

The Structure of Trifluoromethyl Acetylene from the Microwave Spectrum and Electron Diffraction Pattern

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Measurements, in the microwave region, of the $J=3\rightarrow 4$ rotational transitions of trifluoromethyl acetylene and several of its isotopic modifications have been made, and the moments of inertia, I_B (in a.m.u.- Å^2), have been found for the ground vibrational state: for CF_3CCH , 175.61₃, $\text{CF}_3\text{C}^{13}\text{CH}$, 177.02₄, $\text{CF}_3\text{CC}^{13}\text{H}$, 181.30₂, and for CF_3CCD , 187.46₂. Three lines corresponding to $J=3\rightarrow 4$ transitions of CF_3CCH in the excited vibrational state $\nu_{10}=1$, and two lines corresponding to $\nu_{10}=2$ and $\nu_{10}=3$, have also been measured and interpreted according to Nielson's theory of l -type doubling in symmetric tops. From Stark effect measurements at different electric field strengths the dipole moment of CF_3CCH in the ground vibrational state has been found to be 2.36 ± 0.04 Debye units. For the ground vibrational state the microwave data lead to the following bond distances: C-H, $1.056\pm 0.005\text{Å}$; C≡C, $1.201\pm 0.002\text{Å}$. The C-C and C-F distances were calculated from the measured moments of inertia for several assumed values of the FCF angle. Electron diffraction experiments were also made, and the intensity curves calculated for the assumed microwave models were compared with the observed visual curve. From the combination of microwave and electron diffraction results the best agreement was obtained with the following set of parameters: $\angle\text{FCF}$, $107.5\pm 1^\circ$; C-C, $1.464\pm 0.02\text{Å}$; C-F, $1.335\pm 0.01\text{Å}$.

INTRODUCTION

SUBSTITUTED acetylenes have long been known to show pronounced shortening of the single bond distances adjacent to the triple bonds; this has been nicely confirmed in several cases by recent microwave studies.¹⁻⁴ Fluorine compounds often show anomalous bond distances. Of interest in both these respects is trifluoromethyl acetylene, CF_3CCH , for which Anderson, Trambarulo, Sheridan, and Gordy⁴ reported bond

lengths C-F=1.330 Å and C-C=1.493 Å on the basis of measurements on two isotopic species, and on the assumption that C-H=1.056 Å , C≡C=1.207 Å , and $\angle\text{FCF}=109^\circ 28'$. The complete structure of this molecule has now been determined in this laboratory from the combined experimental data afforded by electron diffraction results and by microwave absorption lines for four isotopic species. The acetylenic C-H and C≡C distances together with two relations between the other three parameters were evaluated directly from the microwave spectra. In this way, and for the compound studied, the electron diffraction problem was reduced to one which could be handled relatively rapidly and accurately.

MICROWAVE EXPERIMENTAL PROCEDURE

Since the particular microwave spectroscope used in this research has not previously been described in the literature, a few words about it are in order. Microwave energy is generated by a 2K-50 (K -band) reflex klystron; the radiation passes through a 12-foot absorption cell of X-band copper wave guide provided with an accurately centered steel Stark electrode supported by slotted Teflon strips, and the resulting 50 kc square wave modulated, absorption line envelope is pre-amplified and detected with a heterodyne detector. Provision is made for either oscilloscope or recording meter presentation. A slow motor drive allows frequency sweep rates of 40 mc/min. Frequencies are measured by comparing with the harmonics of a thermostated 10 mc crystal multiplied to the microwave region. The frequency markers are calibrated on the absorption lines of NH_3 gas, which is permanently sealed in a one foot long Stark modulation cell at 50 microns pressure.

A sample of trifluoromethyl acetylene, B.P. = -45° , was obtained through the good offices of Professor

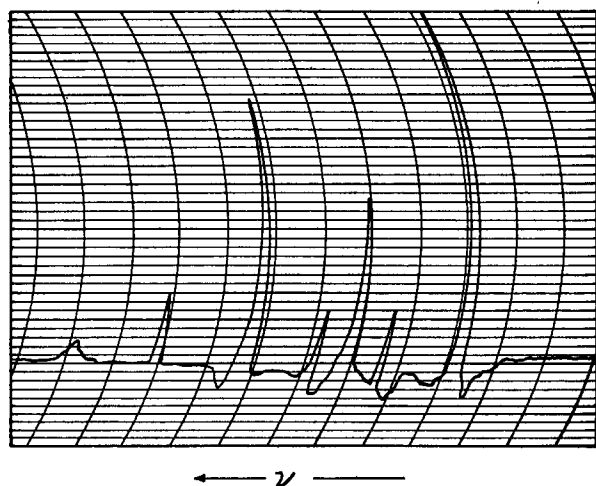


FIG. 1. Microwave absorption of CF_3CCH in the region between 22,980 and 23,200 mc.

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¹ R. Trambarulo and W. Gordy, *J. Chem. Phys.* **18**, 1613 (1950).

² A. A. Westenberg and E. B. Wilson, Jr., *J. Am. Chem. Soc.* **72**, 199 (1950).

³ Westenberg, Goldstein, and Wilson, Jr., *J. Chem. Phys.* **17**, 1319 (1949).

⁴ Anderson, Trambarulo, Sheridan, and Gordy, *Phys. Rev.* **82**, 58 (1951).

A. L. Henne of Ohio State University. Isotopic molecular species, in which C^{13} is substituted for C, are present in 1.1 percent natural abundance. § CF_3CCD was prepared by condensing several cubic centimeters of CF_3CCH vapor at S.T.P. into a tube containing one cubic centimeter of a 50 percent solution of NaOH and NaOD in D_2O . Approximately 50 percent conversion was obtained overnight.

RESULTS OF THE MICROWAVE EXPERIMENTS

Trifluoromethyl acetylene is expected to be a symmetric top similar to methyl acetylene,¹ and observation of a simple microwave spectrum indicates that this is indeed the case. The $J=3 \rightarrow 4$ rotational transitions of several isotopic species were found with the Stark modulated sweep spectroscopy, and their frequencies were measured with the harmonic frequency standard. These are given in Table I. A recording meter trace of the absorption for the most abundant species of CF_3CCH appears in Fig. 1. Lines of the same J and

TABLE I. Measured frequencies for the $J=3 \rightarrow 4$ transition in several isotopic species of CF_3CCH .

Species	Transition	Frequency ^a (mc/sec)
CF_3CCH	$J=3 \rightarrow 4$ Ground state	23,023.4
	$J=3 \rightarrow 4$ Excited state $\nu_{10}=1$ (C-C'≡C'' bending)	23,053.5
		23,067.7
		23,082.4
	$J=3 \rightarrow 4$ Excited state $\nu_{10}=2$	23,111.2
$J=3 \rightarrow 4$ Excited state $\nu_{10}=3$	23,153.0	
$CF_3C^{13}CH$	$J=3 \rightarrow 4$ Ground state	22,839.9
$CF_3CC^{13}H$	$J=3 \rightarrow 4$ Ground state	22,301.0
CF_3CCD	$J=3 \rightarrow 4$ Ground state	21,568.2

^a Absolute frequencies were measured to ± 0.3 mc and relative frequencies to ± 0.1 mc.

different K values should appear at slightly different frequencies, but are not resolved. This results in a broadening of the lines and limits the accuracy of the frequency measurements.

Most of the measurements were made with the square wave amplitude set at 10 to 20 volts and with the bottom of the square wave based on ground potential. A first-order Stark effect was observed. However, the rotational transition of CF_3CCH in the ground vibrational state was completely resolved into its four second-order Stark components by the application of 700 volts dc (1150 volts/cm) to the Stark electrode in addition to the square wave modulation. This identifies it as the $J=3 \rightarrow 4$ transition. The corresponding transitions in the isotopic species $CF_3C^{13}CH$ and $CF_3CC^{13}H$ were identified by their appearance near the predicted frequencies, by their possession of first-order Stark components, and by the presence of excited vibrational

§ The most abundant isotope of carbon, C^{12} , is denoted by the simple symbol C.

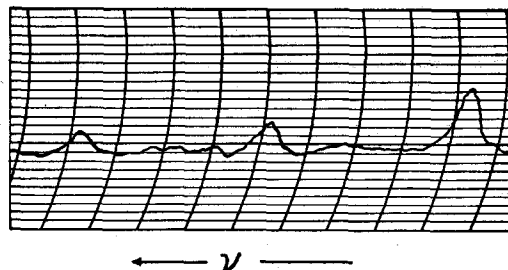


Fig. 2. Microwave absorption of $CF_3CC^{13}H$ in region between 22,280 and 22,380 mc.

state absorptions at slightly higher frequencies. These excited vibrational lines can be seen clearly in Fig. 2.

From relative intensity measurements at room and dry ice temperatures (about -73°), the five lines between 23,053.5 mc and 23,152.9 mc are shown to arise from $J=3 \rightarrow 4$ rotational transitions in CF_3CCH molecules with the degenerate bending vibration ν_{10} excited. The assignments are presented in Table I.

Rotational constants and moments of inertia for the ground vibrational state of four different isotopic species of CF_3CCH are given in Table II.

EXCITED VIBRATIONAL TRANSITIONS

Nielsen's⁵ theory of l -type doubling in symmetric top molecules predicts that the $J=3 \rightarrow 4$ transition for molecules in the first excited degenerate bending vibrational state will consist of six closely spaced lines flanked by two lines split out at nearly equal distances on either side. A broad central line and lines 14.2 mc lower and 14.7 mc higher were actually observed. Solutions for the secular equations given by Nielsen⁵ have been obtained for $J=3$ and $J=4$. Energy levels are obtained which give rise to transitions at the following frequencies:

$$\nu = 8B_v - 256D_J - \frac{60(B_v^2 a / \omega_{10})^2}{(1 - \xi)C_v - B_v}; \quad K=0, l=\pm 1$$

$$\nu = 8B_v - 256D_J - 8D_{JK} + 16(2D_J + D_{JK})\xi \pm 8B_v^2 a / \omega_{10}; \quad K=\pm 1, l=\pm 1$$

TABLE II. Rotational constants for various isotopic species of CF_3CCH in the ground vibrational state, from the $J=3 \rightarrow 4$ transition.

Species	B_0 (mc/sec)	I_B (amu-Å ²)
CF_3CCH	2877.93 ± 0.04^a	175.61 ₃
$CF_3C^{13}CH$	2854.99 ± 0.04	177.02 ₄
$CF_3CC^{13}H$	2787.63 ± 0.04	181.30 ₂
CF_3CCD	2696.02 ± 0.04^a	187.46 ₄

^a These values agree, within experimental error, with those previously reported⁴ for the $J=4 \rightarrow 5$, $6 \rightarrow 7$, and $8 \rightarrow 9$ transitions of CF_3CCH , and $J=5 \rightarrow 6$ and $8 \rightarrow 9$ transitions of CF_3CCD .

⁵ H. H. Nielsen, Phys. Rev. 77, 130 (1950).

TABLE III. Relative intensities I of $v_{10}=2$ and $v_{10}=0$ lines for CF_3CCH .

Temperature	$I(v_{10}=2)/I(v_{10}=0)$ observed	$\omega_{10}(\text{calc})\text{cm}^{-1}$
300°K	24/40	170
200°K	13/40	156

$$\nu = 8B_v - 256D_J - 8D_{JK} - 16(2D_J + D_{JK})\xi - \frac{24(B_e^2 a / \omega_{10})^2}{(1-\xi)C_v - B_v}; \quad K = \pm 1, l = \mp 1$$

$$\nu = 8B_v - 256D_J - 32D_{JK} + 32(2D_J + D_{JK})\xi + \frac{60(B_e^2 a / \omega_{10})^2}{(1-\xi)C_v - B_v}; \quad K = \pm 2, l = \pm 1$$

$$\nu = 8B_v - 256D_J - 32D_{JK} - 32(2D_J + D_{JK})\xi - \frac{28(B_e^2 a / \omega_{10})^2}{3[(1-\xi)C_v - B_v]}; \quad K = \pm 2, l = \mp 1$$

$$\nu = 8B_v - 256D_J - 72D_{JK} + 48(2D_J + D_{JK})\xi + \frac{24(B_e^2 a / \omega_{10})^2}{(1-\xi)C_v - B_v}; \quad K = \pm 3, l = \pm 1$$

$$\nu = 8B_v - 256D_J - 72D_{JK} - 48(2D_J + D_{JK})\xi; \quad K = \pm 3, l = \mp 1.$$

The $K = \pm 1, l = \pm 1$ transitions give rise to two absorption lines spaced $16 B_e^2 a / \omega_{10}$ mc apart. These are the two widely split lines of the l -type multiplet at 23,053.5 and 23,082.4 mc. The other six lines all fall within a one megacycle region centered at 23,067.7 mc. From this assignment $B_e^2 a / \omega_{10}$ is 1.81 mc. This value was also obtained for the $J=4 \rightarrow 5$ and $8 \rightarrow 9$ rotational transitions for molecules in the same excited vibrational state by Anderson *et al.*⁴ If we assume that a is 1.15, as in methyl acetylene,¹ then $\omega_{10} = 176 \text{ cm}^{-1}$.

Relative intensities were measured for the $v_{10}=2$ and ground vibrational lines at two different temperatures. These are given in Table III along with values calculated for ω_{10} assuming a Boltzmann distribution. The frequency of the degenerate C-C≡C bending vibration in trifluoromethyl acetylene determined in this way is in the vicinity of 170 cm^{-1} , and is in satisfactory agreement with the theoretical value 176 cm^{-1} for ω_{10} .

TABLE IV. Dipole moment μ from Stark effect measurements for $J=3 \rightarrow 4$ transition of CF_3CCH in ground vibrational state.

$E^2(\text{ESU}/\text{cm})^2$	$\Delta\nu_{M=3} - \Delta\nu_{M=2}$ mc/sec	μ , Debye	$\Delta\nu_{M=3} - \Delta\nu_{M=1}$ mc/sec	μ , Debye
32.40	12.39	2.314	19.82	2.315
23.25	9.49	2.415	14.77	2.378
20.20	7.92	2.362	12.47	2.343
16.55	6.45	2.360	10.30	2.356
Average $\mu = 2.36 \pm 0.04$ Debye				

STARK EFFECT MEASUREMENTS AND DIPOLE MOMENT

When the electric field in the absorption cell was increased from zero to 1700 volts/cm by the application of a dc voltage to the Stark electrode, the first-order Stark components of the $J=3 \rightarrow 4$ transition of CF_3CCH in the ground vibrational state could be seen to move away rapidly from the original frequency, and then second order components gradually appeared. Complete resolution of the second-order pattern was obtained at 1150 volts/cm.

The change in energy of the levels of a symmetric top molecule having a dipole moment μ and in an electric field E is given by⁶

$$W_{JKM} = -\mu E \frac{KM}{J(J+1)} + \frac{\mu^2 E^2}{2B} \left\{ \frac{\left(\frac{3K^2}{J(J+1)} - 1 \right) \left(\frac{3M^2}{J(J+1)} - 1 \right)}{(2J-1)(2J+3)} - \frac{M^2 K^2}{J^3(J+1)^3} \right\}. \quad (1)$$

Since the electric field is parallel to the electric vector of the microwave radiation, the selection rule $\Delta M = 0$ applies. Transitions for which only the second-order Stark effect occurs are those with either K or M equal to zero; therefore, Eq. (1) reduces to the expression for the frequency shift in a linear molecule

$$\Delta\nu = \frac{3M^2(16J^2 + 32J + 10) - 8J(J+1)^2(J+2) \mu^2 E^2}{J(J+2)(2J-1)(2J+3)(2J+5) h^2 \nu_0} \quad (2)$$

where the transition is from $J \rightarrow J+1$, M is the spatial quantum number, ν_0 is the frequency of the rotational transition when $E=0$, and $\Delta\nu$ is the difference in frequency between ν_0 and the frequency of the Stark component. For $J=3$, $|M|=0$ and $|M|=1$, the components move to lower frequencies; and for $|M|=2$ and $|M|=3$, the components move to higher frequencies. When $M=0$, values of K should be substituted for M in equation (2). Measurements of the difference in frequency of the $M=3$ and $M=2$ components, and of the $|M|=3$ and $|M|=1$ components were made at four different field strengths. From Eq. (2) and the appropriate numerical values for ν_0 and h the expressions

$$\mu^2 = 14.02(\Delta\nu_{M=3} - \Delta\nu_{M=2})/E^2 \quad (3)$$

$$\mu^2 = 8.76(\Delta\nu_{M=3} - \Delta\nu_{M=1})/E^2 \quad (4)$$

are easily derived. Table IV gives the splittings at different field strengths and the values of μ corresponding to these measurements. The error quoted is the sum of the precision error of the measurement and the systematic error due to uncertainty in the electrode spacing.

⁶ D. K. Coles, *Advances in Electronics* (1950), Vol. II, p. 310.

MICROWAVE CONTRIBUTION TO DETERMINATION OF THE MOLECULAR STRUCTURE

In a rigid molecule with a figure axis, the distance of a particular atom on the figure axis from the center of gravity of the unsubstituted molecule is given by

$$Z = \{(I_B' - I_B)(M + \Delta m) / M \Delta m\}^{1/2}, \quad (5)$$

where $I_B' - I_B$ is the difference in the moments of inertia for the unsubstituted molecule and one in which the particular atom has been replaced by a different isotope, M is the original molecular weight, and Δm is the increase in mass as a result of the substitution.

The total moment of inertia of the symmetric top $F_3C-C' \equiv C''-H$ may be written

$$I_B = \frac{3}{2} M_F X_F^2 + 3 M_F Z_F^2 + M_C Z_C^2 + M_{C'} Z_{C'}^2 + M_{C''} Z_{C''}^2 + M_H Z_H^2, \quad (6)$$

where X_F is the perpendicular distance of the fluorine atoms from the figure axis, and the Z 's are the components of the distance of each atom from the center of mass, measured along the figure axis.

Interatomic distances were computed using the following atomic masses ($O^{16} = 16.00000$): H, 1.00813; D, 2.01471; C^{12} , 12.00382; C^{13} , 13.00761; and F, 19.00450. From Eq. (5) and the data of Table II the distance from the center of mass can be calculated for the atoms C' , C'' , and H. The following two bond distances are immediately determined:

$$r_0(C \equiv C) = 1.201 \pm 0.002 \text{ \AA}$$

$$r_0(C-H) = 1.056 \pm 0.005 \text{ \AA}$$

In estimating the limits of error, it must be remembered that Eqs. (5) and (6) hold strictly only for a rigid molecule. We have calculated average, or effective, values for the bond distances for molecules in the ground vibrational state. These effective bond distances differ by very small amounts in going from one isotopic species to another because of changes in zero point vibration frequencies. In carrying out the calculation we multiply these small uncertainties by a factor which depends upon the sensitivity of the calculation to small changes in the moments of inertia. The net result is that, even though the moments of inertia are measured with an accuracy of one part in 10^5 , the interatomic distances calculated from these quantities will not retain this accuracy.

There are five structural parameters in CF_3CCH and measurements have been made for four isotopic species. If one parameter is assumed, the other four can be calculated. The C-H and $C \equiv C$ distances have already been determined unequivocally; therefore, the problem is reduced to one of calculating two of the remaining three parameters for various assumed values of the third. We have chosen to assume several different values for the FCF angle and to calculate the F-C and C-C distances for each of these assumed values from equation (6) and from I_B for CF_3CCH . The results are plotted in

Fig. 3. Each and every set of three parameters obtained by intersecting the two curves and the horizontal coordinate axis of Fig. 3 with a vertical line will be consistent with the measured moments of inertia for CF_3CCH .

A choice of the FCF angle can easily be made by means of electron diffraction results, if the microwave data are assumed to be correct, for there then remains only one shape parameter. It is also true that, except perhaps for the C-H distance, a complete structure determination could be accomplished by means of electron diffraction alone, but the accuracy and elegance of the determination would be decreased.

ELECTRON DIFFRACTION PROCEDURES

Photographs were taken in the apparatus described by Brockway⁷ with sample-bulb temperatures of -68°

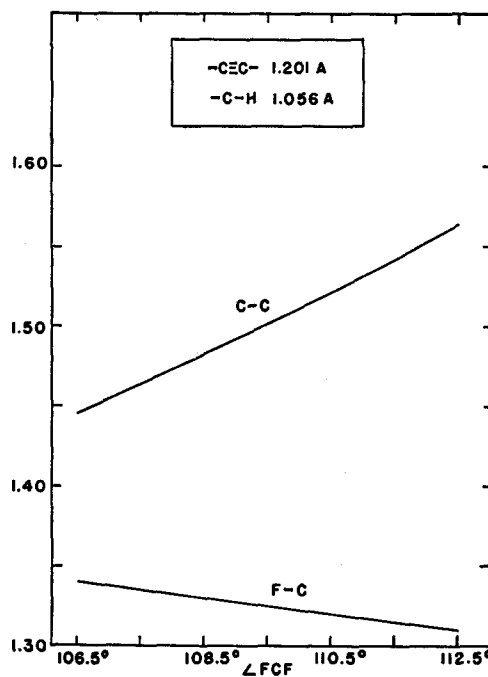


FIG. 3. Parameters of CF_3CCH from microwave spectrum.

to -100° . The camera distance was 10.94 cm, and the electron wavelength, calibrated by means of zinc oxide,⁸ was 0.0606 Å. Corrections for film expansion were made.

The radial distribution curve of Fig. 4 was calculated from the equation,^{9,10}

$$rD(r) = \sum_{q=1, 2, \dots}^{q_{\max}} I(q) \exp(-aq^2) \sin \frac{\pi qr}{10}$$

⁷ L. O. Brockway, *Revs. Modern Phys.* **8**, 231 (1936).

⁸ C. S. Lu and E. W. Malmberg, *Rev. Sci. Instr.* **14**, 271 (1943). ($a = 3.2492 \text{ \AA}$, $c = 5.20353 \text{ \AA}$.)

⁹ R. Spurr and V. Schomaker, *J. Am. Chem. Soc.* **64**, 2693 (1942).

¹⁰ Shaffer, Jr., Schomaker, and Pauling, *J. Chem. Phys.* **14**, 659 (1946).

by the use of punched cards.^{10,11} The visual intensity curve, $I(q)$, was drawn to represent the appearance of the photographs, and the constant a was chosen to make $\exp(-aq^2)$ equal to 0.1 at q equals 100. Peaks

CORRELATION OF VISUAL AND THEORETICAL INTENSITY CURVES

Intensity curves were calculated^{10,11} from the equation⁹

$$I(q) = \sum_{i,j} Z_i Z_j r_{ij}^{-1} \exp(-a_{ij} q^2) \sin \frac{\pi r_{ij} q}{10}$$

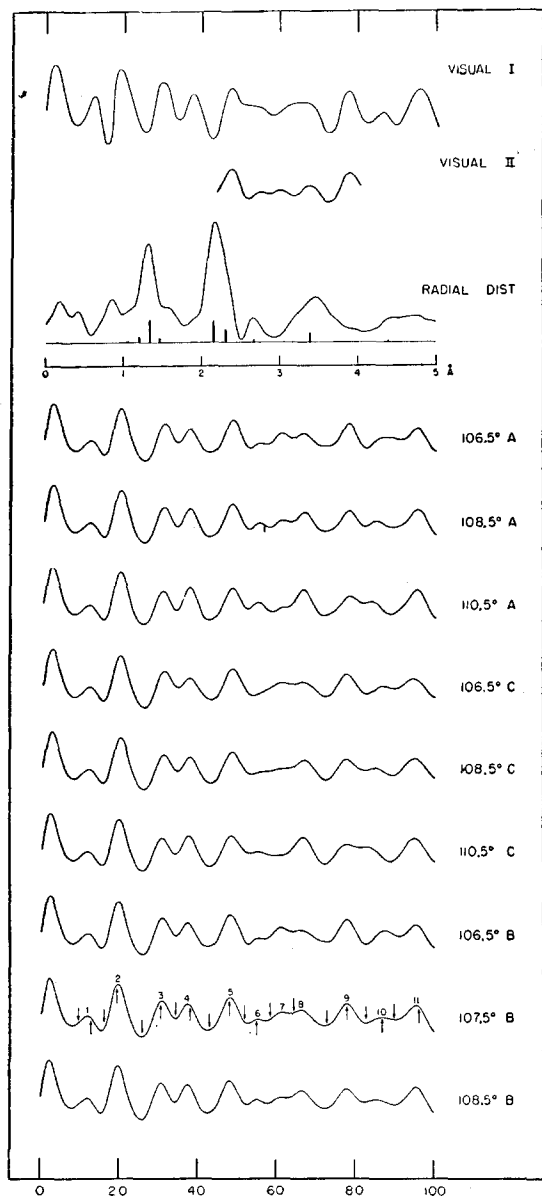


FIG. 4. Electron diffraction intensity functions and radial distribution function.

occur at 0.86Å (error), 1.315Å (C—F), 2.18Å (F···F and C'···F), 2.66Å (C···C''), and 3.46Å (C''···F and error). The heavy lines below the radial distribution curve indicate distances and weights $nZ_i Z_j / r_{ij}$ of the final model.

¹¹ Shaffer, Jr., Schomaker, and Pauling, J. Chem. Phys. 14, 648 (1946).

for models consistent with the microwave data (see Fig. 3) for FCF angles in the range 106.5°–112.5° and the three sets of a_{ij} values shown in Table V. Curves for \angle FCF = 107.5° with further variations of a_{ij} for C'···F and C''···F were also calculated. The significant variations, however, are the ones shown in the Table for C'···F, C''···F, and F···F.

Models 110.5°A and 110.5°C are clearly unacceptable in the region of maxima 8–11 and in the relative heights of maxima, 2, 3, 4, and 5, and only models with the FCF angle less than 108.5° are acceptable if maximum 8 is to be considerably weaker than maximum 9. Since maxima 6, 7, and 8 appear to increase in intensity in the order, 6, 7, 8, models with the FCF angle less than 106.5° are unacceptable. Besides, a weak ring appears at about $q=72$ on model 106.5°A, and maximum 7 disappears in 106.5°C: two objections to 106.5° models which, however, could perhaps be overcome by careful adjustment to the temperature factors.

Maximum 10 and the neighboring minima change very rapidly with \angle FCF and so are very important for the choice of best value and limits of error. According to Visual I they would lead to a choice of about 108°, but it is not certain that the relative depths of the minima are just those shown: the photographs sometimes give the impression that minimum 11 is the weaker, possibly as much as would correspond to an angle of 107°. The position of maximum 10 seems to afford the most sensitive indication, the measured value (which seems to be quite precise) definitely favoring the 107.5° models over the others. In general, all the 107.5° curves calculated are in good agreement with the visual curve. The lack of agreement in the relative depths of minima 2 and 3 and of minima 6 and 7 apparently cannot be resolved by changes in the

TABLE V. Relative temperature factor coefficients, in Å².

Atom pair	$a_{ij} \cdot 10^4$		
	Set A	Set B	Set C
CF	0.15	0.15	0.15
C'F	1.04	0.90	2.08
C''F	2.00	2.55	5.53
FF	0.68	0.68	1.04
FH	5.94	7.25	7.68
CC'	0.10	0.10	0.10
CC''	0.46	0.46	0.46
(C'C'')	0.00	0.00	(0.00)
CH	3.04	3.04	3.04
C'H	2.58	2.58	2.58
C''H	2.22	2.22	2.22

model and presumably arise from errors in the visual curve.¹²

Table VI shows the comparison of measured q values with those read from Curve 107.5°B. The average deviations for 106.5°B and 108.5°B are 0.0075 and 0.0074, both appreciably greater than that, 0.0057, for 107.5°B. The value 1.002 of $\langle q_{\text{calc}}/q_{\text{obs}} \rangle_{\text{AV}}$ is in excellent agreement with the microwave data. This average is satisfactorily stable with respect to changes in the weights, and, perhaps significantly, more so for 107.5°B than for any of the other curves. The parameters of the structure of trifluoromethyl acetylene, with limits of error, are given in Table VII.

ADVANTAGES OF COORDINATED STRUCTURE DETERMINATIONS

The interrelation of electron diffraction and microwave data may be expressed in terms of the intersection of a geometric surface, which defines limits of error for electron diffraction, in the N -dimensional parameter space, with the sheet of $(N-n)$ dimensions which approximately represents the freedom remaining in the choice of parameters when n moments of inertia are known from microwave spectra. On this microwave sheet, limits based on more general knowledge of molecular structures may be drawn; these limits are equally available for the electron diffraction determination. In the ideal case, the model in best agreement with

TABLE VI. Electron diffraction data.

Min (See Fig. 4)	Max	$q(\text{obs})$, Å^{-1}	$q(\text{calc})/$ $q(\text{obs})^*$	Min (See Fig. 4)	Max	$q(\text{obs})$, Å^{-1}	$q(\text{calc})/$ $q(\text{obs})^*$
1		9.5	(0.844)	8		64.1	(0.985)
	1	12.6	(0.942)		8
2		15.9	(0.961)	9		72.5	0.995
	2	19.2	1.019		9	77.7	1.001*
3		25.7	1.001*	10		82.4	1.003
	3	30.3	1.017		10	86.6	1.003*
4		34.17	1.002*	11		89.5	1.008
	4	37.9	0.987		11	95.8	0.995
5		42.8	0.989*	12		99.9	1.008
	5	47.8	1.009*		12	105.6	1.006
6		51.7	(1.016)				
	6	54.8	(1.008)		Average		1.002
7		58.1	(0.980)				
	7		Average deviation		0.0057

* Model 107.5°B. Values in parentheses were omitted from average; those with an asterisk were given double weight.

¹² Having inspected the theoretical intensity curves before studying the photographs, V. S. was unable to make as unbiased an interpretation as was desired, but it seems obvious to him that minimum 6 is very much deeper than shown by Visual I, which was drawn by W. S. Dr. Kenneth Hedberg, who was unacquainted with the details of the investigation, was asked to examine the photographs over the region between what we here call maxima 5 and 9. His representation (Visual II) confirms the conclusion that Visual I is in error in regard to the depths of minima 6 and 7. The consensus on the relative depths of minima 7 and 8, however, is that in this regard Visual I is more nearly correct than Visual II.

TABLE VII. Structure of trifluoromethyl acetylene.

Parameter	Value	Limits of error ^a
C-F	1.335 Å	$\pm 0.01\text{Å}$
C-C'	1.464 Å	$\pm 0.02\text{Å}$
C'≡C''	1.201 Å	$\pm 0.002\text{Å}$
C''-H	1.056 Å	$\pm 0.005\text{Å}$
∠FCF	107.5°	$\pm 1.0^\circ$

^a The C-F, C-C', and ∠FCF values are less certain than the C'≡C'' and C''-H values because the electron diffraction data only restrict the three related parameters of Fig. 3 to a region of parameter space, of size corresponding to the listed limits of error.

the electron diffraction data lies on the microwave sheet and at the center of the electron diffraction limiting surface.

The advantage accruing from the use of electron diffraction data is the reduction of limits based on a general knowledge of molecular structure to diffraction limits of error; the advantages accruing from the use of microwave data are the usually very sharp limitation of the position of the model with respect to certain directions in parameter space, including often some corresponding to the positions of atoms which do not scatter electrons strongly. The most valuable sort of combination is one which minimizes the area of the microwave sheet included by the diffraction limit-of-error surface and the fraction of the volume bounded by this limit-of-error surface which is allowed by the microwave sheet. For particular arbitrary parameters the total range of allowed variation may be minimized under circumstances which do not correspond to this criterion. In any case, the situation for a certain molecule will not be a matter of choice unless the possibility of using only some of the accessible isotopic species is under consideration.

In trifluoromethyl acetylene there is a fortunate combination of methods. Two parameters of direct interest (C-H and C≡C), neither one well determined by electron diffraction, are accurately determined by the microwave data, and the fifth, the sole remaining one, being easily found from electron diffraction.

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