tend to impart lower apicophilicities to the leaving group and hence favor a retention mechanism compared to softer nucleophiles.

Conclusions

With a constant nucleophile, the experimental LG order, $Cl^- > F^- \sim SH^- > OH^- > H^-$, and tendency toward inversion, $Cl^- > F \sim SH^- > OH^- > H^-$, are reflected in the context of these calculations by (1) an increase in overlap population of the Si–LG bond, $Cl^- < F^- < SH^- < OH^- < H^-$ (Figure 2), and (2), with the exception of SH^-, a decrease in apicophilicity of the LG (Figure 3). For example, with Nu = H^-, the apicophilicity decreases in the order $Cl^- > SH^- > F^- > OH^- > H^-$. These results support retention proceeding via the pseudorotation mechanism, increasing in this order. Since there is no correlation between the apicophilicity of the nucleophile and the experimental tendency toward inversion or retention, this calculation provides no support of a retention mechanism involving equatorial attack. Together with the evidence presented elsewhere,[6] namely, the relative high energy of edge attack, we can rule out equatorial attack as a feasible mechanism.

With a constant LG, the apicophilicity of the LG is affected by the nucleophile. For example, with LG = Cl^-, the apicophilicity of Cl^- decreases as the nucleophile is varied in the order (of nucleophiles) Cl > H > SH > F ~ OH. A change in nucleophile alters to a different extent the overlap population of the LG in both axial and equatorial positions (Figure 4) and the apicophilicity of the LG varies with the hard–soft character of the nucleophile. Softer nucleophiles increase the apicophilicity of the LG, which favor inversion, and harder nucleophiles decrease the apicophilicity of the LG, which favors retention (Figure 5).

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Registry No. SiH_4, 7803-62-5; SiH_3OH, 14475-38-8; SiH_3SH, 14044-97-4; SiH_3F, 13537-33-2; SiH_3Cl, 13465-78-6; H^-, 12184-88-2; F^-, 16984-48-8; OH^-, 14280-30-9; SH^-, 15035-72-0; Cl^-, 16887-00-6; Si, 7440-21-3.

Supplementary Material Available: Relative energy, charge density, overlap populations, and bond distances for $[SiH_3XY]^-$ (Table SI) (3 pages). Ordering information is given on any current masthead page.

The Microwave Spectra, Electric Dipole Moment, and Molecular Structure of 1,1,2,2-Tetrafluorocyclopropane

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Abstract: The microwave spectra of the normal, monodeuteriated, dideuteriated, and carbon-13 isotopic species of 1,1,2,2-tetrafluorocyclopropane have been investigated and assigned in the region 26.5–40.0 GHz. The spectral assignments have yielded sufficient data to enable a complete determination of the molecular geometry in the frameworks of both the normal and dideuteriated isotopic species. The partial r_s parameters in the framework of the normal isotopic species are $r(C_1C_2)$ = 1.471 (3) Å, $r(C_3C_{1,2})$ = 1.497 (10) Å, $r(C_{1,2}F)$ = 1.344 (4) Å, $r(C_3H)$ = 1.088 (5) Å, $\theta(FC_{1,2}F)$ = 109.9 (4)° and $\theta(HC_3H)$ = 118.0 (4)°. The electric dipole moment is determined to be 2.16 (3) D. The rotational spectra and symmetry of two low lying vibrational modes were assigned in the dideuteriated isotopic species. The frequencies of the modes were determined from relative intensity measurements to be 188 (9) cm^{-1} for the symmetric (A) vibrational state and 178 (13) cm^{-1} for the antisymmetric (B) vibrational state in accord with the previous vibrational assignments. All the ring bonds in 1,1,2,2-tetrafluorocyclopropane are found to shorten relative to cyclopropane with the greater reduction occurring in the C_1–C_2 bond. The FCF and HCH methylene angles, however, are larger in 1,1,2,2-tetrafluorocyclopropane than in 1,1-difluorocyclopropane. These results are related to structural trends established by several experimental and theoretical studies which examined the effect of fluorine substitution on the geometry of substituted cyclopropanes and oxiranes.

A number of experimental[1-10] and theoretical[11-15] investigations have been conducted to elucidate the effect of fluorine substitution upon the ring geometries of the fluorinated cyclopropanes and ethylene oxides. In the latter series, microwave spectroscopic studies have enabled the determination of complete molecular structures for ethylene oxide,[16] *cis*- and *trans*-1,2-difluoroethylene oxide[8,9] and 1,1,2,2-tetrafluoroethylene oxide.[10] The carbon–oxygen and carbon–carbon ring bond lengths of the 1,2-difluoroethylene oxides are found to shorten, relative to ethylene oxide, with the greater reduction occuring in the trans isomer.[9] A near-linear reduction in ring bond lengths is found to occur from ethylene oxide to *cis*-1,2-difluoroethylene oxide to 1,1,2,2-tetrafluoroethylene oxide.[10]

Molecular structures of *cis*- and *trans*-1,2-difluorocyclopropane[4,5] have recently been obtained from analysis of microwave spectra. The C_1–C_2 and C_3–$C_{1,2}$ ring bond lengths of both species are found to shorten, relative to cyclopropane,[17] with the greater reduction occurring in the trans isomer.[5] These results parallel

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(1) Perretta, A. T.; Laurie, V. W. *J. Chem. Phys.* **1975**, *62*, 2469–2473.
(2) Laurie, V. W.; Stigliani, W. M. *Mol. Spectrosc. Symp.* **1975**, *30*, TF5.
(3) Gillies, C. W. *J. Mol. Spectrosc.* **1976**, *59*, 482–492.
(4) Sengupta, S. K.; Justnes, H.; Gillies, C. W.; Craig, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 876–880.
(5) Justnes, H.; Zozom, J.; Gillies, C. W.; Sengupta, S. K.; Craig, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 881–887.
(6) Beauchamp, R. N.; Agopovich, J. W.; Gillies, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 2552–2560.
(7) Chiang, J. F.; Bernett, W. A. *Tetrahedron* **1971**, *27*, 975–980.
(8) Gillies, C. W. *J. Mol. Spectrosc.* **1978**, *71*, 85–100.
(9) LaBrecque, G.; Gillies, C. W.; Raw, T. T.; Agopovich, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 6171–6175.
(10) Agopovich, J. W.; Alexander, J.; Gillies, C. W.; Raw, T. T. *J. Am. Chem. Soc.* **1984**, *106*, 2250–2254.
(11) Deakyne, C. A.; Allen, L. C.; Craig, N. C. *J. Am. Chem. Soc.* **1977**, *99*, 3895–3903.
(12) Deakyne, C. A.; Cravero, J. P.; Hobson, W. S. *J. Phys. Chem.* **1984**, *88*, 5975–5981.
(13) Skancke, A.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 4063–4067.

0002-7863/87/1509-1696$01.50/0

Table I. Rotational Transitions (MHz) of the Normal and Deuteriated Isotopic Species of 1,1,2,2-Tetrafluorocyclopropane

	$\mathrm{CF_2CF_2CH_2}$		$\mathrm{CF_2CF_2CHD}$		$\mathrm{CF_2CF_2CD_2}$	
transition	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$
$3_{30}-4_{40}$	29 144.05	0.01	28 197.96	-0.05	27 321.07	0.03
$3_{31}-4_{41}$	29 163.60	-0.02	28 216.07	0.04	27 337.32	0.01
$4_{04}-5_{14}$	28 558.47	0.06	27 872.50	0.09	27 204.35	0.06
$4_{13}-5_{23}$	27 840.78	0.03	27 210.60	0.07		
$4_{14}-5_{24}$	29 857.71	0.03	29 094.61	-0.06	28 366.97	0.03
$4_{22}-5_{32}$	29 995.08	0.03	29 235.48	0.01	28 527.36	0.06
$4_{23}-5_{33}$	31 121.81	-0.01	30 282.07	-0.04	29 492.51	0.07
$4_{31}-5_{41}$	33 609.86	0.09	32 612.84	0.10	31 686.84	0.02
$4_{32}-5_{42}$	33 735.14	-0.09	32 728.32	-0.02	31 791.34	0.02
$4_{40}-5_{50}$					34 505.76	-0.05
$4_{41}-5_{51}$					34 507.96	-0.03
$5_{05}-6_{15}$			33 922.83	-0.06	33 090.74	-0.01
$5_{14}-6_{24}$	33 330.00	-0.09	32 573.12	0.01	31 838.17	-0.05
$5_{15}-6_{25}$			34 642.45	-0.02	33 781.61	-0.02
$5_{23}-6_{33}$	34 366.01	-0.03	33 557.38	-0.04	32 796.67	-0.06
$5_{24}-6_{34}$					34 394.59	-0.04

[a] $\Delta\nu = \nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}$ from the rigid rotor fits. The estimated accuracy of ν_{obsd} is ±0.05 MHz.

structural trends observed in the fluorinated ethylene oxides. It will be shown later in this paper that a near-linear reduction in ring bond lengths likely occurs from cyclopropane to *cis*-1,2-difluorocyclopropane to 1,1,2,2-tetrafluorocyclopropane.

Utilizing charge density difference maps obtained from ab initio wave functions, Deakyne, Allen, and Craig have analyzed the effect of fluorine-induced charge redistributions on the ring geometries of a number of fluorinated cyclopropanes.[11] The study predicts that the C_1–C_2 bond in *cis*-1,2-difluorocyclopropane will be intermediate to values of that bond length in cyclopropane and 1,1,2,2-tetrafluorocyclopropane. The $C_3C_{1,2}$ bond lengths in *cis*-1,2-difluorocyclopropane and 1,1,2,2-tetrafluorocyclopropane, however, are predicted to be essentially unchanged, compared to cyclopropane. A similar study of the fluorinated ethylene oxides[12] predicted shortening of all the ring bonds in *cis*-1,2-difluoroethylene oxide and 1,1,2,2-tetrafluoroethylene oxide, compared to ethylene oxide, with the shortening in the tetrafluoro species being twice that in *cis*-1,2-difluoroethylene oxide.

The present study describes the microwave investigation of several isotopic species of 1,1,2,2-tetrafluorocyclopropane. A complete gas-phase molecular structure is obtained in each of two different frameworks from the rotational constant data. Coordinates are calculated in a number of ways to establish the reliability of the resulting parameters. The structural results are interpreted in the context of the known gas-phase structures of similar molecules. They are also considered in relation to theoretical predictions which have been made concerning the ring bond geometry in 1,1,2,2-tetrafluorocyclopropane.

Experimental Section

Synthesis. 1,1,2,2-Tetrafluorocyclopropane-*3,3-d_2* was prepared by photolysis from a mixture of dideuterioketene and tetrafluoroethylene.[18] 1,1,2,2-Tetrafluorocyclopropane-3-d_1 was synthesized by heating a 1:6 mixture of difluorodiazirine and 1,1-difluoroethylene-2-d_1 at 160 °C. Both of these samples originate from a vibrational spectral analysis of 1,1,2,2-tetrafluorocyclopropane-d_0, -d_1, and -d_2.[18] In that study, final sample purity was estimated to be greater than 99.5% for the d_2 species and approximately 99% for the d_1 species, based on gas chromatographic analysis. Isotopic purity was greater than 99% for the d_2 species, based on mass and infrared spectra, and approximately 95% for the d_1 species, based on the solid-phase infrared spectrum.

1,1,2,2-Tetrafluorocyclopropane-d_0 was prepared by heating an equimolar mixture of 1,1-difluoroethylene and perfluoropropylene oxide at 190 °C for 10 h.[19] Distillation through −110 and −196 °C traps was employed to remove the trifluoroacetyl fluoride and $CF_2{=}CF_2$ byproducts and unreacted $CF_2{=}CH_2$. The known microwave spectrum[2] served to identify 1,1,2,2-tetrafluorocyclopropane-d_0. Subsequent microwave assignments were made without additional sample purification.

Spectroscopy. All microwave spectra were recorded with a Hewlett-Packard 8400C MRR spectrometer in the region from 26.5 to 40.0 GHz. Transition frequencies of the normal and enriched isotopic species were measured to an estimated accuracy of ±0.05 MHz at sample pressures of 15 mtorr (relative to air on a Hastings DV-6M vacuum gauge tube). Signal-to-noise enhancement for ground-state rotational transitions was achieved by cooling the absorption cell to dry ice temperature.

All carbon-13 isotopic species were studied in natural abundance at dry-ice temperature. In order to improve sensitivity, a 3-m absorption cell was used in a system employing 95 KHz Stark modulation.[10] Sufficient sensitivity was obtained to enable the characterization of a number of low *J* carbon-13 lines by their Stark effects. Transition frequencies were determined to an estimated accuracy of ±0.05 MHz.

Electric dipole measurements of the dideuteriated isotopic species were made with the 8400C spectrometer by coupling the dc bias to the 33.3-KHz square wave. One HP Stark cell and one HP-8421B Stark modulator were used in the measurements. The dc bias was determined by using a Keithley 177 Microvolt DMM voltmeter which was periodically calibrated to an estimated ±0.1% accuracy. The average Stark electrode spacing was determined by using the $J = 2 \rightarrow 3$ Stark transitions of $^{16}O^{12}C^{32}S$.[20]

Spectra. The experimental spectrum of 1,1,2,2-tetrafluorocyclopropane is fairly sparse with relatively strong c-type transitions. Low *J* R-branch transitions of the species $\mathrm{CF_2CF_2CH_2}$, $\mathrm{CF_2CF_2CD_2}$, and $^{13}\mathrm{CF_2CF_2CD_2}$ were identified by using spectral constants previously determined by Laurie and Stigliani.[2] Transition frequencies of these species are listed in Tables I and II and spectral constants obtained from the rigid rotor fits are given in Table III. The assignments are supported by Stark effects, line intensities, proximity to predicted transition frequencies, and the quality of the rigid rotor fit.

Data from the normal and d_2 assignments sufficed to predict the low *J* R-branch transition frequencies of the d_1 isotopic species within ±2 MHz of the experimental values. Transition frequencies and spectral constants obtained from the rigid rotor fit are given in Tables I and III, respectively. Stark effects and line intensities are consistent with the assignment. Spectral constants of the species $\mathrm{CF_2CF_2CD_2}$, $^{13}\mathrm{CF_2CF_2CD_2}$; and $\mathrm{CF_2CF_2CH_2}$ were used in conjunction with one nontrivial center of mass condition and one assumed parameter to calculate an approximate molecular structure for 1,1,2,2-tetrafluorocyclopropane in the d_2 isotopic species framework. From this approximate structure the low *J* R-branch transitions of $\mathrm{CF_2CF_2{}^{13}CD_2}$ were located within ±1 MHz of their predicted frequencies. The accumulated spectral data then enabled location of the low *J* R-branch transitions of $^{13}\mathrm{CF_2CF_2CH_2}$ and $\mathrm{CF_2CF_2{}^{13}CH_2}$ with similar precision. Transition frequencies of $\mathrm{CF_2CF_2{}^{13}CD_2}$, $^{13}\mathrm{CF_2CF_2CH_2}$, and $\mathrm{CF_2CF_2{}^{13}CH_2}$ are listed in Table II. Spectral constants obtained from the rigid rotor fits are given in Table

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(14) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800–3810, 3811–3819.

(15) Durmaz, S.; Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 6942–6945.

(16) Hirose, C. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1311–1318.

(17) Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* **1964**, *42*, 2259–2263. Butcher, R. J.; Jones, W. J. *J. Mol. Spectrosc.* **1973**, *47*, 64–83.

(18) Craig, N. C.; Anderson, G. J.; Cueller-Ferreira, E.; Koepke, J. W.; Marytn, P. H. *Spectrochim. Acta* **1972**, *28A*, 1175–1193.

(19) Craig, N. C.; Fleming, G. F.; Pranata, J. *J. Phys. Chem.* **1985**, *89*, 100–105.

(20) Reinartz, J. M. L. J.; Dymanus, A. *Chem. Phys. Lett.* **1974**, *24*, 346–351.

Table II. Rotational Transitions (MHz) of Carbon-13 Isotopic Species of 1,1,2,2-Tetrafluorocyclopropane

	$\overline{^{13}CF_2CF_2CH_2}$		$\overline{CF_2CF_2{}^{13}CH_2}$		$\overline{^{13}CF_2CF_2CD_2}$		$\overline{CF_2CF_2{}^{13}CD_2}$	
transition	ν_{obsd}	$\Delta\nu$[a]	ν_{obsd}	$\Delta\nu$[a]	ν_{obsd}	$\Delta\nu$[a]	ν_{obsd}	$\Delta\nu$[a]
$3_{30}-4_{40}$			28 743.35	0.06	27 317.06	−0.03	26 987.44	0.05
$3_{31}-4_{41}$			28 761.45	−0.01	27 333.15	0.12	27 002.43	0.06
$4_{04}-5_{14}$	28 491.17	0.08			27 142.91	0.02		
$4_{13}-5_{23}$	27 785.66	0.04	27 536.10	0.03				
$4_{14}-5_{24}$	29 808.70	−0.09			28 322.38	−0.01		
$4_{22}-5_{32}$	29 967.66	0.01	29 671.62	−0.02	28 502.07	−0.01	28 256.11	0.07
$4_{23}-5_{33}$	31 087.70	−0.17	30 747.10	0.01	29 461.53	−0.05	29 175.27	0.01
$4_{31}-5_{41}$			33 187.02	0.01	31 673.07	−0.01	31 333.69	−0.07
$4_{32}-5_{42}$	33 717.72	0.10	33 303.63	−0.07	31 775.65	0.01	31 430.30	−0.01
$4_{40}-5_{50}$					34 502.06	−0.01	34 079.33	−0.06
$4_{41}-5_{51}$					34 504.17	−0.03		
$5_{05}-6_{15}$	34 700.58	0.01						
$5_{14}-6_{24}$	33 253.72	−0.02	32 947.08	−0.02	31 768.68	0.01		
$5_{15}-6_{25}$					33 723.89	−0.01	33 408.43	−0.04
$5_{23}-6_{33}$	34 320.91	0.05	34 009.26	0.02	32 755.33	0.03	32 494.86	−0.06
$5_{24}-6_{34}$					34 349.11	−0.02	34 028.75	0.08

[a] $\Delta\nu = \nu_{obsd} - \nu_{calcd}$ from the rigid rotor fits. The estimated accuracy of ν_{obsd} is ±0.05 MHz.

Table III. Rotational Constants (MHz) and Principal Moments of Inertia (uÅ^2) of 1,1,2,2-Tetrafluorocyclopropane

	A	B	C	I_A	I_B	I_C
$\overline{CF_2CF_2CH_2}$	3841.18 (1)[a]	2518.11 (1)	1969.68 (2)	131.5686 (2)[b]	200.6981 (3)	256.5799 (21)
$\overline{CF_2CF_2CHD}$	3709.93 (1)	2472.37 (1)	1962.60 (1)	136.2233 (2)	204.4108 (3)	257.5046 (18)
$\overline{CF_2CF_2CD_2}$	3588.43 (1)	2427.40 (1)	1956.48 (1)	140.8359 (1)	208.1975 (3)	258.3104 (12)
$\overline{^{13}CF_2CF_2CH_2}$	3841.25 (2)	2511.39 (1)	1965.56 (3)	131.5662 (6)	201.2350 (7)	257.1167 (37)
$\overline{CF_2CF_2{}^{13}CH_2}$	3785.72 (1)	2494.30 (1)	1969.66 (1)	133.4963 (1)	202.6133 (2)	256.5819 (16)
$\overline{^{13}CF_2CF_2CD_2}$	3588.60 (1)	2421.20 (1)	1952.42 (1)	140.8289 (1)	208.7310 (3)	258.8470 (12)
$\overline{CF_2CF_2{}^{13}CD_2}$	3542.34 (1)	2406.37 (1)	1956.44 (2)	142.6682 (2)	210.0173 (4)	258.3156 (21)

[a] The uncertainty in parentheses represents one standard deviation in the rigid rotor fit. [b] The conversion factor is equal to 505379.1 uÅ^2·MHz.

III. The assignments are supported by observation of correct Stark effects, line intensities, and the quality of the rigid rotor fit. Relative intensity measurements[21] at dry ice and room temperature indicate that the assigned transitions originate from the ground vibrational state.

Two normal modes have been observed below 200 cm^{-1} in the vibrational spectra of 1,1,2,2-tetrafluorocyclopropane-d_0, -d_1, and -d_2.[18] The rotational spectra and symmetry of vibrational satellites arising from these modes have been assigned in the d_2 isotopic species. Transition frequencies and spectral constants of the satellites are given in Table IV. The energy and symmetry of the vibrational states were determined from relative intensity measurements at room temperature.[21] Results of the determinations are given in Table V. The uncertainties in the energies derive from the standard deviation of all the relative intensity measurements for a given mode.

The spectral assignments confirm the anticipated C_{2v} symmetry of 1,1,2,2-tetrafluorocyclopropane-d_0 and -d_2. The observation of exclusively μ_c-type transitions implies the presence of a C_2 axis of symmetry in those species. The negligible change in the C rotational constant accompanying carbon-13 substitution at the C_3 position confirms the location of atom C_3 on the symmetry axis. Spin statistics predict that symmetric/antisymmetric rotational levels will be weighted 28/36 and 78/66 in the normal and d_2 isotopic species, respectively. An intensity alternation consistent with the foregoing prediction was observed for a number of lines in both the normal and d_2 species, confirming the C_{2v} symmetry of the latter two species. No intensity alternation attributable to spin statistics was observed for the d_1 isotopic species, indicating the absence of a C_2 axis of symmetry in that species.

Electric Dipole Moment. Stark shifts of three transitions were used to determine the electric dipole moment of the d_2 isotopic species in the ground vibrational state. The data were least-squares fit to second-order perturbation theory yielding the Stark coefficients and dipole moment given in Table VI. The quality of the fit to one dipole component is consistent with the presence of a C_2 axis of symmetry in the ground-state d_2 isotopic species.

Structure. 1,1,2,2-Tetrafluorocyclopropane possesses eight unique atomic coordinates. Moment of inertia data from the seven isotopic species may be combined with one nontrivial center of mass condition ($\Sigma_i m_i c_i = 0$) to calculate the molecular structure in both the normal and dideuteriated isotopic species framework. The Kraitchman substitution method may be used to calculate the coordinates of the hydrogen (deuterium) and carbon atoms with the single exception of the small $C_{1,2}$ c-coordinate.[22] A substitution value for the small $C_{1,2}$ c-coordinate may be obtained by using the Pierce second-difference method.[23] The fluorine coordinates may then be calculated from a least-squares fit to the three second moment relations of each of the isotopic species not used in the substitution calculations as well as the three second moment relations and the nontrivial center of mass condition of the parent isotopic species.

Table IV. Rotational Transitions (MHz) and Spectral Constants (MHz) of Vibrational Satellites of 1,1,2,2-Tetrafluorocyclopropane-d_2

	V(1)		V(2)	
transition	ν_{obsd}	$\Delta\nu$[a]	ν_{obsd}	$\Delta\nu$[a]
$3_{30}-4_{40}$	27319.31	−0.05	27337.95	−0.02
$3_{31}-4_{41}$	37339.61	−0.03	27350.57	0.04
$4_{04}-5_{14}$	27609.80	−0.09	26756.32	0.01
$4_{14}-5_{24}$	28632.51	0.16		
$4_{22}-5_{32}$	28605.62	−0.08	28465.25	0.03
$4_{23}-5_{33}$	29647.52	−0.01	29339.57	−0.05
$4_{31}-5_{41}$	31716.07	0.04	31669.51	−0.04
$4_{32}-5_{42}$	31844.69	0.05	31751.32	0.03
constants	V(1)		V(2)	
A	3585.44 (1)[b]		3593.82 (1)	
B	2462.27 (1)		2389.74 (1)	
C	1958.11 (4)		1954.70 (2)	

[a] $\Delta\nu = \nu_{obsd} - \nu_{calcd}$ from the rigid rotor fits. The estimated accuracy of ν_{obsd} is ±0.05 MHz. [b] The uncertainty in parentheses represents one standard deviation in the rigid rotor fit. [c] The conversion factor is equal to 505379.1 uÅ^2·MHz.

The structural fitting program STRFIT was used to calculate the molecular structure in the manner described above.[24] Substitution coordinates of the hydrogen (deuterium) atoms were determined by using

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(21) Esbitt, A. S.; Wilson, E. B., Jr. *Rev. Sci. Instrum.* **1963**, *34*, 901–907.

(22) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17–24.

(23) Pierce, L. *J. Mol. Spectrosc.* **1959**, *3*, 575–580. Krisher, L. C.; Pierce, L. *J. Chem. Phys.* **1960**, *32*, 1619–1625.

(24) STRFIT was developed by Dr. R. H. Schwendeman, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

Table V. Symmetry Assignment of Vibrational Satellites

microwave assignment						vibrational assignment[d]		
mode	transition	$\mathrm{sym_{rot}}$	intensity ratios	E_{vib}, cm^{-1}	$\mathrm{sym_{vib}}$	mode	E_{vib}, cm^{-1}	$\mathrm{sym_{vib}}$
V(1)	$4_{41}-3_{31}$	anti[a]	0.488[b] 0.409	188 (9)[c]	A	V_{11}	192	A_2
	$5_{32}-4_{22}$	sym	0.383 0.388					
V(2)	$5_{33}-4_{23}$	anti	0.458 0.525	178 (13)	B	V_{21}	178	B_2
	$5_{32}-4_{22}$	sym	0.347 0.371					

[a] Symmetry of rotational states. [b] The ν^2 dependence of the intensities has been taken into account for all transitions. The intensity ratios of the excited-to-ground vibrational state rotational transitions were obtained at 22 °C. [c] The uncertainty in parentheses is one standard deviation in the energy derived from four relative intensity measurements. [d] Reference 18.

Table VI. Stark Coefficients and Electric Dipole Moment (Debyes) of 1,1,2,2-Tetrafluorocyclopropane-d_2

transition	$(\Delta\nu/E^2) \times 10^5$ $[\mathrm{MHz/(V/cm)^2}]$[a] obsd	$(\Delta\nu/E^2) \times 10^5$ $[\mathrm{MHz/(V/cm)^2}]$[a] calcd
$4_{23}-5_{33}$ $M_J = 0$	0.07013	0.07216
$4_{23}-5_{33}$ $M_J = 1$	-0.5960	-0.5845
$4_{23}-5_{33}$ $M_J = 2$	-2.577	-2.555
$\mu_{total} = \mu_c = 2.16$ (3) D[b]		

[a] The Stark coefficients were calculated by using the conversion factor 0.503404 [MHz/(DV/cm)]. [b] The quantity in parentheses is the estimated uncertainty in the last digit of the parameter cited, as obtained from one standard deviation of the least-squares fit.

Kraitchman's equations for single substitution as well as Chutjian's equations for double substitution.[25] Error analysis indicated that the double substitution result had the lesser uncertainty. The C_3 c-coordinate and $C_{1,2}$ a-coordinate were calculated by using the single-substitution method. The evaluation of the small $C_{1,2}$ c-coordinate was accomplished by using an adaptation of the Pierce second-difference method developed by Rudolph.[26] Four isotopic species were required for the calculations with substitution in each of two different frameworks. The coordinate transformation between the two frameworks, in this case simply a translation, was determined both from Chutjian coordinates of the hydrogen (deuterium) atoms and from Kraitchman coordinates of the C_3 carbon. The calculation utilized $\Delta\Delta I_a$ rather than $\Delta\Delta P_c$ as the second-difference in moments, since $\Delta\Delta I_a$ had the lesser experimental uncertainty.[27] Least-squares fitting of the fluorine coordinates to thirteen moment relations yielded the atomic coordinates listed in Tables VII and VIII. The partial r_s structures derived from these coordinates are presented in Table IX.

As a check on the second-difference result, a second calculation was undertaken in which substitution coordinates were used wherever possible with the exception of the small $C_{1,2}$ c-coordinate and the fluorine coordinates, which were fit to the same moment relations employed in the previous partial r_s calculation. Values of the small $C_{1,2}$ c-coordinate obtained in this manner are listed in Tables VII and VIII. C_3–$C_{1,2}$ bond distances obtained from the calculation are presented in Table IX. Quantities resulting from this calculation compare favorably with previous partial r_s results. The somewhat larger discrepancy encountered in the d_2 isotopic frame is not unexpected, since the $C_{1,2}$ c-coordinate is smaller in that frame than in the normal isotopic species frame.[28]

A complete r_0 structure was calculated by least-squares fitting the eight atomic coordinates to the three second moment relations of each of all seven isotopic species as well as the nontrivial center of mass relation. Atomic coordinates obtained from the calculation are listed in Tables VII and VIII. The corresponding structural parameters are presented in Table IX.

An element of ambiguity is introduced into the determination of in-plane coordinates (x,y) by finite pseudoinertial defect differences, $\delta_{zz} = \Delta I_z - \Delta I_x - \Delta I_y$, accompanying isotopic substitution in an xy symmetry plane.[28] Equating δ_{zz} to zero enables the elimination of one of the ΔI's from Kraitchman's equations and the formulation of "specialized" forms of Kraitchman's equations.[27,29] Coordinates calculated from specialized forms of Kraitchman's equation differ from their unspecialized counterpart by an amount approximately equal to $(4\mu x)^{-1} |\delta_{zz}|$, where μ is the reduced mass for the substitution and x is the magnitude of the substitution coordinate.[29] This quantity was used to estimate Costain uncertainties in the substitution coordinates obtained for the C_3 c-coordinate and $C_{1,2}$ a-coordinate. Similar expressions were developed to evaluate the Costain uncertainty in the hydrogen (deuterium) atom coordinates calculated by using Chutjian's equations for double substitution. Costain uncertainties in the C_3 c-coordinate, $C_{1,2}$ a-coordinate, and hydrogen (deuterium) atom b- and c-coordinates were then algebraically added to experimental uncertainties derived from uncertainty in the pertinent rotational constants to generate the aggregate uncertainty in these coordinates.

Since the $C_{1,2}$ c-coordinate was determined from second-differences in moments, vibrational effects should have been reduced to a greater degree than is typically obtained from the use of Kraitchman or Chutjian equations.[23] The aggregate uncertainty in that coordinate was derived from the experimental uncertainty in $\Delta\Delta I_a$ and the aggregate uncertainty in the coordinate transformation. Costain uncertainties in the fluorine coordinates were estimated as $0.0015X^{-1}$, where x is the magnitude of the coordinate and a typical pseudoinertial defect difference of 0.006 μ $Å^2$ is assumed.[27] Aggregate uncertainties in the fluorine coordinates were obtained from the summation of Costain uncertainties and fitting uncertainties from the least-squares fitting routine. The aggregate coordinate uncertainties were then propagated into the structural parameters through the standard relation for propagation of random error.[27] The resulting structural uncertainties that are listed with the partial r_s parameters in Table IX are intended to reflect investigator confidence in the reported parameters as estimates of equilibrium parameters. Structural uncertainties derived from the least-squares fitting routine are listed alongside the complete r_0 parameters for comparison.

Discussion

Ring Structure. Table X compares the structural parameters experimentally determined for a series of fluorinated cyclopropanes. In each case, the introduction of fluorine has resulted in a contraction of the carbon–carbon bond adjacent to the substitution site, relative to cyclopropane. The results in Table X also suggest a near-linear variation in carbon–carbon bond lengths from cyclopropane to *cis*-1,2-difluorocyclopropane to 1,1,2,2-tetrafluorocyclopropane. The comparison is less certain with regard to the C_3–$C_{1,2}$ bond in 1,1,2,2-tetrafluorocyclopropane due to the uncertainty associated with that parameter. A near-linear variation of all ring bond lengths is clearly evident in the analogous fluorinated oxirane series.[10]

Deakyne, Allen, and Craig rationalized the ring bond effects observed in 1,1-difluorocyclopropane[1] and 1,1,2,2-tetrafluorocyclopropane[2] by analyzing charge density difference maps of these species in the context of the Hellmann–Feynmann theorem.[11] Consideration of trends in atomic charge distributions led the authors to conclude that successive fluorination would modify the cyclopropyl ring structure in an additive manner. Theoretical results for 1,1-difluorocyclopropane were used in conjunction with the additivity postulate to correctly predict the observed shortening of the ring bonds for *cis,cis*-trifluorocyclopropane.[3] The observed shortening of the ring bonds in *cis*-1,2-difluorocyclopropane and

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(25) Chutjian, A. *J. Mol. Spectrosc.* **1964**, *14*, 361–370.

(26) Rudolph, H. D. *J. Mol. Spectrosc.* **1981**, *89*, 430–439.

(27) Schwendeman, R. H. *Critical Evaluation of Chemical and Physical Structural Information*; National Academy of Sciences: Washington, DC, 1974; pp 94–115. Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619–626.

(28) Costain, C. C. *J. Chem. Phys.* **1958**, *29*, 864–874.

(29) Rudolph, H. D. *J. Mol. Spectrosc.* **1981**, *89*, 460–464.

Table VII. Atomic Coordinates (Å)[a] of the Normal Isotopic Species of 1,1,2,2-Tetrafluorocyclopropane

atom	a-coord		b-coord		c-coord	
$C_{1,2}$	±0.7355	(±0.7368)	0.0	(0.0)	0.0860[b,c]	(0.0872)
C_3	0.0	(0.0)	0.0	(0.0)	1.3896	(1.3907)
H	0.0	(0.0)	±0.9323[d]	(±0.9324)	1.9498[d]	(1.9496)
F	±1.4043	(±1.4041)	±1.1001	(±1.1001)	−0.2991	(−0.2988)

[a] Entries enclosed in parentheses are r_0 coordinates; entries not enclosed in parentheses are partial r_s coordinates. [b] This coordinate was obtained by the Pierce second-difference method utilizing Chutjian coordinates of the hydrogens to define the coordinate transformation. A value of 0.0833 Å is obtained if Kraitchman coordinates of the C_3 carbon are used to define the transformation. [c] A value of 0.0895 Å is obtained if the coordinate is fit to the moment relations described in the text. [d] These coordinates were obtained by using Chutjian's equations. The corresponding Kraitchman coordinates are ±0.9346 and 1.9476 Å.

Table VIII. Atomic Coordinates (Å)[a] of the d_2 Isotopic Species of 1,1,2,2-Tetrafluorocyclopropane

atom	a-coord		b-coord		c-coord	
$C_{1,2}$	±0.7358	(±0.7368)	0.0	(0.0)	0.0521[b,c]	(0.0534)
C_3	0.0	(0.0)	0.0	(0.0)	1.3539	(1.3569)
H	0.0	(0.0)	±0.9323[d]	(±0.9324)	1.9159[d]	(1.9158)
F	±1.4042	(±1.4041)	±1.1001	(±1.1001)	−0.3337	(−0.3327)

[a] Entries enclosed in parentheses are r_0 coordinates; entries not enclosed in parentheses are partial r_s coordinates. [b] This coordinate was obtained by the Pierce second-difference method utilizing Chutjian coordinates of the hydrogens to define the coordinate transformation. A value of 0.0476 Å is obtained if Kraitchman coordinates of the C_3 carbon are used to define the transformation. [c] A value of 0.0598 Å is obtained if the coordinate is fit to the moment relations described in the text. [d] These coordinates were obtained by using Chutjian's equations. The corresponding Kraitchman coordinates are ±0.9298 and 1.9182 Å.

Table IX. Structural Parameters[a] of 1,1,2,2-Tetrafluorocyclopropane

	partial r_s(I)[b]	partial r_s(II)[b]	r_0
$r(C_1C_2)$	1.471 (1)	1.472 (2)	1.474 (6)
$r(C_3C_{1,2})$	1.497 (10)[c]	1.495 (12)[c]	1.497 (5)
$r(C_{1,2}F)$	1.344 (4)	1.344 (4)	1.343 (2)
$r(C_3H)$	1.088 (5)[d]	1.089 (5)[d]	1.087 (2)
$\theta(FC_{1,2}F)$	109.9 (4)	109.9 (5)	110.0 (3)
$\theta(HC_3H)$	118.0 (4)[d]	117.8 (4)[d]	118.1 (2)
F···Fgem	2.200 (1)	2.200 (2)	2.200 (1)
F···Fvic	2.809 (3)	2.808 (2)	2.808 (1)
$\theta(C_1C_2F_p)$[e]	150.1 (1)	150.0 (1)	150.0 (1)
$\theta(C_3C_{1,2}F_p)$[e]	149.4 (1)	149.5 (1)	149.5 (1)

[a] All distances are in Å; all angles are in deg. Quantities in parentheses are estimated uncertainties in the last digit(s) of the parameter cited. [b] Structure I is the partial r_s structure obtained in the normal isotopic species frame. Structure II is the partial r_s structure obtained in the d_2 isotopic species frame. [c] The alternate Pierce substitution coordinates obtained by using Kraitchman coordinates of the C_3 carbon (Tables VIII and IX) yield a value of 1.499 Å for this parameter in both isotopic species frames. The fitted $C_{1,2}$ c-coordinates yield values of 1.494 and 1.489 Å for this parameter in the normal and d_2 isotopic species frames, respectively. [d] Kraitchman coordinates of the hydrogens (deuteriums) yield r(CH) = 1.088 Å, r(CD) = 1.088 Å and θ(HCH) = 118.3°, θ(DCD) = 117.5° in the normal and d_2 isotopic species frames, respectively. [e] F_p denotes the projection of the fluorine atom in the cyclopropyl ring plane.

1,1,2,2-tetrafluorocyclopropane are not completely consistent with the ab initio results.[11] The theoretical work predicts a shortening of the C_1–C_2 bond in these two related cyclopropanes which is in qualitative agreement with the microwave results listed in Table X. However, the ab initio results find no shortening of the C_3–$C_{1,2}$ bond contrary to the observed bond contractions of 0.01 and 0.02 Å, respectively, in this bond for these two fluorinated cyclopropanes.

Recently, it was suggested that the discrepancy arises from difficulty in the interpretation of the charge density difference maps.[5] These maps showed charge redistributions associated with the C_1 and C_2 carbons in 1,1,2,2-tetrafluorocyclopropane that tended to displace them toward the center of the ring. Such an atom movement for C_1 and C_2 carbons leads to a C_1–C_2 bond shortening which is in agreement with the microwave results listed in Table X.

The charge density difference maps revealed charge gains both behind and in front of the C_3 carbon of 1,1,2,2-tetrafluorocyclopropane.[11] On the basis of an analogous charge redistribution accompanying the "molecular formation" of Be_2, Deakyne and co-workers concluded that the charge gain behind the C_3 carbon would dominate, resulting in the displacement of the C_3 carbon away from the C_1–C_2 bond.[11] The net effect of the displacements, the authors reasoned, was to leave the C_3–$C_{1,2}$ bond distance in 1,1,2,2-tetrafluorocyclopropane essentially unchanged, relative to cyclopropane. Extension of the preceeding argument to *cis*-1,2-difluorocyclopropane led to the prediction that the C_3–$C_{1,2}$ bond distance in that species would also remain essentially unchanged, compared to cyclopropane.[11]

The recent microwave results demonstrate that the C_3–$C_{1,2}$ bond distance for *cis*-1,2-difluorocyclopropane is shortened relative to cyclopropane.[5] As shown in Table X, the C_3–$C_{1,2}$ bond length in 1,1,2,2-tetrafluorocyclopropane follows the same trend. Since the C_1–C_2 bond shortening predicted by the charge density dif-

Table X. Comparison of Structural Parameters[a] of the Fluorinated Cyclopropanes

	bond length, Å						methylene angle, deg		
compound	C_1–C_2	C_2–C_3	C_1–H	C_1–F	C_3–H	C_3–F	$\theta(XC_1Y)$	$\theta(XC_3Y)$	reference
$CH_2CH_2CH_2$	1.514 (3)	1.514 (3)	1.081 (3)		1.081 (3)		114.9 (7)	114.9 (7)	17
cis-CHFCHFCH$_2$	1.488 (3)	1.503 (4)	1.093 (4)	1.368 (6)	*b*		111.3 (4)	*b*	5
trans-CHFCFHCH$_2$	1.466 (4)	1.488 (5)	1.090 (4)	1.383 (3)	1.083 (2)		111.3 (4)	116.8 (2)	4
$CF_2CH_2CH_2$	1.464 (2)	1.553 (1)		1.355 (2)	1.082 (2)		108.4 (2)	116.9 (2)	1
cis,cis-CHFCHFCHF	1.507 (1)	1.507 (1)	1.095 (2)	1.354 (2)	1.095 (2)	1.354 (2)	112.3 (2)	112.3 (2)	3
cis,-trans-CHFCHFCFH	1.500 (3)	1.478 (10)[c]	1.076 (6)	1.367 (8)	1.085 (16)	1.387 (8)	109.4 (8)	114.7 (15)	6
$CF_2CF_2CH_2$	1.471 (3)	1.497 (10)		1.344 (4)	1.088 (5)		109.9 (4)	118.0 (4)	this work
$CF_2CF_2CF_2$	1.505 (3)	1.505 (3)		1.314 (1)		1.314 (1)	112.2 (10)	112.2 (10)	7

[a] All distances are in Å; all angles are in deg. Quantities in parentheses are estimated uncertainties in the last digit(s) of the parameter cited. [b] This parameter is not well-determined. [c] C_3 denotes the unique carbon.

Table XI. Fluorine-Fluorine Nonbonded Distances (Å)

compound	geminal	vicinal	ref
CF_2CF_2	2.19	2.78	*a*
$CHFCF_2$	2.20	2.75	*a*
cis-$CHFCHF$		2.74	*b*
cis-$CHFCHFCH_2$		2.73	5
$CF_2CH_2CH_2$	2.20		1
$CF_2CF_2CH_2$	2.20	2.81	this work
$CF_2CF_2CF_2$	2.18	2.77	7

[a] Landolt-Bornstein, *Numerical Data and Functional Relationships in Science and Technology*; 1976; New Series, II/7. [b] Laurie, V. W.; Pence, D. T. *J. Chem. Phys.* **1963**, *38*, 2693-2697.

ference maps is in agreement with the microwave results, it appears that the problem lies with the prediction of the C_3 displacement. If the charge gain in front of the C_3 carbon and behind the C_3 carbon cancel out, there can be no C_3 atomic displacement.[5] This reasoning predicts a C_3–$C_{1,2}$ bond shortening in agreement with experiment.

FCF and HCH Groups. Table X demonstrates that the carbon-fluorine bond distance decreases from 1,1-difluorocyclopropane to 1,1,2,2-tetrafluorocyclopropane to perfluorocyclopropane. The FCF methylene angle decreases in the reverse order. The combination of the shorter CF bond distance and larger FCF methylene angle in 1,1,2,2-tetrafluorocyclopropane, compared to 1,1-difluorocyclopropane, results in equivalent geminal fluorine-fluorine nonbonded distances in the two species. A near constancy in the geminal fluorine-fluorine nonbonded distance is found for the fluorinated molecules listed in Table XI.

A majority of the molecules listed in Table XI possess vicinal fluorine-fluorine nonbonded distances very close to 2.7 Å, the sum of two fluorine van der Waals radii.[30] In 1,1,2,2-tetrafluorocyclopropane this same distance is about 0.1 Å longer. The CF and C_1C_2 bond lengths are shorter in 1,1,2,2-tetrafluorocyclopropane than in *cis*-1,2-difluorocyclopropane. Either of these factors would tend to decrease the vicinal fluorine-fluorine nonbonded distance in 1,1,2,2-tetrafluorocyclopropane, relative to *cis*-1,2-difluorocyclopropane. Hence, it must be the angular orientation of the CF bonds in 1,1,2,2-tetrafluorocyclopropane which accounts for the larger vicinal fluorine-fluorine nonbonded distance in that species.

The CF bond orientation in 1,1,2,2-tetrafluorocyclopropane and *cis*-1,2-difluorocyclopropane may be described quantitatively by specifying two angles, designated $\omega(F)$ and $\tau(F)$. $\omega(F)$ denotes the angle between the C-F bond and the ring plane. $\tau(F)$ denotes the angle between the projection of the CF bond in the ring plane and the bisector of angle $C_3C_1C_2$, taken in a positive sense if the displacement is toward C_3. $\tau(F)$ is almost zero in both 1,1,2,2-tetrafluorocyclopropane (0.3 ± 0.1°) and *cis*-1,2-difluorocyclopropane (0.5 ± 0.9°), indicating that the fluorines are not preferentially displaced toward either of the opposing (fluoro) methylene groups.[5] $\omega(F)$, however, is significantly less in 1,1,2,2-tetrafluorocyclopropane (55.0 ± 0.2°) than in *cis*-1,2-difluorocyclopropane (58.5 ± 0.3°). It is the closing of this angle in 1,1,2,2-tetrafluorocyclopropane, compared to *cis*-1,2-difluorocyclopropane, which causes the larger vicinal fluorine-fluorine nonbonded distance in the tetrafluoro species.

The carbon-hydrogen bond length in 1,1,2,2-tetrafluorocyclopropane ($r(CH) = 1.088 \pm 0.005°$) compares closely with values of that parameter obtained for other fluorinated cyclopropanes. The HCH methylene angle in 1,1,2,2-tetrafluorocyclopropane is unusually large for a fluorinated cyclopropane. A systematic increase in that angle occurs from cyclopropane (114.9 ± 0.7°) to 1,1-difluorocyclopropane (116.9 ± 0.2°) to 1,1,2,2-tetrafluorocyclopropane (118.0 ± 0.4°). Opening of the HCH methylene angle in the latter two species leads to reduction in the vicinal hydrogen-fluorine distances.[6]

Table XII. Second Moment Differences (uÅ^2)[a] of the Two Lowest Excited Vibrational States of CF_2CF_2O and $CF_2CF_2CD_2$

	CF_2CF_2O[b]		$CF_2CF_2CD_2$	
	B_2	A_2	B_2	A_2
ΔP_{aa}	0.6372	−0.5007	1.8643	−1.6400
ΔP_{bb}	−0.5403	0.4516	−1.6284	1.4253
ΔP_{cc}	0.4177	−0.3551	1.4170	−1.3079

[a] $\Delta P_{xx} = P_{xx}$ (excited state) $-P_{xx}$ (ground state) where $P_{xx} = 1/2(I_{yy} + I_{zz} - I_{xx})$. [b] Reference 10.

Vibrational States. Two depolarized Raman bands were observed in the liquid-phase Raman spectrum of 1,1,2,2-tetrafluorocyclopropane-d_2 below 200 cm^{-1}.[18] The assignment of these features was accomplished by analogy to the 1,1,2,2-tetrafluorocyclopropane-d_0 assignment,[18] where gas-phase far-IR and liquid-phase Raman spectra demonstrated the symmetry of the two lowest energy excited vibrational states. Zero-order normal coordinate calculations suggested that these modes primarily involve motions associated with the CF_2 groups. The vibrational assignments demonstrated that the energies of the two modes were relatively unaffected by deuterium substitution. The next higher energy mode of 1,1,2,2-tetrafluorocyclopropane-d_2 was observed at 289 cm^{-1} in both gas-phase IR and liquid-phase Raman spectra.[18]

In the present study, a consideration of nuclear spin statistics enabled the assignment of the symmetries of the modes producing the two vibrational satellites of 1,1,2,2-tetrafluorocyclopropane-d_2. Relative intensities were analyzed by Boltzmann statistics to confirm that the satellites corresponded to the two lowest energy excited state modes observed in the vibrational study. Transitions arising from symmetric rotational levels had the same intensity relative to the ground state as transitions arising from antisymmetric rotational levels in the satellite designated V(1) in Tables IV and V, indicating that the mode involved has either A_1 or A_2 symmetry. Relative intensities of transitions arising from symmetric/antisymmetric rotational levels were weighted (66/78)/(78/66) in the satellite designated V(2), indicating that the mode involved in that case possesses either B_1 or B_2 symmetry. An alternative symmetry assignment was considered for the two satellites but was discounted on the basis of the large standard deviation in the vibrational energies that would result.

Additional, albeit indirect, evidence supporting the symmetry assignments comes from comparison of the second moment differences between the ground state and the two lowest excited vibrational states of 1,1,2,2-tetrafluorooxirane[10] and 1,1,2,2-tetrafluorocyclopropane. Table XII demonstrates that the sign and magnitude of the differences are highly correlated ($r^2 > 0.99$, overall) between the two species. This result would be expected if structural differences between the ground state and two lowest excited vibrational states of 1,1,2,2-tetrafluorocyclopropane were in parallel with those of their tetrafluorooxiranyl counterparts.

Conclusion

Microwave spectral analysis has enabled the determination of a complete gas-phase molecular structure for 1,1,2,2-tetrafluorocyclopropane. All the ring bonds have shortened relative to cyclopropane, with the greater reduction occurring in the C_1–C_2 bond. An ab initio study by Deakyne et al. using charge density difference maps predicts the observed C_1–C_2 bond shortening. However, it does not predict ring bond contraction for the C_3–$C_{1,2}$ bond which is contrary to the observed shortening of 0.017 Å. The discrepancy may result from difficulty in determining the force which acts upon C_3 from the charge density difference plots.

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Registry No. 1,1,2,2-Tetrafluorocyclopropane, 3899-71-6.

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(30) Pauling, L. *Nature of the Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, New York, 1945; p 189.