[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Microwave Spectra and Structure of $CF_2{=}CH_2$, $CF_2{=}CHD$ and $CF_2{=}CD_2$

BY WALTER F. EDGELL, PHILIP A. KINSEY[1] AND JONATHAN W. AMY

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The K-band microwave spectra of CF_2CH_2, CF_2CHD and CF_2CD_2 have been recorded and analyzed. With the assumptions that $\angle HCH{=}DCD = 120°$ and $r_{CD} = r_{CH} = 0.009$ Å., the following structural parameters have been calculated: $r_{CF} = 1.321 \pm 0.005$ Å., $r_{CC} = 1.311 \pm 0.005$ Å., $\angle FCF = 109° 15' \pm 25'$, $r_{CH} = 1.10 \pm 0.05$ Å.

The structure of CF_2CH_2 is of interest since it provides further information as to the changes in molecular configuration resulting from multiple fluorine substitution in simple hydrocarbons. Such information for the series of fluorinated methanes was summarized by Lide[1]; the carbon–halogen bonds become progressively shorter as the number of fluorine substituents is increased.

CF_2CH_2 has previously been studied by microwave spectroscopy[2] and by electron diffraction.[3] It was felt that it was worthwhile to repeat the microwave investigation, since the frequencies were measured to an accuracy of only 3 mc. The spectra of the deuterated species were studied to reduce the number of assumptions needed to calculate the structure of the molecule. However, with the data given here it is still necessary to assume a value for one of the structural parameters, and for the extent to which the geometry of the molecule is changed by isotopic substitution.

Experimental

The CF_2CH_2, CF_2CHD and CF_2CD_2 used in these experiments were part of the samples prepared by Edgell and Ultee[4] for the study of the infrared and Raman spectra. The purity of the CF_2CD_2 and CF_2CHD was checked by mass spectrographic analysis. The per cent. of CF_2CHD in CF_2CD_2 was 5.3%. The main impurity in CF_2CHD was 2% of CF_2CH_2. There was also evidence of about 0.4% of CF_2CD_2.

Observations were made with a Stark-effect sweep spectrometer of the Hughes–Wilson type[5] using a 100 kc. square wave for modulation.

The modulating voltages ranged up to about 800 practical volts. All measurements were made in a 10 ft. K-band wave guide absorption cell at Dry Ice temperature. 1N26 crystal detectors were used and a Bendix radio range compass (ARN-7) was modified for use as a receiver. The sensitivity of the system was sufficient to detect NH_3 lines with an intensity of 1×10^{-7} cm.$^{-1}$.

Frequency measurements were made using harmonics from a UHF signal source[6] which was calibrated by comparison with the standard frequencies broadcast by station WWV. It is felt that the frequencies given are accurate to ±0.3 mc., unless otherwise noted.

Analysis of the Spectra; CF_2CH_2.—As pointed out by Roberts and Edgell,[2] CF_2CH_2 is an oblate slightly asymmetric rotor, and to account for the microwave spectrum the dipole must be along the axis of the least moment of inertia. The two Q branch transitions which would be observed for the limiting symmetric rotor each split into a series of lines as a result of the asymmetry. The band heads of these two sub-branches are near 26,700 mc., and one series extends to higher, one to lower frequencies. In addition two R transitions should be found in the region near these Q sub-branch band heads. The whole region should also be covered with lines originating from high J transitions, or from other Q sub-branches whose origins are outside the region of observation.

An initial search of the region from 17,000 to 30,000 mc. yielded approximately 80 lines. Stark patterns indicated that most of these lines had fairly high *J*-values. Analysis of the spectrum essentially confirmed the assignments previously made.[2] In addition the $2_{02} \rightarrow 3_{03}$ and $2_{12} \rightarrow 3_{13}$ lines were found at the frequencies predicted on the basis of these assignments, and displayed the expected resolved Stark patterns. Table I gives the calculated and observed frequencies of all identified transitions. The observed but unidentified lines for CF_2CH_2 are listed in Table II. The rotational constants are (in mc./sec.) (table).

	CF_2CH_2		CF_2CHD		CF_2CD_2	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
A	11,000.8	11,000.8	10,926.9	10,931.6	10,590.5	10,590.5
B	10,428.8	10,429.5	9,545.5	9,541.6	8,994.1	8,986.7
C	5,345.6	......	5,086.7	......	4,855.9	......
$\Delta = I_C - (I_A - I_B)$	0.234		0.262		0.235	
$\kappa =$	0.79771		0.52692		0.44326	

CF_2CD_2.—More than 50 lines were found in the spectrum of CF_2CD_2 in the region from 19,000 to 35,000 mc. Although it was possible to calculate the general pattern of the spectrum from the assumed model, the great density of lines in the spectrum made an unambiguous assignment of individual transitions difficult. The analysis was greatly facilitated by the fact that the $1_{01} \rightarrow 2_{02}$ and $1_{11} \rightarrow 2_{12}$ lines could be identified on the basis of their Stark patterns. Table I shows the observed and calculated frequencies based on the rotational constants given above.

CF_2CHD.—About 80 lines were seen in the spectrum of CF_2CHD in the region from 18,000 to 36,000 mc. After identifying the $1_{01} \rightarrow 2_{02}$ transition on the basis of its Stark pattern, the analysis was completed by assignment of Q branch transitions. The observed and calculated frequencies

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(1) D. R. Lide, Jr., THIS JOURNAL, **74**, 3548 (1952).

(2) A. Roberts and W. F. Edgell, *J. Chem. Phys.*, **17**, 742 (1950); *Phys. Rev.*, **76**, 178A (1950).

(3) I. L. Karle and J. Karle, *J. Chem. Phys.*, **18**, 963 (1950).

(4) W. F. Edgell and C. J. Ultee, *ibid.*, **22**, 1984 (1954).

(5) R. H. Hughes and E. B. Wilson, Jr., *Phys. Rev.*, **71**, 562 (1947).

(6) The UHF signal source was designed and built by L. C. Hedrick, *Rev. Sci. Instr.*, **24**, 565 (1953).

TABLE I

THE ROTATIONAL TRANSITIONS OBSERVED AND IDENTIFIED OF CF_2CH_2, CF_2CHD AND CF_2CD_2 IN MC./SEC.

Transition	CF_2CH_2	CF_2CHD	CF_2CD_2
$1_{11} \rightarrow 2_{12}$	26,465.6(26,465.6)[a]	24,805.5(24,805.5)	23,561.7(23,561.7)
$1_{01} \rightarrow 2_{02}$	26,991.7(26,991.9)	25,912.7(25,912.7)	24,778.2(24,778.2)
$1_{10} \rightarrow 2_{11}$	36,633[b] (36,632.0)	33,723.1(33,723.1)	....
$2_{02} \rightarrow 3_{03}$	37,461[b] (37,459.0)	35,751.8(35,751.8)	34,178.2(34,178.2)
$2_{12} \rightarrow 3_{13}$	37,417 (37,415.9)	35,512.2(35.512.4)	33,857.0(33,856.8)
$3_{13} \rightarrow 3_{12}$	26,646.2(26,646.2)	24,595.1(24,598.0)	23,114.4(23,120.8)
$3_{03} \rightarrow 3_{22}$	26,881.2(26,876.2)	25,937.9(25,939.7)	24,950.7(24,955.4)
$3_{12} \rightarrow 3_{31}$	18,075.0(18,078.6)	21,056.0(21,057.1)	21,587.7(21,589.2)
$4_{22} \rightarrow 4_{41}$	19,710.9(19,713.6)	26,327.3(26,329.5)	....
$4_{13} \rightarrow 4_{32}$	27,014.7(27,010.8)	26,815.7(26,818.4)	....
$4_{23} \rightarrow 4_{22}$	26,627.6(26,625.4)	23,004.8(23,007.9)	21,084.9(21,093.0)
$4_{24} \rightarrow 4_{32}$	....	....	26,203.4(26,208.0)
$4_{14} \rightarrow 4_{24}$	....	....	33,619.5(33,628.4)
$4_{04} \rightarrow 4_{23}$	....	35,643.3(35,648.7)	....
$5_{33} \rightarrow 5_{32}$	25,725.2(25,724.3)	20,529.2(20,529.4)	....
$5_{23} \rightarrow 5_{42}$	27,297.0(27,295.7)	28,728.4(28,732.4)	28,933.9(28,938.0)
$5_{24} \rightarrow 5_{23}$	....	34,704.2(37,707.7)	32,567.8(32,578.5)
$5_{32} \rightarrow 5_{51}$	....	33,792.5(33,795.8)	....
$5_{14} \rightarrow 5_{33}$	....	35,643.3(35,648.8)	....
$6_{42} \rightarrow 6_{41}$	25,245.7(25,245.9)	....	....
$6_{43} \rightarrow 6_{41}$	24,771.0(24,771.3)	....	....
$6_{33} \rightarrow 6_{52}$	27,821.2(27,819.9)	32,264.5(32,259.6)	....
$6_{24} \rightarrow 6_{43}$	....	35,922.1(35,924.4)	....
$7_{53} \rightarrow 7_{52}$	23,435.7(23,440.2)	....	....
$7_{43} \rightarrow 7_{62}$	28,696[b] (28,699.3)	....	....
$7_{44} \rightarrow 7_{43}$	....	30,804.8(30,812.0)	....
$8_{63} \rightarrow 8_{62}$	21,745.2(21,749.2)	....	....

[a] Calculated frequencies are in parentheses. [b] These lines are measured with an accuracy of ±1 mc.

TABLE II

OBSERVED BUT UNIDENTIFIED LINES OF CF_3CH_2

17,008[a]	20,957.1	23,270[a]	24,357.4	26,329.0
17,229.3	21,484.0	23,323.0	24,449.6	26,335.6
17,843.8	21,572.6	23.360.4	24.543.3	26,726[a]
17.892.1	21,689.0	23,647.1	24,581.4	26,832.0
18,907.5	22,236.3	23,770.5	24,639.8	27,112.0
19,098.9	22,273.4	23.814.4	24,729.2	27,218.6
19,254[a]	22.386.2	23,994.7	24,809.7	27,680.4
19,660.9	22,394.8	24,020.5	25,352.1	28,177.7
19.723.3	22,744.7	24,149.3	25,448.9	28,414.2
19,726.5	23,180.0	24,293.6	25,516.3	28,438.1
20,038.2	23,208.1	24,323.2	25,742.0	28.455.1
20.345.0	23,215.3	24,353.3	26,116.4	28,945.3

[a] These lines were measured with an accuracy of ±1 mc.

based on the rotational constants above are given in Table I.

Structural Parameters.—For a planar molecule, the moment of inertia about the axis perpendicular to the plane should equal the sum of the other two moments. As a result of zero-point vibrations, this holds only approximately for actual molecules; the small value of the "defect" $\Delta = I_C - (I_A - I_B)$ given above confirms the assumed planarity of CF_2CH_2.

The moment of inertia around the C–C bond in CF_2CH_2 is a function of only two parameters: r_{FF}, the distance between fluorine atoms and r_{HH}, the distance between hydrogen atoms. With the assumption that the geometry of the molecule is unchanged by isotopic substitution one can calculate r_{FF} and r_{HH} directly from the A moments of inertia for CF_2CH_2 and CF_2CD_2. Since this assumption can only be approximately true, it seemed preferable to assume instead a value for δ, the shortening of the C–H distance with deuterium substitution. The value chosen was 0.009 Å., in agreement with the results of Miller, *et al.*,[7] for the methyl halides; it seems unlikely that δ would differ from this value by more than a few thousandths of an ångström. In these calculations it is assumed that the HCH angle is near 120°; the results are almost independent of the precise value.

r_{FF} proves to be very insensitive to δ, changing by only 0.002 Å. if δ is changed from 0 to 0.009 Å. The best value of r_{FF} is 2.154 Å.

The r_{HH} and r_{DD} distances, of course, are more sensitive to δ: for $\delta = 0$, $r_{HH} = r_{DD} = 1.881$ Å.; for $\delta = 0.009$ Å., $r_{HH} = 1.912$ Å., $r_{DD} = 1.897$ Å.

The B moment of inertia of CF_2CH_2 depends on three parameters which may be taken as the projection of the CF distance on the CC axis, the C–C distance and the HCH angle. Although three isotopic species were available, the equation relating the observed moment to these parameters for CF_2CHD is nearly a linear combination of the corresponding equations for CF_2CH_2 and CF_2CD_2, and gives no additional information. It is therefore necessary to assume a value for one parameter in order to determine a structure.

As a result of the small mass of the H atom, the moment depends only slightly on any assumption made about the configuration of the CH_2 group. If the HCH angle is chosen as 120° for all isotopic species, and the isotope effect on the CH distance

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(7) S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes and J. Kraitchman, *J. Chem. Phys.*, **20**, 1112 (1952).

is the same as assumed above, the resulting parameters are those given below along with the results of the electron diffraction study.[3]

	This research	Electron diffraction[3]
<FCF	109° 15′ ± 25′	110°
C–F	1.321 ± 0.005 Å.	1.321
C–C	1.311 ± 0.005 Å.	1.311 ± 0.035 Å.
<HCH	120° (assumed)	117° ± 7°
C–H	1.10 ± 0.05 Å.	1.07 ± 0.02 Å.

The CH distance corresponding to our choice of the HCH angle is 1.10 Å. A change in the angle of 9° changes the CH distance by 0.05 Å., but only changes the other parameters by less than 0.005 Å. Thus the microwave data still leave the geometry of the CH_2 group somewhat uncertain, but defines the remaining parameters quite precisely, since the actual HCH angle can hardly be expected to differ so greatly from 120°.

The measured FCF angle is nearer to the tetrahedral value than to that of 120° expected on the usual assumption that the σ-bonds are formed with sp^2 hybrids. It is interesting to note that near-tetrahedral values of the corresponding angle are not unusual in the substituted ethylenes, though the angle reported for ethylene itself[8] is 119° 55′. The particularly small value of the FCF angle is also in line with that reported[1] for CH_2F_2.

Comparison of the C–C distance with that found for ethylene[8] indicates that there is appreciable triple-bond character in the bond, an effect that may be associated with the closing of the FCF angle.

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(8) W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM SOUTHERN METHODIST UNIVERSITY]

Experimental Investigation of the Distribution of Salicylic Acid between Cyclohexane and Water

BY JOHN J. BANEWICZ, CHARLES W. REED AND MARK E. LEVITCH

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The distribution of salicylic acid between water and cyclohexane was investigated at various temperatures from 24.00 to 55.00° and at concentrations from 10^{-4} to 10^{-2} mole per liter in water and cyclohexane. The concentrations were determined spectrophotometrically. In the more dilute concentrations, the dimerization of salicylic acid in cyclohexane was found to be negligible; and from the data in this region the ionization and distribution constants were obtained. In the more concentrated regions the dimerization became appreciable; and from the data in this region the dimerization constant was calculated. With these constants known as a function of temperature, the heats, entropies and free energies of dimerization, distribution and ionization were calculated.

In spite of the numerous references to salicylic acid in the literature there are very few data on the dimerization of salicylic acid in non-polar solvents. By studying the distribution of salicylic acid between cyclohexane and water not only can the distribution coefficient be obtained, but also the ionization constant of the salicylic acid in water and the dimerization constant in cyclohexane. Furthermore if determinations are made at different temperatures the various enthalpy, free energy and entropy changes can be calculated.

Experimental

Materials.—Matheson practical grade cyclohexane was used. The cyclohexane was purified by passage through a column of activated silica gel in accordance with the procedure of Graff, O'Conner and Skau.[1] Salicylic acid was recrystallized from cyclohexane and then sublimed.

Spectrophotometric Measurements.—The concentrations of salicylic acid in both the cyclohexane and water layers were determined spectrophotometrically using a Beckman DU spectrophotometer. For each solvent, solutions of known concentration were prepared ranging from 10^{-4} to 10^{-2} mole per liter. The standard solutions in each solvent were saturated with respect to each other. Salicylic acid has absorption maxima in water at 231 and 296 mμ and in cyclohexane at 240 and 310 mμ. Beer's law was obeyed at all four peaks.

The following equations were found to relate A, the absorbance, to C_g, the concentration of salicylic acid in grams of acid per gram of solvent

Water	231 mμ	$C_g = 2.09 \times 10^{-5} A$
Cyclohexane	240 mμ	$C_g = 2.08 \times 10^{-5} A$
Water	296 mμ	$C_g = 3.96 \times 10^{-5} A$
Cyclohexane	310 mμ	$C_g = 4.32 \times 10^{-5} A$

All readings were taken in triplicate with an average variation of 0.002 absorbance units.

Distribution Method.—Preliminary measurements were made to determine the approximate relation between equilibrium concentrations of the aqueous and cyclohexane solutions of salicylic acid. With this information seven different mixtures were made up with concentrations varying from about 10^{-2} to 10^{-4} mole per liter. The mixtures were placed in glass-stoppered Pyrex bottles in a constant temperature bath and allowed to equilibrate for three days with occasional shaking. At the end of this time samples were withdrawn from each layer, diluted by weight if necessary to bring the concentration into the spectrophotometric range, and the absorbance determined.

This procedure was repeated daily until constant concentration values were obtained. Almost always equilibrium was obtained within a three-day period. Using the known dilution factor, the concentrations of salicylic acid in the water and cyclohexane layers were calculated. The concentrations were converted to moles per liter, assuming the solutions to be so dilute that the solvent and solution densities could be considered identical.

This procedure was repeated for all the solutions at seven different temperatures, 24.00, 29.50, 32.00, 36.00, 40.05, 47.13 and 55.00°. The temperature was controlled to within 0.01° by a Sargent Thermonitor unit.

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(1) M. M. Graff, R. T. O'Conner, and E. L. Skau, *Ind. Eng. Chem. Anal. Ed.*, **16**, 556 (1944).