BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (7), 1984—1986 (1975)

Molecular Structure of 2-Fluoropropane as Determined By Gas Electron Diffraction

Hironobu KAKUBARI,* Takao IIJIMA, and Masao KIMURA**

Department of Chemistry, Faculty of Sciences, Hokkaido University, Sapporo 060

(Received December 23, 1974)

The skeletal parameters, C–C, C–F, and C···F distances, of 2-fluoropropane have been determined by means of gas electron diffraction. The r_g-values obtained are: C–C 1.514±0.004 Å, C–F 1.405±0.005 Å and C···F 2.366 ±0.006 Å.*** By a joint analysis of the diffraction data and the spectroscopic moments of inertia, determination of the remaining structural parameters has also been attempted, and the ϕ_z value of the CCC angle being found to be 114.6±1.5 °.

It is well-known that systematic elongations of both C–C and C–Cl distances are observed in the series of chloroalkanes, *viz.*, from methyl to ethyl to isopropyl to *t*-butyl chlorides.[1–3] In the corresponding series of fluorides,[4] however, the structure of isopropyl fluoride, or 2-fluoropropane, was not determined until recently. The microwave spectrum of this molecule was observed by Griffiths, Owen, and Sheridan, and the rotational constants were obtained.[5] However, they did not determine the structural parameters since their spectrum was only for the normal species. Saito and co-workers measured the microwave spectra of the normal and six isotopic species and found a reasonable set of the r_0-structure.[6]

The molecule is unfavorable for determining the structure from spectroscopic data, because the central carbon is close to the center of gravity and there is no stable isotope for fluorine. The C–C and C–F distances are especially difficult to determine accurately. Such being the case, it is desirable to obtain information on the skeletal structure by means of gas electron diffraction to complement the spectroscopic r_0-structure.

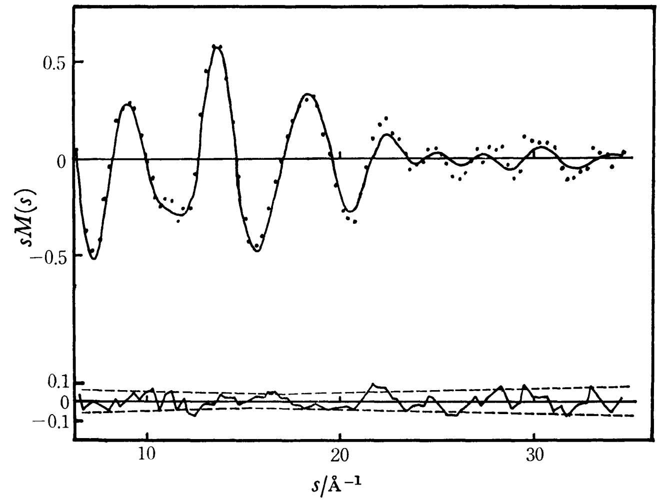

Fig. 1. Molecular intensity curve of 2-fluoropropane. Experimental values (dots) are compared with the best-fit theoretical (solid curve). The residuals are shown below, where the broken curves represent the estimated uncertainty in the intensity measurement.

In the present diffraction study, the C–C and C–F bonded distances and the C···F non-bonded distance were determined. Furthermore, by a joint analysis of the diffraction and spectroscopic data, determination of the complete structure of this molecule was attempted.

Experimental

The sample was synthesized by Dr. Shuji Saito, Sagami Chemical Research Center, the purity being checked by him to be about 99.5% by gas-chromatography. The diffraction photographs were taken at room temperature by a unit with an r^3-sector[7] under the following conditions: camera length, 109.3 mm; accelerating voltage, 40 kV; beam current, 0.2 μA; exposure time, 2—4 min; sample pressure, 50—20 Torr. The scale factor was calibrated by the diffraction pattern of carbon disulfide. The total range of s covered was from 7 to 36 Å^{-1}. Five plates were selected for the least square analysis. The observed reduced molecular intensity is shown in Fig. 1, together with the calculated intensity for the best-fit model.[8]

Analysis of the Diffraction Data

The skeletal parameters, C–C, C–F, and C···F distances, were determined by a least square adjustment for molecular intensity. Routine procedure[9,10] was followed for scattering factors, anharmonicity constants and other details of the analytical processes. The final results obtained from the analysis of five plates are given in Table 1. Other structural parameters were fixed

TABLE 1. RESULTS OF THE LEAST SQUARE ANALYSIS OF THE DIFFRACTION DATA FOR 2-FLUOROPROPANE[a]

Adjusted parameters		Fixed parameters[b]	
r_g(C–F)	1.405(5)	r_a(C···C)	2.535
r_g(C–C)	1.514(4)	r_a(C–H$_{\text{Methyl}}$)	1.091
r_g(C···F)	2.366(6)	r_a(C–H$_{\text{sec}}$)	1.096
index of resolution	0.97—1.05	ϕ_α(CCH$_{\text{sec}}$)	109.2
		ϕ_α(HCH$_{\text{Methyl}}$)	107.7

a) Distances in Å and angles in degrees. The numbers in parentheses indicate the limits of error attached to the last significant digit. For the definitions of r_g, r_a and ϕ_α see Ref. 11. b) Those non-bonded distances not shown in the Table were computed by use of the parameters listed here. The local C_{3v} symmetry of the methyl groups is assumed. The C–H bonds which lie on the CCC plane are in the *trans* position to the C–C bond.

---

* Present address: Oki Electric Industry, Co. Ltd., Higashikanagawa, Hachioji, Tokyo.

** To whom correspondence should be addressed.

*** 1 Å = 100 pm is used throughout this paper.

to appropriately assumed values, also listed in Table 1. Most of the assumed values were taken from the r_s-structure of propane.[12] These values were eventually replaced by those obtained by a joint analysis of the diffraction results and the spectroscopic moments of inertia, given in Table 4, and the least square calculation was repeated for the molecular intensity of a plate or two. The most probable values of the adjusted parameters did not vary significantly.

The mean amplitudes of vibration were also fixed to the calculated values. The force constants were adjusted by the method of Cyvin and Cyvin[13] so as to reproduce the fundamental frequencies observed by Griffiths, Owen and Sheridan[5] and Crowder and Koger.[14] The method is an iterative process based on the relation, $\boldsymbol{F}=\tilde{\boldsymbol{L}}_0^{-1}\boldsymbol{\Lambda}\boldsymbol{L}_0^{-1}$, where $\boldsymbol{L}_0$ is the transformation matrix obtained from a trial set of the force constants, $\boldsymbol{\Lambda}$ is the eigenvalue matrix of the observed values and $\boldsymbol{F}$ is the improved force-constant matrix. The calculation is iteratively repeated until the calculated eigenvalues converge exactly to the observed values. The force constants thus obtained are still approximate, since the set can only be one of the many possible sets which could reproduce the observed vibrational frequencies. However, it is considered to be sufficient for evaluating mean amplitudes as long as the initial trial set is properly chosen.

Table 2. Calculated values of the mean amplitudes of vibration at 298 K (in Å units)

C–F	0.0540	H···H	0.13—0.26[a]
C–C	0.0562	C···H	0.11—0.16
C···F	0.0814	F···H	0.11—0.16
C–H	0.0784		

a) The range indicates the distribution of the calculated values among the non-equivalent non-bonded distances.

The set of force constants of 2-chloropropane determined by Cyvin and Cyvin[13] was used as the initial trial, where the diagonal constant for the C–F stretching of CH_3F,[15] 3.135 mdyn/Å, was used. The mean amplitudes at 298 K thus calculated are listed in Table 2.

Joint Analysis of the Diffraction Results and the Spectroscopic Rotational Constants

Determination of the structural parameters which were not obtained by analysis of the diffraction data was carried out by means of a joint analysis of the diffraction intensity and the rotational constants on the basis of the zero-point average structure. The vibrational corrections for both r_g-distances and rotational constants were carried out by the ordinary method.[16] All the normal modes including the torsional motion of the methyl tops were treated as small-amplitude motions, since the barrier to internal rotation as high as 3.0—3.5 kcal/mol[5] makes it unnecessary to rely on the large-amplitude theory for the vibrational correction.[17,18] The moments of inertia and the calculated values of the vibrational correction are listed in Table 3. The values of r_g—$r_\alpha{}^0$ are 0.0029 Å, 0.0024 Å, and 0.0007 Å for C–F, C–C, and C···F distances, respectively.

Table 3. Moments of inertia of 2-fluoropropane[a] (in amu Å^2 units)

	$I^{(0)}$	ΔI	$I^{(z)}$
a	58.131	0.065	58.196(7)[b]
b	62.373	0.091	62.464(9)
c	105.533	0.064	105.597(7)

a) $I^{(0)}$; Observed effective values for the ground vibrational state (Refs. 5 and 6). Conversion factor 505376 MHz amu Å^2 was used. ΔI; Calculated values of the vibrational correction. $I^{(z)}$; Moments of inertia for the zero-point average structure.
b) Estimated uncertainties to be attached to the last significant digit.

Table 4. Structure parameters of 2-fluoropropane compatible with both the diffraction data and the spectroscopic moments of inertia[a]

C–F	r_g	1.405±0.005
C–C	r_g	1.514±0.004
C···F	r_g	2.366±0.006
∠CCC	ϕ_z	114.6±1.5
C–H$_{\text{Methyl}}$ C–H$_{\text{sec}}$	r_g	1.13±0.03[b]
∠HCH$_{\text{Methyl}}$	ϕ_z	110±3
∠CCH$_{\text{sec}}$	ϕ_z	109.0 (assumed)

a) Distances in Å and angles in degrees. b) The values of $r_g-r_\alpha{}^0$ for C–H$_{\text{Methyl}}$ and C–H$_{\text{sec}}$ are 0.020 Å and 0.016 Å, respectively.

For a complete description of the structure of this molecule, eight independent parameters given in Table 4 are necessary. Three distances from electron diffraction and three moments of inertia from microwave spectroscopy are therefore insufficient. Although the rotational constants of ^{13}C-species and singly deuterated species are available,[6] none of them effectively provide independent additional information. The following two assumptions were then made: (1) The C–H$_{\text{Methyl}}$ and C–H$_{\text{sec}}$ are equivalent in their r_g-values. (2) The CCH$_{\text{sec}}$ angle is within the range of 109±2 °. The implication of the first assumption is essentially the same as the equivalence of C–H distances in r_e-values. As for the second assumption, it was found that the moments of inertia $I^{(z)}$ are very insensitive to the CCH$_{\text{sec}}$ angle. A variation of CCH$_{\text{sec}}$ as much as 2 ° produces changes in $I^{(z)}$ of only about 0.01 amu Å^2.

Since there remain six parameters for the six independent observables, they can be determined uniquely for each combination of the six observed values which are allowed to vary within their stated uncertainties. Therefore, for the three distances from electron diffraction, the uncertainties can not be reduced by the joint analysis as in other more favorable cases.[17,19] The other three parameters can only be determined with large uncertainties, since they are strongly correlated with the three distances from diffraction. Numerical results are summarized in Table 4. The uncertainties for ∠CCC, C–H, and ∠HCH represent the maxima and minima of the ranges of these parameters in which the values compatible with the moments of inertia are found, as the C–F, C–C, and C···F distances are varied within the stated limits of error. The uncertainties associated with the limits of error of $I^{(z)}$ are much smaller. The CCC angle is determined with a reasonable range of uncertainty. The C–H distance and the HCH angle shown in Table 4 are larger than the commonly accepted range of methyl structure. Nevertheless, both C–H and HCH would decrease if the C···F distance decreases. This seems to suggest that the anharmonicity of the non-bonded C···F distances, which was assumed negligible in the present study, is substantially nonzero.

Discussion

The C–C and C–F distances of 2-fluoropropane are compared with those of other fluoroalkanes in Table 5. Although the comparison is somewhat obscured by lack of the r_g-distances for some of the compounds concerned, the trends that both C–C and C–F distances increase from methyl to ethyl, isopropyl, and *t*-butyl are observed in the same way as in the chlorides. The C–C distances of fluorides are smaller than those of *n*-alkanes, *e.g.*, propane.[10] The shortening seems to be similar in nature to that often encountered in fluorine substitution.[23]

Table 5. Comparison of the structural parameters of fluoro-alkanes (in Å units)

		C–C	C–F	Ref.
CH_3F	r_0		1.3852(1)	20
CH_3CH_2F	r_0	1.505(3)	1.398(5)	4
$(CH_3)_2CHF$	r_0	1.515(1)	1.407(2)	6
	r_g	1.514(4)	1.405(5)	a)
$(CH_3)_3CF$	r_0	1.516(5)	1.43(2)	21
	r_g	1.522(8)	1.427(8)	22[b)]
$(CH_3)_2CH_2$	r_g	1.532(3)		10

a) The present study. b) Estimated from the reported r_a-values, 1.520 and 1.425, respectively.

The r_0-structure reported by Saito and co-workers[6] is consistent with the r_g-structure determined in the present study. However, since the difference between r_0 and r_g values is often as large as 0.01 Å, the closeness of r_0 and r_g seen in Table 5 can be fortuitous.

The authors wish to thank Dr. Shuji Saito, Sagami Chemical Research Center, for the sample and for his helpful discussions. Numerical computation was performed on a FACOM 230-60 of the Hokkaido University Computing Center and also on a FACOM 270-20 in the laboratory of Professor Kimio Ohno, to whom the authors' thanks are due.

References

1) D. R. Lide, Jr. and M. Jen, *J. Chem. Phys.*, **38**, 1504 (1963).

2) F. L. Tobiason and R. H. Schwendeman, *ibid.*, **40**, 1014 (1964).

3) R. L. Hilderbrandt and J. D. Wieser, *ibid.*, **56**, 1143 (1972).

4) L. Nygaard, *Spectrochim. Acta*, **22**, 1261 (1966).

5) J. H. Griffiths, N. L. Owen, and J. Sheridan, *J. Chem. Soc. Faraday II*, **69**, 1359 (1973).

6) K. Yoshida, F. Makino, and S. Saito, private communication. A preliminary report was read at the Spring 26 th National Meeting of the Chemical Society of Japan (Tokyo, 1972).

7) Y. Murata, K. Kuchitsu, and M. Kimura, *Jap. J. Appl. Phys.* **9**, 591 (1970).

8) Numerical experimental data of the leveled total intensity and the background, together with the correlation matrix, have been deposited with the Chemical Society of Japan. (Document No. 7514).

9) S. Konaka and M. Kimura, This Bulletin, **43**, 1693 (1970).

10) T. Iijima, *ibid.*, **45**, 1291 (1972).

11) K. Kuchitsu and S. J. Cyvin, "Molecular Structures and Vibrations," ed. by S. J. Cyvin, Chapter 12, Elsevier, Amsterdam (1972).

12) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

13) B. N. Cyvin and S. J. Cyvin, *Acta Chem. Scand.*, **26**, 3943 (1972).

14) G. A. Crowder and T. Koger, *J. Mol. Struct.*, **23**, 311 (1974). The observed values of frequencies are consistent with those given in Ref. 5, although the assignments slightly differ.

15) S. Mizushima and T. Shimanouchi, "Infrared Absorption and Raman Effect," (in Japanese), Kyoritsu, Tokyo (1958).

16) K. Kuchitsu, "MTP International Review of Science. Physical Chemistry Series One," vol. 2, ed. by G. Allen, Chapter 6, Medical and Technical Publishing Co. Ltd., Oxford (1972).

17) T. Iijima and S. Tsuchiya, *J. Mol. Spectrosc.*, **44**, 88 (1972).

18) We also applied the large-amplitude treatment to the analysis of this molecule and found that either method leads to the same result if the distances are represented in terms of the r_g-structure.

19) T. Iijima, This Bulletin, **45**, 3526 (1972).

20) F. A. Andersen, B. Bak, and S. Brodersen, *J. Chem. Phys.*, **24**, 989 (1956).

21) D. R. Lide, Jr. and D. E. Mann, *ibid.*, **29**, 914 (1958).

22) B. Haase, J. Haase, and W. Zeil, *Z. Naturforsch.*, **22a**, 1646 (1967).

23) A. Yokozeki and S.H. Bauer, "The Geometric and Dynamic Structures of Fluorocarbons and Related Compounds," in "Topics in Current Chemistry," Springer Verlag, Berlin (1974).