}$  become comparable in magnitude to  $|\mu|$  itself. In the case of fluoroform, these corrections are 1.17 D if  $\mu$  has the same sign as  $\tilde{\mu}$

and 1.80 D if the signs are opposite. This favors the positive sign for  $\mu$ , but the result would be more satisfying if the vibrational corrections were smaller.

Two different methods have been applied to determine the direction of  $\mu$  in fluoroform. Although each method individually is not entirely convincing, the agreement between the two is strong evidence that the polarity is  $+HCF_3^-$ .

## VII. CONCLUSION

The current work shows that avoided-crossing molecular-beam spectroscopy can be used to determine the rotational constant about the symmetry axis for a broad range of molecules. The main limitation is the difficulty in generating the high electric fields required with sufficient homogeneity. For the lowest possible ( $\Delta J = 0$ ) crossing field, namely, that due to the anticrossing ( $J, K = (1, 0) \leftrightarrow (1, \pm 1)$ ), this limit at the present stage of development can be expressed as  $[(B_0 - C_0)/\mu] \leq 5$  GHz/D. Although the current work was concerned with an oblate top, there are no essential differences for a prolate rotor and the same limit applies with  $(B_0 - C_0)$  replaced by  $(A_0 - B_0)$ . The absolute accuracy in  $(B_0 - C_0)$  or  $(A_0 - B_0)$  is usually determined by the long term stability and resettability of the voltage source to be 0.002%. It should be possible to determine  $C_0$  or  $A_0$  for a large number of symmetric rotors in the ground vibronic state, thereby helping one to obtain or improve the structure determination.

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