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Rotational Spectrum and Structure of 1,2-Dichloro-3,3,4,4-tetrafluorocyclobutene: Comparison of Spectroscopy, Diffraction, and ab Initio Results

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The rotational spectra of four isotopomers of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene have been measured with a Fourier transform microwave spectrometer. The ring parameters determined from the inertial data were $r(C_1{=}C_2) = 1.311(15)$ Å, $r(C_2{-}C_3) = 1.487(15)$ Å, and $r(C_3{-}C_4) = 1.551(15)$ Å, with the angles $(C_1{=}C_2{-}C_3) = 94.6(6)°$ and $(C_2{-}C_3{-}C_4) = 85.4(6)°$. The $C_3{-}C_4$ bond is found to be shorter by 0.05 Å than the value obtained from an electron diffraction study, although consistent with a previous microwave study of the closely related molecule hexafluorocyclobutene. The $C_1{=}C_2$ bond is also 0.04 Å shorter than the electron diffraction data and about 0.02−0.03 Å shorter than microwave spectroscopy studies of other tetrafluorocyclobutenes. The reasons for these differences are unclear. The chlorine nuclear quadrupole coupling constants were determined; the axis of the principal nuclear quadrupole coupling tensor is essentially parallel to the carbon−chlorine bond axis. Comparisons with theoretical calculations and electron diffraction results are made, along with comparisons with similar molecules.

Introduction

This paper reports the structure of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (CFCB). This study was stimulated by several recent reports on hexafluorocyclobutene (HFCB) and related halogenated cyclobutenes. Structural parameters from experimental studies of HFCB by microwave spectroscopy (MW) and electron diffraction (ED)[1,2] along with two subsequent ab initio calculations[3,4] are listed in Table 1 (numbering scheme in Figure 1) and show a variation in the ring parameters. It is well-known that MW, ED and ab initio analyses measure operationally different structural parameters due to zero point vibrational effects, and the discrepancies among the results in Table 1 likely arise in part from these effects. Vibrational corrections were made in the ED analysis which should greatly reduce discrepancies with the MW ground vibrational state structure, yet the appreciable differences which remained were considered puzzling and unexplained.[1,2] The two ab initio studies were undertaken to shed light on this deviance but instead served to further enhance the puzzle since ref 3 preferred results having a long $F_2C{-}CF_2$ distance (1.584 Å), close to the ED analysis while ref 4 reported a shorter distance (1.555 Å) more consistent with the MW analysis.

The results for two related halogenated cyclobutenes were similarly divergent; they gave for the $F_2C{-}CF_2$ distance: 1.539(6) Å in 3,3,4,4,-tetrafluorocyclobutene[5] (MW) and 1.599(10) Å in CFCB[6] (ED). This has been a concern since one of the questions structural chemists would like to resolve is whether there is a systematic contraction in most (all) distances in four-membered rings upon substitution with halogens and especially fluorine. A shortening trend is often seen in experiments and calculations with fluorinated acyclic systems. Because of the considerable interest in the effects of fluorination on the properties of small hydrocarbons,[7] we decided to analyze the MW spectrum of CFCB to compare it with the ED study.

TABLE 1: Comparison of Ring Structural Parameters for Cyclobutene and Hexafluorocyclobutene[a]

distance or angle	hexafluorocyclobutene MW[1]	ED[2]	ab initio[3 b]	ab initio[4 c]	cyclobutene MW[19]
$C_1{=}C_2$	1.333(6)	1.325(24)	1.344	1.348	1.342(4)
$C_2{-}C_3$	1.478(6)	1.500(5)	1.502	1.497	1.517(3)
$C_3{-}C_4$	1.552(6)	1.582(8)	1.584	1.555	1.566(3)
$\angle C_1{-}C_2{-}C_3$	94.3(2)	94.9(5)	94.6	93.6	94.2(3)
$\angle C_1{-}C_4{-}C_3$	85.7(2)	85.1(5)	85.4	86.4	85.8(2)

[a] See Figure 1 for atom numbering. [b] LDA+BP/TZP level (DFT). [c] MP2−6-31G**.

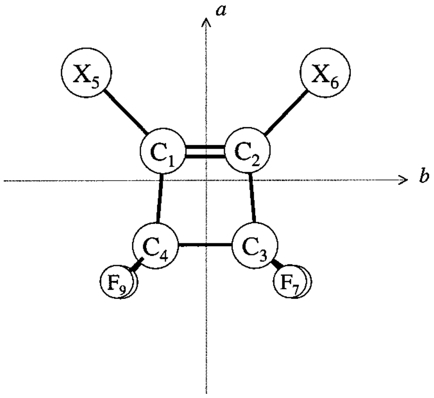

Figure 1. Structure of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene and its derivatives showing the atom numbering scheme. X = Cl for CFCB, X = F for hexafluorocyclobutene and X = H for tetrafluorocyclobutene.

Experimental Section

The rotational spectrum of CFCB was measured in the frequency range between 6 and 12 GHz using a Fourier transform microwave spectrometer of the Balle-Flygare type.[8] The spectrometer incorporates hardware and software developments from the University of Kiel[9] that enable it to scan large regions unassisted; this feature was utilized in the initial search for the spectrum. The CFCB sample was obtained from

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Lancaster Synthesis Ltd. (Gainesville, FL) and used without further purification. A few milliliters of the liquid were placed in a glass sample bulb to which argon carrier gas was added to give a total backing pressure of around 2−3 bar. This gas mixture was expanded through a General Valve Series 9 solenoid valve into the evacuated Fabry−Pérot cavity perpendicular to the direction of microwave propagation, giving rise to rotational transitions having a full-width at half-maximum (fwhm) of around 30 kHz. This did not afford sufficient resolution to resolve much of the chlorine nuclear hyperfine splittings so a second general valve series 9 nozzle situated just off-center in one of the mirror faces of the Fabry−Pérot cavity was used. This axial nozzle is aligned parallel to the microwave propagation axis. It was able to significantly improve the resolution, giving Doppler doublets split by about 30 kHz with a fwhm of around 10 kHz for each component. The measured frequencies of the rotational transitions (average of the doublets) are typically reproducible to within 4 kHz. Transitions arising from the normal isotopomer were reasonably intense with the strongest transitions averaged for 100−500 shots to achieve signal-to-noise ratios of 30−40. The ^{35}Cl/^{37}Cl species was slightly less intense, as would be expected from the natural abundance of ^{37}Cl (24.5%) and required similar averaging. The assignment of the ^{13}C species, however, required considerable effort due to their low abundance. A total of 25 000 gas pulses were typically averaged to obtain transitions that would allow the hyperfine structure to be unambiguously assigned. This in itself should not have proved too challenging, but additional problems arose since the isotopic shifts for these species (see the rotational constants in Table 3) were small and hence frequently placed the ^{13}C transitions close to transitions arising from the normal species. The considerably more intense hyperfine components belonging to the normal species caused problems when they were within 1 MHz or so of the ^{13}C transitions and careful selection of the transitions to be measured was necessary. Consequently, the number of transitions that could be measured with a high degree of confidence for the ^{13}C species was much less than for the other species. Despite this, good fits of rotational and nuclear quadrupole coupling constants were obtained for these isotopomers and the resulting spectroscopic constants are tabulated in Table 3.

Results

A. Spectra. The four isotopomers (the normal, the ^{35}Cl/^{37}Cl species, the ^{13}C species singly substituted at the single bond, and the ^{13}C species singly substituted at the double bond were all measured in natural abundance (respectively, 54.6%, 35.4%, 1.2%, 1.2%). Structural information from the previous electron diffraction study[6] and ab initio calculations made in this laboratory (to be discussed later) made the initial search for the rotational spectrum of the normal species straightforward, with the hyperfine structure associated with each $J + 1 \leftarrow J$ transition easily located. Only *a*-type transitions were observed for any of the four isotopomers, with each transition split over several megahertz by the nuclear quadrupole hyperfine interactions of the Cl nuclei (which have a nuclear spin quantum number, $I = {}^3/_2$). While the $K = 0$ and $K = 1$ lines fitted reasonably well, initial attempts to fit the hyperfine components for some of the higher K transitions ($K > 1$) led to some rather large residuals until a χ_{ab} term was introduced into the fit. A total of 228 hyperfine components for the normal isotopic species were measured and a representative selection are given in Table 2; the full set of frequencies for the normal and additional isotopomers are available as Supporting Information. The fits were performed with the SPFIT program of H. M. Pickett,[10] which allows for the diagonalization of the complete exact Hamiltonian for an asymmetric rotor with two quadrupolar nuclei. The rotational and nuclear spin angular momentum vectors were coupled according to the scheme, $I = I_{\mathrm{Cl1}} + I_{\mathrm{Cl2}}$, $F = I + J$, so the energy levels in Table 2 are labeled with I, F quantum numbers. The resulting spectroscopic constants from least-squares fitting the rotational transition frequencies to a Watson A-reduced Hamiltonian in the I^r representation[11] are given in Table 3. The $\Delta\nu_{\mathrm{rms}}$ values of the fits for the four isotopomers (Table 3) are all 2−3 kHz, which is well within the range of the estimated accuracy of 4 kHz. The goodness of the fit for the quadrupole multiplets, which are sensitive probes of the I, J, F assignment of the states, ensure the correctness of the assignment of these complex patterns. In addition, the constancy of P_{cc} (the out-of-plane inertial planar moment; see below) and χ_{cc} (32.60 ± 0.10 MHz; the out-of-plane quadrupole coupling constant of a ^{35}Cl nucleus) in all the isotopic species further confirms the assignments. Attempts to study quantitatively the variation in intensities of the transitions were not pursued due to the difficulty in obtaining reliable intensity data with a FTMW spectrometer. The intensities were qualitatively in accordance with expected values.

B. Structure. Measurement of the rotational spectra of four isotopomers of this molecule provided 12 moments of inertia, which allowed a full structure determination of CFCB to be carried out. Inspection of the planar moment data in Table 3 provides some initial insight into the symmetry of the molecule. All the isotopic substitutions were in the *ab* plane so the P_{cc} moment ($P_{xx} = \sum m_i x_i^2$) is not expected to change; the value of P_{cc} in Table 3 can be seen to be 89.303 ± 0.003 u Å^2 for all four isotopic species, confirming that all substituted atoms are in the plane and that only the out-of-plane fluorine atoms contribute to this moment. This also serves to confirm the assignment of the ^{13}C spectra as arising from these species and not an adventitious vibrational satellite. In actuality, this is not expected since population of an excited vibrational state would be very unusual due to the low temperature of the jet expansion.

For a C_{2v} symmetry molecule of this type, eight internal parameters (nine Cartesian coordinates) are required to fully describe the structure. A least-squares fitting of the Cartesian coordinates of all atoms in this molecule to the 12 experimental moments of inertia from the four isotopomers (plus the three center of mass conditions (first moments) for the normal isotopomer) was carried out using the University of Michigan implementation of the STRFIT87 program of Schwendeman.[12] (Note: nine of the experimental inertial second moments and one of the first moments are independent due to the symmetry, and hence an overdetermined set of equations was used in the fitting program.) The principal axis coordinates of the resulting structure are given in Table 4, and the associated structural parameters are given in Table 5. The ΔI_{rms} for this fit was 0.0026 u Å^2. Table 4 also lists the principal axis coordinates of the C and Cl atoms, which were calculated from Kraitchman's equations[13] using the single isotopic substitution data. The corresponding structural parameters calculated from the Kraitchman coordinates are compared in Table 5 with the values from the inertial fit and an ab initio calculation (to be discussed in more detail in the Discussion). Also included in Table 5 are the values obtained from the electron diffraction study.[6] The uncertainties in the structural parameters listed in Table 5 are statistical uncertainties (1σ) that arise from the least-squares fitting procedure and do not include model errors.

TABLE 2: Selected Rotational Transition Frequencies and Residuals for the Normal Isotopic Species of 1,2-Dichloro-3,3,4,4-tetrafluorocyclobutene[a]

$J_{KaKc} \leftarrow J_{KaKc}$	I	F	←	I	F	ν_{obs}/MHz	$\Delta\nu$/MHz[b]
$4_{23} \leftarrow 3_{22}$	3	5		1	4	6110.6656	−0.0001
	3	6		3	5	6112.4807	0.0015
	1	5		3	4	6114.3481	0.0018
	3	3		3	2	6114.8767	0.0021
	1	4		1	3	6117.0010	0.0054
	2	4		0	3	6117.0010	0.0026
$4_{13} \leftarrow 3_{12}$	3	5		3	4	6114.6322	0.0012
	3	5		3	5	6114.9069	0.0006
	0	4		2	3	6115.2675	0.0011
	3	6		3	5	6116.7218	0.0014
	3	3		3	3	6119.0985	0.0007
	3	3		3	2	6119.3164	0.0009
	3	7		3	6	6120.1738	0.0007
$4_{22} \leftarrow 3_{21}$	2	3		0	3	6952.8486	−0.0019
	3	4		3	4	6953.9910	−0.0021
	3	3		3	3	6954.8051	−0.0015
	3	5		3	4	6955.7175	−0.0027
	0	4		0	3	6956.4482	−0.0003
	1	3		1	2	6957.1442	−0.0008
	3	6		3	5	6957.7384	0.0009
	3	4		3	3	6958.3016	−0.0007
	2	5		2	4	6959.1943	−0.0010
	2	2		2	1	6959.5151	−0.0025
	1	5		1	4	6959.5548	−0.0021
	2	6		2	5	6959.8308	−0.0019
	3	7		3	6	6960.0954	−0.0033
	3	5		3	5	6960.1702	−0.0037
	2	3		2	2	6961.1855	0.0000
	2	2		2	2	6961.2986	0.0043
	3	2		3	2	6961.5397	−0.0002
	2	4		2	3	6961.8666	−0.0034
	1	4		1	3	6962.0337	−0.0023
	3	3		3	2	6963.1139	−0.0003
$5_{05} \leftarrow 4_{04}$	3	7		3	7	6542.5376	−0.0010
	0	5		2	5	6544.0969	−0.0013
	2	4		2	4	6544.8378	−0.0007
	3	5		1	5	6545.5506	0.0001
	3	4		1	4	6547.0177	−0.0011
	3	6		3	6	6548.1569	−0.0009
	3	5		3	4	6554.6893	0.0016
	3	3		3	2	6554.8230	0.0013
	3	4		3	3	6555.2032	0.0030
	1	4		1	3	6555.5857	0.0018
	3	6		3	5	6555.6707	0.0007
	0	5		0	4	6555.7158	0.0026
	1	6		1	5	6556.2122	−0.0005
	3	7		3	6	6557.0591	0.0000
	1	5		1	4	6557.1905	−0.0010
	2	5		2	4	6557.2144	0.0008
	3	8		3	7	6557.5822	0.0002
	3	5		3	5	6560.3815	−0.0013
	3	3		3	3	6561.1424	−0.0008
	3	2		3	2	6563.0285	0.0010
	1	6		3	6	6563.5321	−0.0007
	3	4		3	4	6566.8057	0.0012
	1	5		1	5	6567.8391	−0.0008
	2	4		0	4	6568.1029	−0.0008
	2	5		2	5	6568.8623	−0.0014
	3	3		3	4	6572.7480	0.0005
	3	3		1	3	6572.8758	−0.0018
$5_{33} \leftarrow 4_{32}$	3	6		3	5	8131.7008	0.0020
	3	4		3	4	8132.1637	−0.0012
	1	4		1	3	8132.8997	0.0019
	3	5		3	4	8132.9779	0.0010
	3	7		3	6	8133.2199	0.0023
	3	6		3	6	8133.8840	0.0015
	1	5		1	5	8134.1916	0.0009
	1	6		1	5	8134.8783	0.0017
	3	3		3	3	8135.0755	−0.0004
	3	4		3	3	8135.4075	0.0018
	3	8		3	7	8136.4050	0.0025
	3	3		3	2	8136.8536	0.0022
	1	5		1	4	8137.1483	0.0026
	0	5		2	4	8137.1483	−0.0030
	3	7		3	7	8137.3912	0.0028
	3	4		1	4	8137.7836	−0.0007
	3	2		3	1	8138.2919	0.0019
$5_{23} \leftarrow 4_{22}$	2	4		0	4	8143.2276	0.0041
	3	5		3	5	8143.2020	0.0034
	3	6		3	5	8143.5546	0.0048
	2	5		0	4	8144.0946	0.0024
	1	4		1	3	8144.8295	0.0026
	3	5		3	4	8144.9283	0.0026
	3	7		3	6	8145.2983	0.0032
	3	4		3	3	8147.6003	0.0023
	3	8		3	7	8148.2347	0.0030
	3	3		3	2	8148.8217	0.0024
	0	5		2	4	8148.9915	0.0014
	1	5		1	4	8149.0062	0.0050
	3	7		3	7	8149.1942	0.0003
	3	4		1	4	8149.6247	0.0013
	2	4		2	4	8149.7510	0.0021
	3	2		3	1	8149.9783	0.0040
$5_{32} \leftarrow 4_{31}$	3	6		3	5	9006.1186	0.0026
	0	5		0	4	9006.6134	0.0005
	1	4		1	3	9007.2126	0.0005
	3	7		3	6	9007.5608	0.0013
	3	5		3	4	9007.6245	0.0005
	3	2		3	2	9008.2909	0.0033
	3	3		3	3	9008.3524	0.0003
	2	6		2	5	9008.6088	0.0008
	1	6		1	5	9008.8630	0.0013
	2	7		2	6	9008.9503	0.0007
	2	5		2	4	9010.2883	0.0000
	1	5		1	4	9010.3249	−0.0003

[a] A full list of the 228 measured hyperfine components for the normal isotopic species is available as Supporting Information. [b] $\Delta\nu = \nu_{obs} - \nu_{calc}$ where ν_{calc} is obtained from the constants in Table 3.

To test the sensitivity of the determined parameters to the fluorine locations since no fluorine substitution is possible, a second inertial fit was carried out. In this second fit, the F—C—F bond angles and C—F bond lengths were fixed at the values from 3,3,4,4-tetrafluorocyclobutene[5] and the following internal coordinates were optimized: the distances C_1—Cl_5, C_1═C_2, C_2—C_3, and C_3—C_4, the angles C_2═C_1—Cl_5 and Y—C_4—C_1. The point Y lies on the angle F—C—F bisector. To maintain C_{2v} symmetry, the angles C_4—C_3—C_2 and C_3—C_4—C_1 and the angles C_4—C_1═C_2 and C_3—C_2═C_1 were set equal during the fitting procedure. The results from this fit (ΔI_{rms} = 0.003 u Å^2) are given in the third column of Table 5. It can be seen that the parameters of interest, namely the C_1═C_2 and the C_3—C_4 bond, change a little, agreeing with the previous inertial fit to within the uncertainties and remain considerably shorter than the electron diffraction values. The other single bond, C_2—C_3 is

TABLE 3: Spectroscopic Constants for the Isotopomers of 1,2-Dichloro-3,3,4,4-tetrafluorocyclobutene

spectroscopic constant	$CF_2C^{35}Cl{=}C^{35}ClCF_2$	$CF_2C^{37}Cl{=}C^{35}ClCF_2$	$CF_2{}^{13}C^{35}Cl{=}C^{35}ClCF_2$	$CF_2C^{35}Cl{=}C^{35}Cl^{13}CF_2$
A/MHz	1022.4403(6)	1015.1143(6)	1021.5761(7)	1021.3103(7)
B/MHz	1001.4502(4)	983.2860(6)	1000.8348(12)	999.6256(11)
C/MHz	616.07373(13)	606.53683(10)	615.52946(9)	614.96664(8)
Δ_J/kHz	0.0103(11)	0.00083(8)	0.0103[a]	0.0103[a]
Δ_K/kHz	0.22(2)	0.34(2)	0.22[a]	0.22[a]
$\chi_{aa}{}^{(5)}$/MHz	−17.635(6)	−49.975(13)	−22.02(22)	−25.47(25)
$\chi_{bb} - \chi_{cc}{}^{(5)}$/MHz	−47.568(6)	−1.416 (75)	−43.41(9)	−39.60(8)
$\chi_{ab}{}^{(5)}$/MHz	−57.887(27)	−26.62(25)	−59.5(22)	−59.1(8)
$\chi_{aa}{}^{(6)}$/MHz	−17.635(6)	29.209(11)	−13.24(21)	−9.76(25)
$\chi_{bb} - \chi_{cc}{}^{(6)}$/MHz	−47.568(6)	−94.412(1)	−51.69(9)	−55.58(6)
$\chi_{ab}{}^{(6)}$/MHz[b]	57.887(27)	35.96(20)	56.2(23)	56.1(8)
N [c]	228	155	49	58
$\Delta\nu_{rms}$/kHz[d]	2.29	2.85	2.17	2.02
P_{aa}/u Å^2	415.3412	424.6680	415.6500	416.2667
P_{bb}/u Å^2	404.9811	408.5528	405.3977	405.5324
P_{cc}/u Å^2	89.3060	89.3016	89.3075	89.3016

[a] Centrifugal distortion constants were fixed at the values for the normal isotopomer during the fitting of the ^{13}C species. [b] The signs of the χ_{ab}'s must be opposite but otherwise cannot be determined from the spectrum. The signs assigned are consistent with a positive (negative), clockwise (counterclockwise) angle θ_{za} for X_5 (X_6) in Figure 1. For the mixed chlorine isotopomer, the $\chi^{(5)}$ set corresponds to ^{37}Cl, $\chi^{(6)}$ to ^{35}Cl. The ^{13}C isotopomers can be correlated to substitution at C_1 and C_3. The sum of both θ_{za} is 88.6 ± 0.3° for the four isotopomers, notwithstanding large axis rotations especially for the ^{37}Cl species. [c] Number of hyperfine components fitted. [d] $\Delta\nu_{rms} = (\sum(\nu_{obs} - \nu_{calc})^2/N)^{1/2}$.

TABLE 4: Principal Axis Coordinates of 1,2-Dichloro-3,3,4,4-tetrafluorocyclobutene Resulting from the Inertial Fit[a]

<table>
<tr><th>atoms</th><th>a</th><th>b</th><th>c</th></tr>
<tr><td>C_1, C_2</td><td>0.55205</td><td>∓0.65228</td><td>0.00000</td></tr>
<tr><td></td><td>|0.54483|</td><td>|0.65554|</td><td>|0.00000|</td></tr>
<tr><td>C_3, C_4</td><td>−0.93831</td><td>±0.77261</td><td>0.00000</td></tr>
<tr><td></td><td>|0.93695|</td><td>|0.77565|</td><td>|0.00000|</td></tr>
<tr><td>Cl_5, Cl_6</td><td>1.75952</td><td>∓1.85155</td><td>0.00000</td></tr>
<tr><td></td><td>|1.75834|</td><td>|1.85299|</td><td>|0.00000|</td></tr>
<tr><td>F_7, F_8</td><td>−1.49731</td><td>1.36062</td><td>∓1.08405</td></tr>
<tr><td>F_9, F_{10}</td><td>−1.49731</td><td>−1.36062</td><td>∓1.08405</td></tr>
</table>

[a] The absolute values of the Kraitchman coordinates obtained from single isotopic substitution are given in brackets. All coordinates are in ångstroms. See Figure 1 for atom numbering and coordinate system.

somewhat shorter than the previous inertial fit although in good agreement with the Kraitchman determination. The differences in the angles are slightly outside the quoted uncertainties, particularly the $C_1{=}C_2{-}C_3$ and $C_2{-}C_3{-}C_4$ angles, which are interestingly 0.24° less than and 0.24° more than the previous inertial fit values, respectively. This calculation indicates that a correlation exists between the fluorine parameters in the least-squares fitting procedure, which makes them less certain[14] and suggests that this can affect the ring parameters determined in an r_0 fit perhaps by as much as 0.01−0.015 Å.

In summary, it is noted that the values compared in Table 5 are different, arising from different analyses. The r_0 geometry that is obtained from the ground-state moments of inertia may differ by a few hundredths of an angstrom from the equilibrium value of the bond length. The r_s quantity is derived from the use of the isotopic substitution equations of Kraitchman. This procedure assumes that the vibrational effects between the normal and substituted isotopomer will be similar and will tend to cancel in the analysis. r_s geometries are often closer to the r_e structure in favorable cases (e.g., for large coordinates). The r_α that comes from the electron diffraction data corresponds to a thermally averaged bond distance. Because of the heavy weighting of the fluorine in the r_0 structure determinations noted above and the possible unfavorable correlations this induces among the parameters in an r_0 fit, we believe the Kraitchman structure ring parameters in Table 5 are the preferred values. The large inertial coordinates (b values) and the ring rigidity should minimize anomalous vibrational effects in the structure determination. Their experimental uncertainties are about 0.0015 Å. Nevertheless, a more conservative estimate of the model errors is that they are within ± 0.015 Å of the r_e values.

C. Interpretation of Nuclear Quadrupole Coupling Constants. Some additional structural information may be obtained from the experimentally determined nuclear quadrupole coupling constants. It is expected that the value of χ_{cc} (the out-of-plane projection of the nuclear quadrupole coupling tensor onto the principal inertial axis system) should be the same in the four species. The following values for χ_{cc} are calculated for chlorine nuclei (1) and (2): $\chi_{cc}{}^{(1)} = \chi_{cc}{}^{(2)} = 32.602(7)$ MHz for the normal species; $\chi_{cc}{}^{(1)} = 32.602(10)$ MHz, $\chi_{cc}{}^{(2)} = 25.696(10)$ MHz for the $^{35}Cl/^{37}Cl$ species; $\chi_{cc}{}^{(1)} = 32.7(2)$ MHz, $\chi_{cc}{}^{(2)} = 32.5(2)$ MHz for the ^{13}C at the single bond; $\chi_{cc}{}^{(1)} = 32.7(2)$ MHz, $\chi_{cc}{}^{(2)} = 32.5(2)$ MHz for the ^{13}C at the double bond. It can be seen that the values of χ_{cc} for the ^{35}Cl nuclei all agree within their uncertainties. The much larger uncertainties in the coupling constants for the ^{13}C species result from the smaller number of transitions in the fit, although the deviation is still less than 1% of the constant's value; this presents no real concern since the rotational constants are well determined and the coupling constants are consistent with the expected values. The ratio of the value of χ_{cc} for the ^{35}Cl nucleus to that of the ^{37}Cl nucleus should agree with the ratio of the magnitudes of the nuclear quadrupole moments; the value of 1.26876 obtained from the above values is in excellent agreement with the value of 1.26878 listed in the literature.[15]

The off-diagonal term χ_{ab} contains some angular information that may be extracted from the relation $2\chi_{ab} = (\chi_{aa} - \chi_{bb}) \tan 2\theta_{za}$, where θ_{za} is the angle between the a inertial axis and the z principal axis of the nuclear quadrupole coupling tensor. Using this relation we obtain a value of 44.34° from the values of χ_{aa}, χ_{bb}, and χ_{ab} for the normal isotopomer. This angle is in very good agreement with the angle between the C−Cl bond and the a inertial axis of 44.80° that is obtained from the inertial fit structure, indicating that the z axis and C−Cl bond axis are collinear to within 0.5°. From the angle θ_{za} we can use the well-known relations[15] between χ_x, χ_y, and χ_z (the coupling constants in the axis system of the nuclear quadrupole tensor) and the projections in the inertial axis system χ_{aa}, χ_{bb}, and χ_{cc}, to obtain the following: $\chi_x = 41.721$ MHz, $\chi_y = 32.602$ MHz, and $\chi_z = -74.322$ MHz. The quadrupole asymmetry parameter, $\eta = (\chi_x$

TABLE 5: Comparison of Fitted and Calculated Structural Parameters for 1,2-Dichloro-3,3,4,4-tetrafluorocyclobutene

parameter	inertial fit r_0[a]	inertial fit r_0[b]	Kraitchman r_s[c]	CCD/6-31G* r_e	electron diffraction, r_α[d]
$r(C_1{=}C_2)$/Å	1.305(4)	1.313(4)	1.311(15)	1.344	1.355(9)
$r(C_2{-}C_3)$/Å	1.495(3)	1.488(2)	1.487(15)	1.508	1.498(6)
$r(C_3{-}C_4)$/Å	1.545(4)	1.540(7)	1.551(15)	1.554	1.596(10)
$r(C_1{-}Cl_5)$/Å	1.702(3)	1.700(2)	1.705(15)	1.694	1.680(3)
$r(C_3{-}F_7)$/Å	1.354(2)	1.358[e]		1.349	1.332(2)
$\theta(Cl_5{-}C_1{=}C_2)$/deg	134.80(20)	134.60(11)	134.62(60)	134.94	133.9(3)
$\theta(C_1{=}C_2{-}C_3)$/deg	94.62(23)	94.38(11)	94.63(60)	93.98	94.6(2)
$\theta(C_2{-}C_3{-}C_4)$/deg	85.38(20)	85.62(14)	85.37(60)	86.02	85.4(2)
$\theta(F_7{-}C_3{-}F_8)$/deg	106.38(19)	106.2[e]		108.30	108.2(4)
$\theta(F_7{-}C_3{-}C_2)$/deg	116.52(13)	116.50(12)		116.04	116.5(5)

[a] From a fit of Cartesian coordinates for all atoms to I_a, I_b, and I_c using STRFIT87. [b] From a fit of I_a and I_b for all isotopomers fixing some C—F parameters. [c] Preferred values; see text for discussion of uncertainties. [d] Electron diffraction data taken from ref 6. [e] Values fixed from the structure of 3,3,4,4-tetrafluorocyclobutene.[5]

TABLE 6: Comparison of ab Initio Structural Parameters and Computed Rotational Constants for 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene

parameter	HF/6-31G* [a]	HF/AUG-cc-pVDZ	B3LYP/6-31G*	B3LYP/cc-pVDZ	CCD/6-31G*	CCD/cc-pVDZ
$r(C_1{=}C_2)$/Å	1.322	1.326	1.347	1.351	1.344	1.354
$r(C_2{-}C_3)$/Å	1.502	1.504	1.512	1.514	1.508	1.517
$r(C_3{-}C_4)$/Å	1.543	1.550	1.568	1.571	1.554	1.566
$r(C_1{-}Cl_5)$/Å	1.692	1.697	1.702	1.705	1.694	1.703
$r(C_3{-}F_7)$/Å	1.325	1.327	1.350	1.352	1.349	1.344
$\theta(Cl_5{-}C_1{=}C_2)$/deg	134.86	134.71	134.76	134.64	134.94	134.85
$\theta(C_1{=}C_2{-}C_3)$/deg	94.23	94.28	94.19	94.17	93.98	94.01
$\theta(C_2{-}C_3{-}C_4)$/deg	85.77	85.72	85.81	85.84	86.02	85.99
$\theta(F_7{-}C_3{-}F_8)$/deg	108.02	107.62	108.22	107.78	108.30	108.10
$\theta(F_7{-}C_3{-}C_2)$/deg	116.06	116.14	116.14	116.19	116.04	115.98
A/MHz	1037.914	1032.184	1011.247	1007.909	1017.340	1010.155
B/MHz	1013.078	1008.127	989.759	986.609	997.197	991.687
C/MHz	623.000	618.959	610.001	607.155	614.923	608.919

[a] This calculation appeared in the electron diffraction paper[6] and is included here for comparison purposes.

$- \chi_y)/\chi_z$ is calculated to be -0.123 in this case. These values of χ_x, χ_y, χ_z, and η are consistent with the values in similar Cl-containing compounds such as *cis*-1,2-dichloroethylene ($\chi_x = 39.3(3)$ MHz, $\chi_y = 31.36(9)$ MHz, and $\chi_z = -70.7(3)$ MHz with $\eta = -0.112$)[16] and 1,1-dichloroethylene ($\chi_x = 43.5(7)$ MHz, $\chi_y = 34.36(15)$ MHz, and $\chi_z = -77.9(5)$ MHz with $\eta = -0.117$).[16]

Discussion

The initial assignments of the spectra for the isotopic species of CFCB were guided by ab initio calculations carried out using Gaussian 94[17] and 98.[18] Table 5 lists the structural parameters from a CCD/6-31G* calculation that best reproduced the experimental rotational constants with those values obtained from the inertial and Kraitchman fit. Structural parameters from several other ab initio calculations are listed in Table 6 for comparison. The computed rotational constants for the theoretical (CCD/6-31G*) structure are in excellent agreement with the experimental values in Table 3, with the coupled cluster calculation giving $A = 1017.340$ MHz, $B = 997.197$ MHz, and $C = 614.923$ MHz, underestimating the experimental rotational constants by 5.10, 4.25, and 1.15 MHz, respectively. This calculated structure was very helpful at predicting isotopic shifts for the ^{13}C species and allowed quick location of the transitions of interest. An inspection of Table 6 reveals surprisingly little variation in many of the structural parameters at the various levels of theory. The C═C double bond lengths for the SCF calculations are much closer to the experimental determination although the DFT and CCD results are 0.02−0.03 Å larger. Likewise, the C—F bond lengths in the SCF calculation are some 0.02 - 0.03 Å shorter than the higher level calculations. The considerably shorter C═C and C—F bonds at the SCF level compared to correlated levels is consistent with previous ab initio calculations on substituted cyclobutenes.[4]

An examination of the $C_1{=}C_2$ and $C_3{-}C_4$ distances in Table 5 reveals that they are both about 0.04−0.05 Å shorter than the electron diffraction values. The $C_1{=}C_2$ value is also about 0.03−0.04 Å shorter than the ab initio (CCD/6-31G**) value while the $C_3{-}C_4$ distance is within 0.01 Å of the calculated value. The $C_2{-}C_3$, $C_3{-}F_7$ and $C_1{-}Cl_5$ bond lengths are within 0.01−0.02 Å of the ab initio and ED values.

A comparison with the electron diffraction data[6] reveals that all angles, with the exception of the F—C—F angle, agree to within the experimental uncertainties. The value of θ_{za} calculated from the ab initio structure is found to be 44.94° (again assuming that the z axis and the C—Cl bond are coincident). Indeed, the ab initio values of this angle for the calculations listed in Table 6 give angles in the range 44.8 ± 0.2°, remarkably constant and in essentially perfect agreement with the angle obtained from our inertial fit structure. This is even more remarkable (and perhaps fortuitous) since the proximity of this angle to 45° leads to very rapidly changing values of functions, which cause the projections of the coupling constants onto the principal inertial axis system to be quite sensitive to this angle. It is therefore helpful in cases such as this to have a good guess for this angle to allow accurate predictions of the nuclear quadrupole coupling constant projections to accelerate assignment of the hyperfine splittings. The value of the angle θ_{za} (the angle of the C—Cl bond with respect to the a-axis) from the electron diffraction data is 43.9(3)°, which agrees with the value of θ_{za} derived from χ_{ab} (for the normal species) to within the uncertainties.

The initial impetus for this work was to determine whether the $F_2C{-}CF_2$ bond distance (i.e., $C_3{-}C_4$) in CFCB would be around 1.55 Å as in the MW study of HFCB or around 1.58−

TABLE 7: Comparison of Experimental Structural Parameters for 1,2-Dichloro-3,3,4,4-tetrafluorocyclobutene and Related Molecules

	1,2-dichloro-3,3,4,4-tetrafluorocyclobutene, this work[a]	cyclobutene[b]	3,3,4,4,-tetrafluoro-cyclobutene[c]	hexafluoro-cyclobutene[d]
r(C═C)/Å	1.311(15)	1.342(4)	1.348(3)	1.333(6)
r(═C—C)/Å	1.487(15)	1.517(3)	1.502(3)	1.478(6)
r(C—C)/Å	1.551(15)	1.566(3)	1.536(3)	1.552(6)
r(C—Cl)/Å	1.705(15)			
r(C—F)/Å	1.354(15)		1.358(2)	1.358[e]
r(C—H)/Å		1.083(5)		
θ(C═C—C)/deg	94.6(6)	94.2(3)	93.6(1)	94.3(2)
θ(C—C—C)/deg	85.4(6)	85.8(2)	86.4(2)	85.7(2)
θ(F—C—F)/deg	106.4(6)		106.2(2)	106.0(2)
θ(C—C—H)/deg		132.3(5)		

[a] Kraitchman (r_s) values from Table 5. [b] Reference 19. [c] Reference 5. [d] Reference 1. [e] Assumed.

1.60 Å as in ED studies of CFCB and HFCB. It can be seen that the value obtained of about 1.55 Å is more consistent with the spectroscopic values for cyclobutene,[19] tetrafluorocyclobutene,[5] and hexafluorocyclobutene.[1] The distances and angles for these molecules are compared in Table 7.

In comparison, the C_1═C_2 distances of 1.311 Å seemed initially somewhat short. It is about 0.04 Å shorter than in tetrafluorocyclobutene (MW),[5] 0.01−0.02 Å shorter than in hexafluorocyclobutene[1,2] (MW and ED values), and about 0.03−0.04 Å shorter than most of the higher level ab initio calculations in Table 6. However, a broader literature review of some related prototype alkenes provided a greater range of results. The C═C distance in 1,2-dichloroethene was reported to be 1.319 Å[16] (cis, MW), 1.305 Å (trans, IR),[20] 1.337 − 1.345 Å (cis, ED),[21,22] and 1.332 Å[22] (trans, ED). Ab initio calculations of these dichloroethenes and tetrachloroethene gave values between 1.308 and 1.324 Å.[23,24] The experimental values for 1,2-difluoroethene were 1.324 Å[25] (cis, MW) and 1.319 Å[26] (trans, IR), and for C_2F_4, 1.311 Å[27] (ED). Ab initio values for these fluorinated species cluster between 1.30 and 1.34 Å with a few results even shorter or longer.[23,28−35] This indicates that the C═C distance in CFCB reported here, while short, is not patently unreasonable or unprecedented compared to other results in substituted ethenes. Nevertheless, a reason for the shortening compared to HFCB and the ab initio calculations is unclear to us.

Some previous ab initio studies of CFCB and other closely related molecules have been reported. A recent study by Han et al. attempted to resolve the differences between the microwave and electron diffraction geometries of hexafluorocyclobutene.[4] In that study, an MP2/6-31G* optimization of CFCB was also presented, giving a value for the C_3—C_4 bond of 1.554 Å, while the C_1═C_2 bond was calculated to be 1.354 Å, showing a pattern that is consistent with our own ab initio results in Table 6.

In summary, in reviewing the structures for the cyclobutenes and halogenated ethenes, the variability in the parameters obtained in the ab initio, spectroscopic, and diffraction analyses continues to be noteworthy. While some variability is expected since the three approaches derive operationally different parameters due to vibrational effects, the discrepancies are somewhat larger than usually found for nonhalogenated hydrocarbon systems. The discrepancies are certainly not actually large on an absolute scale but warrant further attention if for no other reason than the pursuit of intellectual rigor.

As a means of beginning to resolve the spectroscopic ambiguities, it is attractive to consider determining equilibrium structures (r_e) using ab initio calculations of the vibration−rotation interaction constants (α's) to correct the ground-state constants. There are recent examples of this approach,[36−38] which was discussed at a recent symposium.[39] There is reason to think that ab initio calculations without enormous (and impractical) basis sets may prove reliable enough for calculating the anharmonic and harmonic force constants so that relatively accurate equilibrium structures can be achieved. Whether this approach can be easily extended to the kinds of halogenated hydrocarbons discussed in this work is a question for future investigation.

Conclusions

The spectroscopic data for CFCB are consistent with a noticeable shortening of the ring distances in this halogenated system compared to cyclobutene. For some parameters, this shrinkage appears greater than in previous spectroscopic and electron diffraction results on the same or similar compounds. The C═C and C_3—C_4 distances in the CFCB depend only on the *b* coordinates of the carbon atoms, which should be well determined by using the spectroscopic isotopic shift data.

The ab initio results agree well with the present determination in all but the C═C bond length. As noted in the Discussion section, the ab initio calculations provided a useful means of obtaining the angle θ_{za} and the structure of the CCD/6-31G* calculation was sufficiently good to allow easy location of the ^{13}C isotopic species. The source of the differences between the electron diffraction, microwave, and ab initio determinations are still not fully understood but may be resolvable by further ab initio calculations, as proposed in the Discussion.

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Supporting Information Available: Table of rotational transition frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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