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High-Resolution Microwave and Infrared Molecular-Beam Studies of the Conformers of 1,1,2,2-Tetrafluoroethane

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High-resolution microwave and infrared molecular-beam spectra have been measured for 1,1,2,2-tetrafluoroethane (HFC134). For the higher energy, polar, C_2 symmetry, *gauche* conformer, microwave spectra have been recorded for the normal and mono-^{13}C isotopomers and analyzed to determine a C–C bond length of 1.512(4) Å, in good agreement with a recent *ab initio* value (MP2/6-31G**) of 1.515 Å [S. Papasavva, K. H. Illinger, and J. E. Kenny, *J. Phys. Chem.* **100,** 10100–10110 (1996)]. A tunable microwave-sideband CO_2 laser and electric-resonance optothermal spectrometer have been used to measure the infrared spectrum of the ν_6, C–C stretch of the *gauche* conformer near 906 cm^{-1}. Microwave-infrared double resonance and precise ground state combination differences provided by the microwave measurements guide the assignment of the spectrum. The observation of a *c*-type spectrum definitively establishes that the upper state vibration is of A symmetry in the C_2 point group. The spectrum is fit to a Watson asymmetric-top Hamiltonian to a standard deviation of 0.24 MHz. A weak perturbation shifts the line positions for transitions near $J = K_c = 20$ by as much as 12 MHz. The identity of the perturber is unknown. Pulsed slit-jet diode-laser spectra have been recorded for the ν_{16} vibration of the *anti* conformer near 1127 cm^{-1}. An *a*- and *c*-type hybrid band is observed, consistent with a B_u symmetry mode. Previous low-resolution studies have attributed the 1127-cm^{-1} mode to either a B_u or an A_u symmetry vibration. A total of 522 nonblended transitions were assigned and fit to determine ground and excited state constants. The ground state constants of $A = 5134.952(65)$ MHz, $B = 3148.277(27)$ MHz, and $C = 2067.106(43)$ MHz are the first experimental determinations of the rotational constants for this conformer. Here, type A standard uncertainties are given in the parentheses. © 1998 Academic Press

I. INTRODUCTION

The fluorinated ethanes and their derivatives furnish simple model systems for the study of photoinitiated conformational isomerization reactions (*1*). Here, the isomerization coordinate is the rotation angle about the C–C bond. Typically, these studies have been undertaken on substituted ethane molecules trapped in rare-gas or nitrogen matrices. Matrix isolation studies have shown, e.g., that 2-fluoroethanol isomerizes from the *gauche* to the *anti* form when a C–H or O–H stretching vibration is excited (*1*), and that 1,2-difluoroethane isomerizes from *anti* to *gauche* upon excitation of a C–F stretch fundamental (*2*). Of particular interest is the relative importance of inter- and intramolecular coupling in driving the isomerization processes. However, in the matrix both types of coupling are present, which makes it difficult to assess their relative importance in these studies.

This fact has motivated the direct study of the intramolecular couplings in these systems using the techniques of high-resolution infrared molecular-beam spectroscopy (*3–9*). Philips and coworkers (*3–6*) examined the molecular-beam infrared spectra of a series of fluorinated ethanes, 2-fluoroethanol (*3*), 1,2-difluoroethane (*4, 5*), 1-chloro,2-fluoroethane (*6*), and 1,1,2-

trifluoroethane (*5*), to examine the role of steric and electrostatic interactions on their vibrational dynamics. In these experiments, they found that as the strength and extent of the intramolecular interactions increase, the vibrational mode coupling, as determined by the number of perturbing states, also increases. The perturbing states usually contain significant torsional excitation, suggesting an intramolecular mechanism for energy to flow into the isomerization reaction coordinate. More recently, Hudspeth *et al.* (*9*) for 2-fluoroethanol have used infrared-microwave double resonance to find direct evidence for vibrational couplings between two molecular conformations in the gas phase, when the molecule is vibrationally excited above the barrier to conformational isomerization.

An additional motivation for the study of fluorinated ethanes results from their role as potential replacement refrigerants for the chlorofluorocarbons (CFCs). Indeed, the most promising alternatives for the CFCs to date are the hydrofluorocarbon (HFC) derivatives of methane and ethane (*10*). One of the two tetrafluoroethane isomers, 1,1,1,2-tetrafluoroethane (HFC134a), is already in use in car air conditioners. To address environmental, economic, and industrial concerns, it is necessary to characterize the HFCs as fully as possible. In particular, spectroscopic measurements on these compounds provide data for thermodynamic calculations, atmospheric modeling, and remote sensing.

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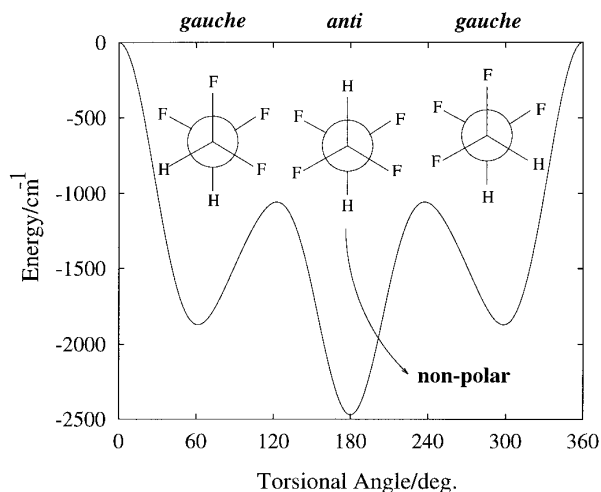
FIG. 1. A theoretical torsional potential energy surface for 1,1,2,2-tetrafluoroethane taken from Chen *et al.* (*11*). Experimentally, the energy difference between the *gauche* and *anti* conformers is approximately 400 cm^{-1}.

In the present work we investigate the microwave and infrared spectra of 1,1,2,2-tetrafluoroethane (HFC134). This molecule exists in two conformers, differing by the torsional angle about the C–C bond. The theoretical potential energy surface for the torsional coordinate shown in Fig. 1 (*11*) is primarily qualitative, as the experimental values for the energy difference vary (*12–14*), with the most recent calculation giving a value of 577 cm^{-1} (*15*). The higher energy *gauche* conformer has a permanent electric dipole moment, and thus has a pure rotational spectrum. The dipole moment also allows

deflection of the molecule by an inhomogeneous field, important for infrared experiments with the NIST electric-resonance optothermal spectrometer (*16*). The lower energy *anti* isomer is centrosymmetric and, thus, does not have a permanent electric dipole moment. This high symmetry forbids the observation of a microwave spectrum, and, in most cases, prevents deflection by an inhomogeneous electric field (*17*).

The present microwave spectra of the ^{12}C and mono-^{13}C *gauche* conformers provide a precise determination for the torsional angle ($\angle$HCCH) of 66.8(5)°. This value for the angle differs by 7° from the totally staggered configuration and by 10° from the electron-diffraction value. The infrared spectrum of the ν_6, C–C stretch fundamental at 906 cm^{-1} was recorded at 2.5 MHz resolution with a tunable microwave-sideband CO$_2$ laser in an electric-resonance, optothermal spectrometer. The spectrum is fit to a standard deviation of 0.3 MHz. A weak perturbation is observed near $J = K_c = 20$, but the identity of the perturbing state has not been determined.

For the *anti* conformer, the direct-absorption diode-laser infrared molecular-beam spectrum for the ν_{16}, CF$_2$ stretch fundamental at 1127 cm^{-1} has been recorded. The unperturbed hybrid *a/c* band furnishes 398 ground state combination differences, which provide the first determination of the ground state rotational constants for this conformer. The absence of large perturbations in the above two bands contrasts with previous results on substituted ethanes which reveal tunneling splittings induced by interactions between the fundamental vibration and modes containing high-torsional excitation.

TABLE 1
Microwave Transition Frequencies in MHz for *gauche*-1,1,2,2-Tetrafluoroethane

J_{K_a,K_b}	^{12}C	^{13}C
$2_{02} - 1_{10}$	7896.649(10)	—
$1_{10} - 0_{00}$	8091.418(10)	—
$3_{21} - 3_{13}$	8935.631(10)	—
$4_{22} - 4_{14}$	9946.861(2)	—
$5_{33} - 5_{23}$	12147.026(2)	—
$4_{32} - 4_{22}$	12555.267(2)	—
$3_{03} - 2_{11}$	12774.041(2)	12735.290(2)
$3_{31} - 3_{21}$	12778.057(2)	—
$3_{30} - 3_{22}$	12940.247(2)	—
$4_{31} - 4_{23}$	13036.635(2)	—
$5_{24} - 4_{32}$	13605.520(2)	—
$6_{33} - 6_{25}$	13620.414(2)	—
$2_{11} - 1_{01}$	13766.470(2)	13724.282(2)
$4_{13} - 3_{21}$	15030.624(2)	—
$5_{15} - 4_{23}$	16261.285(2)	—
$4_{04} - 3_{12}$	17325.484(2)	17277.813(2)
$4_{41} - 4_{31}$	18019.193(5)	—
$4_{40} - 4_{32}$	18033.034(5)	—
$2_{20} - 1_{10}$	18296.706(2)	18249.381(2)
$2_{21} - 1_{11}$	18599.162(5)	18549.646(5)
$3_{12} - 2_{02}$	19619.948(5)	—

[a] Experimental uncertainties on the line positions are one standard deviation (1σ).

TABLE 2
Spectroscopic Constants for Normal and Mono-^{13}C and *gauche*-1,1,2,2-Tetrafluoroethane

Constant	[12]C	[13]C	ν_6
A/MHz	5253.8859(6)[a]	5240.590(1)[b]	5241.007(7)
B/MHz	2837.5750(5)	2827.946(1)	2840.390(2)
C/MHz	2502.6175(3)	2495.623(1)	2488.730(1)
δ_J/kHz	0.492(5)	c	0.489(2)
δ_K/kHz	14.49(6)	c	14.2(2)
Δ_J/kHz	1.706(9)	c	1.688(5)
Δ_{JK}/kHz	-2.94(2)	c	-3.24(7)
Δ_K/kHz	3.25(3)	c	5.05(54)
ν_0/cm^{-1}	----	----	905.83395(2)
σ^d/MHz	0.002	—	0.24

[a] Experimental uncertainties on the line positions are one standard deviation (1σ).

[b] Due to the limited data set these uncertainties are estimated.

[c] Fixed at values for the ^{12}C species.

[d] Standard deviation of the least-squares fit.

II. EXPERIMENTAL

Microwave spectra of the *gauche* conformer were obtained with the NIST Fourier transform microwave spectrometer, which has been described previously (*18*). Briefly, the spectrometer is of the Balle–Flygare type (*19*), with the expansion nozzle placed in the center of one of the Fabry–Perot cavity's mirrors, for increased resolution and sensitivity (*20*). A mixture consisting of 1% by volume tetrafluoroethane and 20% by volume helium in neon was expanded at a pressure of 100 kPa through a 0.5-mm-diameter nozzle. The use of a He/Ne carrier gas leads to a molecular beam with a warmer vibrational temperature than argon, thus allowing the higher energy *gauche* conformer to be populated.

The microwave-sideband CO_2 laser system (*16, 21, 22*) used to examine the ν_6 vibration of the *gauche* conformer is built around a thin-slab GaAs waveguide modulator. In the modulator, radiation from a Lamb-dip-stabilized CO_2 laser is mixed with 7–18.4 GHz radiation from a 20-W traveling-wave-tube amplifier driven by a microwave synthesizer. Several milliwatts of sideband output power result primarily at frequencies $\nu_{out} = \nu_{CO_2} \pm \nu_{microwave}$. The laser beam enters the vacuum chamber, where it multipasses with the molecular beam of the sample.

The tetrafluoroethane was diluted to 3% by volume in helium and expanded at a pressure of 100 kPa (1 atm) through a 60-μm-diameter nozzle. A 1-mm skimmer collimates the supersonic jet into a molecular beam. After the skimmer, the molecular beam enters an electric field of quadrupolar symme-
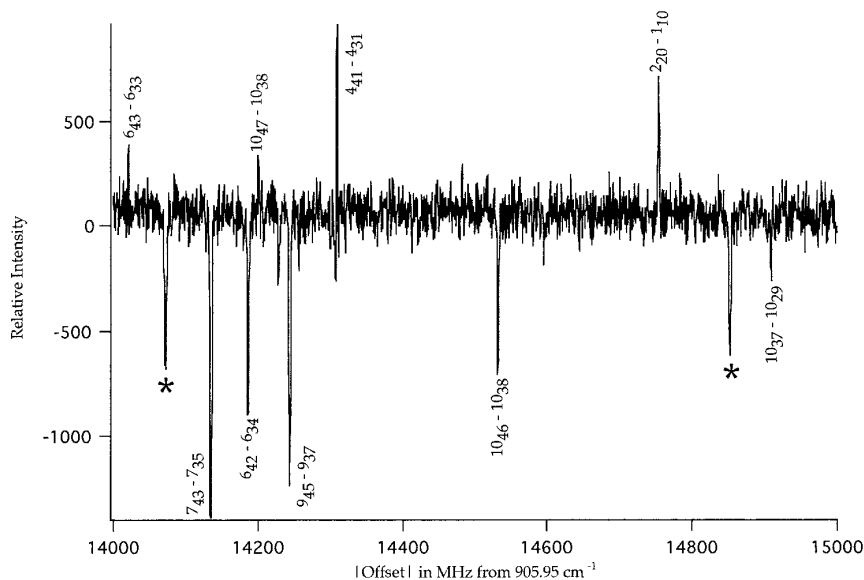
FIG. 2. A section of the CO_2 sideband spectrum of the ν_6, C–C stretch fundamental vibration of *gauche*-1,1,2,2-tetrafluoroethane. Both positive and negative peaks are observed due to the focusing/defocusing nature of the quadrupole fields.

TABLE 3
Transition Frequencies in cm^{-1} for the ν_6 Band of *gauche*-1,1,2,2,-Tetrafluoroethane[a]

6	2	4	7	3	4	904.180755	30	1	30	30	0	30	905.427805	6	3	4	6	2	4	906.209196
10	2	8	11	1	10	904.228729	30	0	30	30	1	30	905.427805[b]	5	2	3	5	1	5	906.210941
11	4	8	12	3	10	904.292907	13	3	10	13	4	10	905.433238	5	3	3	5	2	3	906.231949
9	3	6	10	2	8	904.328062	19	4	15	19	5	15	905.442058	4	3	2	4	2	2	906.247131
6	1	5	7	2	5	904.332294	5	1	5	5	2	3	905.442845	12	4	9	12	3	9	906.248795
4	3	2	5	4	2	904.333787	6	2	4	6	3	4	905.445940	3	3	1	3	2	1	906.255841
4	3	1	5	4	1	904.334289	29	1	29	29	0	29	905.454753	3	0	3	2	1	1	906.257290
9	2	7	10	1	9	904.344180	29	0	29	29	1	29	905.454753[b]	3	3	0	3	2	2	906.261260
5	2	3	6	3	3	904.346889	28	1	28	28	0	28	905.480760	4	3	1	4	2	3	906.263255
10	4	7	11	3	9	904.460796	28	0	28	28	1	28	905.480760[b]	6	2	4	6	1	6	906.276408
8	2	6	9	1	8	904.473855	14	3	11	14	4	11	905.485924	6	3	3	6	2	5	906.280105
13	4	10	13	5	8	905.036099	4	1	4	4	2	2	905.495181	7	3	4	7	2	6	906.300344
12	4	9	12	5	7	905.043608	27	1	27	27	0	27	905.505858	8	3	5	8	2	7	906.332929
11	4	8	11	5	6	905.047228	27	0	27	27	1	27	905.505858[b]	7	2	5	7	1	7	906.359345
10	4	7	10	5	5	905.048663	8	2	6	8	3	6	905.507576	9	3	6	9	2	8	906.381201
9	4	6	9	5	4	905.049158	26	1	26	26	0	26	905.530030	21	6	16	21	5	16	906.390946
8	4	5	8	5	3	905.049420	26	0	26	26	1	26	905.530030[b]	8	4	5	8	3	5	906.392621
2	1	1	3	2	1	905.051918	3	1	3	3	2	1	905.531712	4	0	4	3	1	2	906.406612
9	4	5	9	5	5	905.054198	15	3	12	15	4	12	905.538122	7	4	4	7	3	4	906.408061
11	2	10	11	3	8	905.090395	25	1	25	25	0	25	905.553278	6	4	3	6	3	3	906.417857
4	2	2	5	1	4	905.138237	25	0	25	25	1	25	905.553278[b]	7	4	3	7	3	5	906.421658
11	3	9	11	4	7	905.169569	2	1	2	2	2	0	905.555382	6	4	2	6	3	4	906.423377
2	0	2	3	1	2	905.178294	24	1	24	24	0	24	905.575615	5	4	2	5	3	2	906.423851
10	2	9	10	3	7	905.182321	24	0	24	24	1	24	905.575615[b]	9	4	5	9	3	7	906.425307
10	3	8	10	4	6	905.193858	16	3	13	16	4	13	905.586729	4	4	1	4	3	1	906.427485
7	3	5	7	4	3	905.222152	2	2	1	3	1	3	905.590203	10	4	6	10	3	8	906.434892
1	1	0	2	2	0	905.223318	23	1	23	23	0	23	905.597012	2	2	0	1	1	0	906.442299
6	3	4	6	4	2	905.224570	23	0	23	23	1	23	905.597012[b]	10	3	7	10	2	9	906.447477
6	3	3	6	4	3	905.230907	22	1	22	22	0	22	905.617485	11	4	7	11	3	9	906.453624
7	3	4	7	4	4	905.237644	22	0	22	22	1	22	905.617485[b]	14	5	10	14	4	10	906.463296
8	3	5	8	4	5	905.250243	11	2	9	11	3	9	905.625278	12	4	8	12	3	10	906.485006
9	2	8	9	3	6	905.254445	21	1	21	21	0	21	905.636982[b]	3	1	2	2	0	2	906.487541
3	1	2	4	0	4	905.255174	21	0	21	21	1	21	905.636982[b]	13	5	9	13	4	9	906.501714
7	1	7	7	2	5	905.283927	5	1	4	5	2	4	905.651315	5	1	4	4	2	2	906.523934
8	2	7	8	3	5	905.307939	20	1	20	20	0	20	905.656093[b]	12	5	8	12	4	8	906.530577
32	1	32	32	0	32	905.371172	20	0	20	20	1	20	905.656093[b]	5	2	3	4	1	3	906.958306
32	0	32	32	1	32	905.371172[b]	12	2	10	12	3	10	905.661868	4	3	1	3	2	1	906.969581
6	1	6	6	2	4	905.372650	19	1	19	19	0	19	905.673514[b]	20	8	13	20	7	13	907.004197
18	4	14	18	5	14	905.377909	19	0	19	19	1	19	905.673514[b]	8	1	7	7	2	5	907.033744
4	2	3	4	3	1	905.394361	6	1	5	6	2	5	905.677359	6	1	5	5	0	5	907.117514
31	1	31	31	0	31	905.399961	9	3	7	9	2	7	906.053248	9	2	7	8	3	5	907.127754
31	0	31	31	1	31	905.399961[b]	15	4	12	15	3	12	906.071835	6	2	4	5	1	4	907.138919
3	2	1	3	3	1	905.405097	9	3	7	9	2	7	906.099415	5	3	2	4	2	2	907.141373
2	1	1	3	0	3	905.407347	8	3	6	8	2	6	906.141839	9	1	8	8	2	6	907.172807
4	2	2	4	3	2	905.411994	7	3	5	7	2	5	906.178895	13	5	9	12	6	7	907.201918
5	2	3	5	3	3	905.425270														

[a] Experimental uncertainties on the line positions are approximately 0.25 MHz (1σ).

[b] Transition weighted zero in the least-squares fit.

try. The quadrupolar field focuses or defocuses the polar molecules in the molecular beam onto a liquid-He-cooled bolometer detector. The focusing/defocusing properties of a molecule in the quadrupole field depend on the quantum state of the molecule. The quadrupole field increases our sensitivity for polar molecules by approximately an order of magnitude.

Between the nozzle and the skimmer, in the region where the multipass mirror assembly is located, a *K*-band waveguide and a radio frequency antenna are used for double-resonance experiments to guide the assignment of the spectrum. With the laser fixed on an infrared transition, known ground state mi-

crowave or radio frequency transitions are probed. Once two distinct double resonance signals are observed, the lower state of the infrared transition is unambiguously established.

The Pacific Northwest Laboratory's molecular-beam diode-laser system also has been previously described (*23, 24*). The beam from a lead–salt diode laser is collimated by a parabolic mirror and filtered by a monochromator for single-mode operation. The light then encounters a three-way rotating mirror, which reflects the laser to a 295-MHz fixed étalon, a reference cell, or the vacuum chamber. The étalon and reference cell share a detector and provide signals for relative and absolute
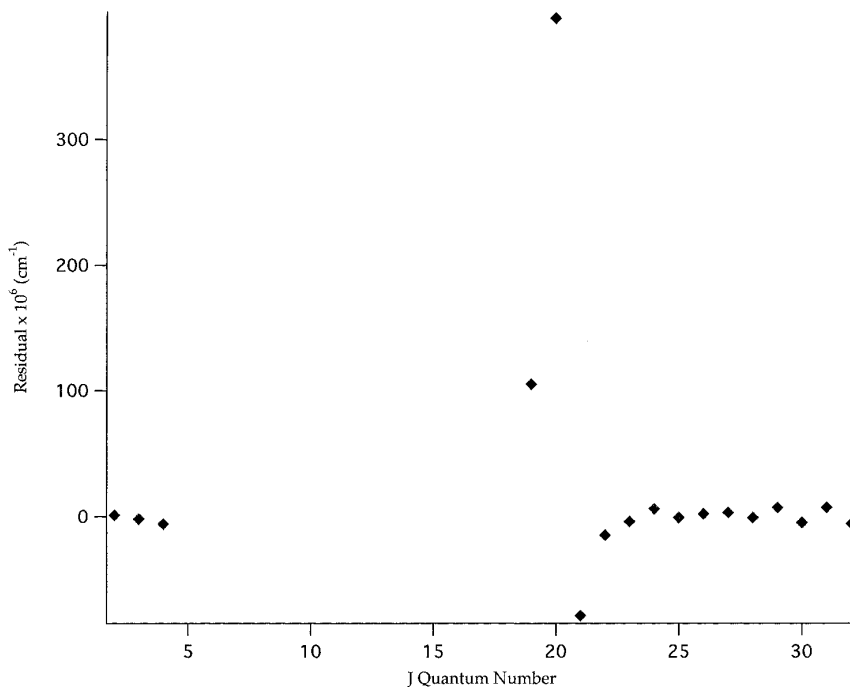
FIG. 3. A plot of the observed–calculated residuals as a function of J for the $K_a = 0$ excited state of *gauche*-1,1,2,2-tetrafluoroethane. The abrupt change of sign at approximately $J = 20$ suggests a resonance.

calibration, respectively. In the chamber, the light multipasses the molecular beam approximately 32 times using a white cell. The molecular beam is formed by expanding 1% by volume 1,1,2,2,-tetrafluoroethane in argon at 100 kPa through a 12 cm × 100 μm pulsed slit nozzle at a repetition rate of 3 Hz.

III. RESULTS AND DISCUSSION

A. Gauche Conformer—Microwave Spectrum

Since the *gauche* conformer contains a C_2 symmetry axis coincident with the c inertial axis, only c-type rotational transitions are allowed. Twenty-one transitions were measured for the ^{12}C isotopomer and are listed in Table 1. For the lower natural abundance mono-^{13}C isotopomer, only five transitions were observed (see Table 1). Both sets of transitions are fit to within experimental uncertainty to the A-reduced Watson Hamiltonian (*25*) in the I^r representation, giving the spectroscopic constants listed in Table 2. This analysis allows determination of all five quartic centrifugal distortion constants for the primary isotopomer. The current results correct many misassignments in the previous microwave study of *gauche*-HFC134 (*26*). The rotational constants determined in the present study, $A = 5254$ MHz, $B = 2838$ MHz, and $C = 2503$ MHz, can be compared with the *ab initio* values of Papasavva *et al.* (*15*) calculated at the MP2/6-31G** level, $A = 5178$ MHz, $B = 2867$ MHz, and $C = 2512$ MHz.

B. Gauche Conformer—Infrared Spectrum

A section of the $K_a = 4$–3 Q branch of the CO_2 sideband spectrum of the ν_6, C–C stretch fundamental (*14*) at 905.8 cm^{-1} is shown in Fig. 2. The spectrum contains both positive and negative peaks due to the focusing/defocusing effect of the quadrupole field. A total of 119 unique c-type infrared transitions are assigned and listed in Table 3. The observation of a c-type spectrum verifies that the 905.8-cm^{-1} vibration is of A symmetry in the C_2 point group, consistent with the previous results of Kalasinky *et al.* (*14*). The spectroscopic constants determined by a fit of the transitions to the Watson Hamiltonian are listed in Table 2. Here we have only determined the upper state constants by constraining the ground state constants to the precise microwave values determined above.

Three strong transitions, assigned to the $J = 19$, 20, and 21 Q-branch transitions of the $J = K_c$ series, are shifted from their calculated frequencies, with the largest deviation (for $J = 20$) being approximately 12 MHz. Figure 3 shows the observed–calculated residuals of the fit as a function of J for the $K_a = 0$ excited states. The plot suggests a resonance is responsible for the large residuals. Observation of a transition to the dark state for the $J = 20$ level, which would verify the presence of a perturbation, is prevented in the CO_2 laser experiments due to the limited signal-to-noise ratio.

It is interesting to speculate on the possible nature of the perturbing state. Because of the low frequency of the torsional mode of approximately 78 cm^{-1} (*11*), a large number of

TABLE 4
Transition Frequencies in cm^{-1} for the ν_{16} Band of *anti*-1,1,2,2,-Tetrafluoroethane[a]

J	K_a	K_c	J	K_a	K_c	Frequency	J	K_a	K_c	J	K_a	K_c	Frequency	J	K_a	K_c	J	K_a	K_c	Frequency
17	6	11	18	6	12	1123.975867	8	5	3	9	5	4	1125.733480	1	1	1	2	2	1	1126.814056
12	6	7	13	7	7	1123.979619	5	3	2	6	4	2	1125.800186	3	1	3	4	1	4	1126.822340
11	7	5	12	8	5	1123.991699	10	0	10	11	0	11	1125.804910	6	1	5	6	3	4	1126.825446
12	0	12	13	1	12	1124.009357	5	2	4	6	3	4	1125.859078	1	1	0	2	2	0	1126.839733
12	6	6	13	7	6	1124.050740	8	3	6	9	3	7	1125.868590	12	5	7	12	6	7	1126.853700
16	7	9	17	7	10	1124.057086	7	5	2	8	5	3	1125.941160	2	1	1	3	1	2	1126.865170
13	5	8	14	6	8	1124.092542	9	0	9	10	0	10	1125.952290	2	2	0	3	2	1	1126.868610
12	4	9	13	5	9	1124.105815	4	3	1	5	4	1	1125.962951	7	2	6	7	2	5	1126.871088
17	5	12	18	5	13	1124.138402	7	4	4	8	4	5	1125.966520	5	0	5	5	2	4	1126.873471
17	6	12	18	6	13	1124.154436	5	2	3	6	3	3	1125.973995	9	4	5	9	5	5	1126.890320
11	6	6	12	7	6	1124.168181	8	2	7	9	2	8	1125.979300	5	3	2	5	4	2	1126.894587
16	12	4	17	12	5	1124.171684	5	1	4	6	2	4	1125.986982	2	2	1	3	2	2	1126.907780
11	6	5	12	7	5	1124.198970	7	3	5	8	3	6	1126.024850	5	3	3	6	2	5	1126.921132
16	7	10	17	7	11	1124.225560	6	3	3	7	3	4	1126.073310	5	1	5	5	1	4	1126.933480
8	4	4	9	6	3	1124.286388	4	2	3	5	3	3	1126.080076	1	0	1	2	1	1	1126.947847
11	4	8	12	5	8	1124.359978	8	0	8	9	0	9	1126.098790	2	0	2	3	0	3	1126.949760
10	6	4	11	7	4	1124.361664	8	4	4	9	3	6	1126.106464	6	3	3	6	4	3	1126.954708
11	2	9	12	3	9	1124.365774	6	4	2	7	4	3	1126.114755	2	1	2	3	1	3	1126.970320
15	9	6	16	9	7	1124.381113	7	1	6	8	1	7	1126.119844	10	4	6	10	5	6	1127.001659
17	3	14	18	3	15	1124.391301	6	2	4	7	2	5	1126.123063	8	3	6	8	3	5	1127.005190
15	7	9	16	7	10	1124.405644	7	2	6	8	2	7	1126.125792	6	2	5	6	2	4	1127.033420
11	5	6	12	6	6	1124.445669	6	5	2	7	5	3	1126.141547	7	3	4	7	4	4	1127.037315
14	6	8	15	6	9	1124.465874	6	4	3	7	4	4	1126.148172	1	1	0	2	1	1	1127.049380
11	3	8	12	4	8	1124.486093	4	2	2	5	3	2	1126.156811	4	1	4	4	1	3	1127.080030
14	6	9	15	6	10	1124.639340	13	2	11	13	4	10	1126.159693	1	0	1	2	0	2	1127.097340
10	2	8	11	3	8	1124.654478	6	3	4	7	3	5	1126.186210	1	1	1	2	1	2	1127.120820
16	2	14	17	2	15	1124.663860	4	1	3	5	2	3	1126.240008	8	3	5	8	4	5	1127.130643
13	6	7	14	6	8	1124.674950	5	3	2	6	3	3	1126.281122	9	4	6	9	4	5	1127.156658
13	5	8	14	5	9	1124.703610	5	2	3	6	2	4	1126.286662	11	5	7	11	5	6	1127.158325
14	4	10	15	4	11	1124.712280	5	4	1	6	4	2	1126.321986	7	3	5	7	3	4	1127.162298
7	7	1	8	8	1	1124.714840	5	4	2	6	4	3	1126.333887	13	6	8	13	6	7	1127.163268
14	5	10	15	5	11	1124.732540	5	3	3	6	3	4	1126.355660	5	2	4	5	2	3	1127.179944
9	5	4	10	6	4	1124.737625	3	1	3	4	2	3	1126.374475	15	14	2	15	14	1	1127.185331
13	7	6	14	7	7	1124.741630	11	2	9	11	4	8	1126.417536	14	14	0	14	14	1	1127.192534
13	12	2	14	12	3	1124.749811	5	2	4	6	2	5	1126.425170	12	4	8	12	5	8	1127.209736
13	11	2	14	11	3	1124.765159	4	2	2	5	2	3	1126.469200	15	13	2	15	13	3	1127.212393
10	3	7	11	4	7	1124.782527	9	4	6	10	3	8	1126.472134	3	1	3	3	1	2	1127.214686
10	4	6	11	5	6	1124.789660	11	3	9	11	3	8	1126.475763	21	1	21	21	0	21	1127.216358
8	4	5	9	5	5	1125.035466	2	2	0	3	3	0	1126.489116	14	13	2	14	13	1	1127.218839
12	5	8	13	5	9	1125.050864	4	3	1	5	3	2	1126.493570	13	13	0	13	13	1	1127.224987
15	0	15	16	0	16	1125.054120	4	4	0	5	4	1	1126.516871	2	1	1	2	2	1	1127.233741
11	5	6	12	5	7	1125.073856	4	4	1	5	4	2	1126.519927	15	12	4	15	12	3	1127.237280
5	4	2	6	5	2	1125.603058	4	1	3	5	1	4	1126.538133	6	2	4	6	3	4	1127.239307
5	4	1	6	5	1	1125.605635	9	2	7	9	4	6	1126.615650	14	12	2	14	12	3	1127.243788
6	1	6	7	2	6	1125.619071	7	1	7	7	1	6	1126.650008	13	12	2	13	12	1	1127.249784
9	4	6	10	4	7	1125.622248	2	1	1	3	2	1	1126.661607	12	12	0	12	12	1	1127.255902
11	5	6	12	4	8	1125.627072	3	2	1	4	2	2	1126.665020	0	0	0	1	0	1	1127.260370
6	0	6	7	1	6	1125.629321	4	0	4	5	0	5	1126.672800	14	7	8	14	7	7	1127.264792
6	3	3	7	4	3	1125.643280	4	1	4	5	1	5	1126.677350	14	11	4	14	11	3	1127.266617
11	0	11	12	0	12	1125.656690	3	1	2	4	1	3	1126.693220	13	11	2	13	11	3	1127.272787
8	4	4	9	4	5	1125.680520	2	0	2	3	1	2	1126.715288	10	5	6	10	5	5	1127.276102
10	1	9	11	1	10	1125.685040	3	2	2	4	2	3	1126.740280	12	11	2	12	11	1	1127.279086
9	2	7	10	2	8	1125.702710	7	1	6	7	3	5	1126.747937	14	10	4	14	10	5	1127.288288
8	3	5	9	3	6	1125.706990	6	1	6	6	1	5	1126.788279	13	10	4	13	10	3	1127.294036
6	1	5	7	2	5	1125.709137	13	5	9	13	5	8	1126.792879	4	2	3	4	2	2	1127.297353
9	3	7	10	3	8	1125.716230	11	4	8	11	4	7	1126.801995	12	10	2	12	10	3	1127.299733

[a] The experimental uncertainties on the line positions are approximately 7.5 MHz (1σ).

potential perturbing states are expected for the ν_6 normal mode. Ignoring anharmonicity and coupling to the *anti* conformer, 12 vibrational modes are predicted to lie in a 50-cm^{-1} window centered around ν_6. Two of these modes, $\nu_8 + \nu_{18}$ at 903 cm^{-1} and $\nu_{9\ +\ 2\nu_{10}} + \nu_{18}$ at 908 cm^{-1}, are of very low order and are predicted sufficiently close to ν_6 to be judged as viable perturbing states. Both modes are of B symmetry and can couple to ν_6 by weak Coriolis interactions.

C. Anti Conformer—Infrared Spectrum

For the diode-laser spectrum of ν_{16}, the CF$_2$ stretch of the nonpolar, *anti* conformer (*14*), the spectral regions between 1123.8 and 1125.1 cm^{-1}, 1125.6 and 1128.5 cm^{-1}, and 1128.8 and 1131.4 cm^{-1} were studied. The observation of an *a/c* hybrid band established that the vibration is of B_u symmetry. Previous researchers have assigned the CF$_2$ vibration at 1127

TABLE 4—*Continued*

J	K_a	K_c	J	K_a	K_c	Frequency	J	K_a	K_c	J	K_a	K_c	Frequency	J	K_a	K_c	J	K_a	K_c	Frequency
11	10	2	11	10	1	1127.304976	2	1	2	1	1	1	1127.742860	9	3	6	8	3	5	1129.112500
10	10	0	10	10	1	1127.309904	4	3	2	4	2	2	1127.747136	7	2	5	6	1	5	1129.123921
0	0	0	0	0	0	1127.321649	12	5	7	12	5	8	1127.766153	9	4	5	8	4	4	1129.133000
15	1	15	15	0	15	1127.321649	2	0	2	1	0	1	1127.768980	10	8	2	9	8	1	1129.135960
11	9	2	11	9	3	1127.323878	4	1	3	4	1	4	1127.773317	6	3	3	5	1	4	1129.168520
4	1	3	4	2	3	1127.325954	7	4	4	7	3	4	1127.785498	10	6	5	9	6	4	1129.187660
10	9	2	10	9	1	1127.328965	10	4	6	10	4	7	1127.797841	10	6	4	9	6	3	1129.198429
9	9	0	9	9	1	1127.333277	3	3	1	3	2	1	1127.799857	13	0	13	12	0	12	1129.202200
14	1	14	14	0	14	1127.335559	6	2	4	6	2	5	1127.804477	7	2	6	6	1	6	1129.205343
10	8	2	10	8	3	1127.345989	8	3	5	8	3	6	1127.811508	11	2	9	10	2	8	1129.205955
13	1	13	13	0	13	1127.348813	3	2	2	3	0	3	1127.814590	6	5	2	5	4	2	1129.208919
9	8	2	9	8	1	1127.350225	2	1	1	1	1	0	1127.816120	10	3	7	9	3	6	1129.249570
8	8	0	8	8	1	1127.354950	4	2	3	4	0	4	1127.880562	7	4	4	6	3	4	1129.261250
10	7	4	10	7	3	1127.360557	3	1	3	2	1	2	1127.890470	11	10	2	10	10	1	1129.266046
8	7	2	8	7	1	1127.369352	3	0	3	2	0	2	1127.912100	10	5	5	9	5	4	1129.272080
7	7	0	7	7	1	1127.372807	5	4	2	5	3	2	1127.938598	11	9	2	10	9	1	1129.291680
3	2	2	3	2	1	1127.377176	3	2	2	2	2	1	1127.949440	11	4	8	10	4	7	1129.308831
8	5	4	8	5	3	1127.379150	4	1	4	3	1	3	1128.032280	11	8	4	10	8	3	1129.318070
6	6	0	6	6	1	1127.389003	4	0	4	3	0	3	1128.044380	11	7	5	10	7	4	1129.345890
6	1	5	6	2	5	1127.391046	4	2	3	3	2	2	1128.111740	11	7	4	10	7	3	1129.348572
6	5	2	6	5	1	1127.399909	4	3	2	3	3	1	1128.133780	6	6	1	5	5	1	1129.362074
4	3	2	4	3	1	1127.405638	4	1	3	3	1	2	1128.166385	11	5	7	10	5	6	1129.370667
5	4	2	5	4	1	1127.408494	3	2	1	2	1	1	1128.199722	11	6	6	10	6	5	1129.372626
2	2	1	2	2	0	1127.417723	8	4	4	8	3	6	1128.211353	7	5	2	6	4	2	1129.374141
3	3	1	3	3	0	1127.420738	3	2	2	2	1	2	1128.256270	7	5	3	6	4	3	1129.385953
4	1	4	4	0	4	1127.433503	5	2	4	4	2	3	1128.265900	8	2	6	7	1	6	1129.397472
4	3	1	4	3	2	1127.436543	7	6	2	7	5	2	1128.274734	11	6	5	10	6	4	1129.401730
2	2	0	2	2	1	1127.440456	7	6	1	7	5	3	1128.278563	8	3	6	7	2	6	1129.441220
6	2	5	6	1	5	1127.442768	6	1	6	5	1	5	1128.302586	12	4	9	11	4	8	1129.446509
3	1	3	3	0	3	1127.448920	6	0	6	5	0	5	1128.304609	13	2	11	12	2	10	1129.453777
7	4	3	7	4	4	1127.458743	5	4	2	4	4	1	1128.306354	8	4	5	7	3	5	1129.467883
8	3	6	8	2	6	1127.462923	5	3	3	4	3	2	1128.308572	12	9	4	11	9	3	1129.472130
12	6	6	12	6	7	1127.466882	5	3	2	4	3	1	1128.349290	12	3	9	11	3	8	1129.478700
1	1	0	1	1	1	1127.469110	3	3	0	2	2	0	1128.363393	11	5	6	10	5	5	1129.494530
2	1	2	2	0	2	1127.472595	5	2	3	4	2	2	1128.383940	11	4	7	10	4	6	1129.506110
5	3	2	5	3	3	1127.473577	4	2	2	3	1	2	1128.394749	12	5	8	11	5	7	1129.531580
3	2	1	3	2	2	1127.478694	4	1	3	3	0	3	1128.400395	12	7	6	11	7	5	1129.533346
10	4	7	10	3	7	1127.496269	6	2	5	5	2	4	1128.412280	12	7	5	11	7	4	1129.542130
1	1	1	1	0	1	1127.498947	6	1	5	5	1	4	1128.444040	12	6	7	11	6	6	1129.554500
10	5	5	10	5	6	1127.501627	6	5	2	5	5	1	1128.473240	16	0	16	15	0	15	1129.573620
7	3	5	7	2	5	1127.521870	6	3	4	5	3	3	1128.477370	15	1	14	14	1	13	1129.575370
4	2	3	4	1	3	1127.526452	6	4	3	5	4	2	1128.487020	13	3	10	12	3	9	1129.593730
8	4	4	8	4	5	1127.530071	6	4	2	5	4	1	1128.500440	12	6	6	11	6	5	1129.619360
2	1	1	2	1	2	1127.540070	8	6	3	7	6	2	1128.818518	13	10	4	12	10	3	1129.624460
4	2	2	4	2	3	1127.554333	6	3	3	5	2	3	1128.870710	12	4	8	11	4	7	1129.651150
13	6	7	13	6	8	1127.568837	5	4	2	4	3	2	1128.882855	9	2	7	8	1	7	1129.664449
9	4	6	9	3	6	1127.582453	9	6	4	8	6	3	1129.002010	13	5	9	12	5	8	1129.681959
6	3	4	6	2	4	1127.597008	9	5	5	8	5	4	1129.020930	13	8	5	12	8	4	1129.690151
11	5	6	11	5	7	1127.611837	6	4	2	5	3	2	1129.030067	17	0	17	16	0	16	1129.695400
2	2	1	2	1	1	1127.627585	9	5	4	8	5	3	1129.055040	16	1	15	15	1	14	1129.698160
7	3	4	7	3	5	1127.664991	10	3	8	9	3	7	1129.067540	15	2	13	14	2	12	1129.701170
5	2	3	5	2	4	1127.666068	11	1	10	10	1	9	1129.074580	14	4	11	13	4	10	1129.705023
5	3	3	5	2	3	1127.676458	12	0	12	11	0	11	1129.076730	14	3	11	13	3	10	1129.711680
8	4	5	8	3	5	1127.683670	10	2	8	9	2	7	1129.084690	13	7	7	12	7	6	1129.720620
1	1	0	0	0	0	1127.709239								13	6	8	12	6	7	1129.730220
14	6	8	14	6	9	1127.719807								13	7	6	12	7	5	1129.744750

cm^{-1} to either a B_u (*11, 16*) or a A_u (*13*) symmetry mode. Our results verify that the former is correct. The relative intensities of the *a*-type to *c*-type lines suggest that the *c* dipole-moment component is approximately 40% of the value of the *a* dipole-moment component.

Five hundred twenty-two nonblended transitions (see Table 4) were assigned and included in a fit to the Watson asymmetric-rotor Hamiltonian. The assigned transitions provide 398 ground state combination differences, which were fit to give ground state rotational constants for this conformer. These ground state constants were then used with the infrared transitions to fit the excited state constants. Table 5 summarizes the results, and Fig. 4 compares the experimental and calculated spectra. The ground state constants of 5145, 3148, and 2067 MHz can be compared with the MP2/6-31G** *ab initio* values of 5026, 3179, and 2062 MHz.

TABLE 4—*Continued*

J	K_a	K_c	J	K_a	K_c	Frequency	J	K_a	K_c	J	K_a	K_c	Frequency	J	K_a	K_c	J	K_a	K_c	Frequency
9	5	5	8	4	5	1129.755791	16	5	11	15	5	10	1130.278810	12	6	6	11	4	7	1130.821896
10	4	6	9	3	6	1129.758533	22	0	22	21	0	21	1130.290520	11	10	1	10	9	1	1130.825764
13	4	9	12	4	8	1129.770380	20	2	18	19	2	17	1130.306810	18	7	11	17	7	10	1130.827546
14	11	4	13	11	3	1129.774460	17	11	6	16	11	5	1130.320173	20	7	14	19	7	13	1130.830011
14	10	4	13	10	3	1129.805700	18	5	14	17	5	13	1130.326279	14	4	10	13	3	10	1130.836353
18	0	18	17	0	17	1129.815990	9	9	1	8	8	1	1130.334228	12	5	7	11	3	8	1130.840985
17	1	16	16	1	15	1129.819890	10	4	6	9	2	7	1130.354866	19	9	10	18	9	9	1130.861785
14	5	10	13	5	9	1129.822090	17	10	8	16	10	7	1130.360996	13	8	5	12	7	5	1130.864812
16	2	14	15	2	13	1129.823870	17	10	7	16	10	6	1130.362463	14	5	10	13	4	10	1130.867393
7	4	4	6	2	5	1129.826935	11	7	4	10	6	4	1130.371667	20	6	14	19	6	13	1130.870168
15	4	12	14	4	11	1129.829520	17	5	12	16	5	11	1130.377346	13	8	6	12	7	6	1130.872517
15	3	12	14	3	11	1129.832402	12	3	9	11	2	9	1130.385784	15	6	9	14	5	9	1130.883133
14	9	6	13	9	5	1129.839690	12	5	8	11	4	8	1130.391337	20	11	9	19	11	8	1130.886510
13	6	7	12	6	6	1129.847300	12	4	9	11	3	9	1130.403386	14	3	11	13	2	11	1130.896462
8	7	1	7	6	1	1129.862302	23	0	23	22	0	22	1130.406492	14	4	11	13	3	11	1130.899373
14	4	10	13	4	9	1129.876801	22	1	21	21	1	20	1130.415624	24	3	21	23	3	20	1130.901700
9	6	4	8	5	4	1129.885484	17	7	11	16	7	10	1130.416688	9	7	2	8	5	3	1130.904851
13	5	8	12	5	7	1129.893670	17	9	8	16	9	7	1130.421066	23	4	19	22	4	18	1130.915934
14	6	9	13	6	8	1129.896530	16	7	9	15	7	8	1130.424801	14	7	8	13	6	8	1130.920344
10	4	7	9	3	7	1129.918263	12	3	10	11	2	10	1130.431972	20	8	13	19	8	12	1130.929937
15	12	4	14	12	3	1129.922123	20	3	17	19	3	16	1130.434251	14	1	13	13	0	13	1130.950101
10	2	8	9	1	8	1129.924502	12	6	7	11	5	7	1130.438767	20	9	12	19	9	11	1130.962588
10	3	8	9	2	8	1129.933155	16	6	10	15	6	9	1130.442689	20	10	10	19	10	9	1130.964451
19	0	19	18	0	18	1129.935870	19	5	15	18	5	14	1130.445830	11	11	0	10	10	0	1130.969998
18	1	17	17	1	16	1129.940850	18	12	6	17	12	5	1130.463485	19	7	12	18	7	11	1130.975787
17	2	15	16	2	14	1129.945950	18	5	13	17	5	12	1130.481469	12	10	3	11	9	3	1130.998386
16	3	13	15	3	12	1129.953599	10	9	1	9	8	1	1130.507201	19	8	11	18	8	10	1131.000070
15	5	11	14	5	10	1129.954790	22	2	20	21	2	19	1130.541238	13	6	7	12	4	8	1131.028908
14	7	7	13	7	6	1129.961250	21	3	18	20	3	17	1130.551849	24	4	20	23	4	19	1131.031183
15	4	11	14	4	10	1129.983490	19	6	14	18	6	13	1130.579904	10	7	3	9	5	4	1131.040328
15	10	6	14	10	5	1129.988710	19	5	14	18	5	13	1130.590852	11	6	6	10	4	7	1131.042657
9	4	5	8	2	6	1129.995759	18	8	11	17	8	10	1130.612320	14	8	7	13	7	7	1131.043866
11	4	7	10	3	7	1130.009706	9	6	4	8	4	5	1130.620025	21	11	11	20	11	10	1131.074839
8	8	1	7	7	1	1130.012304	13	5	9	12	4	9	1130.625895	22	6	16	21	6	15	1131.078956
10	6	4	9	5	5	1130.032413	18	9	9	17	9	8	1130.633570	21	11	10	20	11	9	1131.084730
14	5	9	13	5	8	1130.049715	24	1	23	23	1	22	1130.647765	20	7	13	19	7	12	1131.087544
15	6	10	14	6	9	1130.051074	10	10	1	9	9	1	1130.653336	15	6	10	14	5	10	1131.088948
20	0	20	19	0	19	1130.055197	23	2	21	22	2	20	1130.658572	11	3	8	10	1	9	1131.093264
19	1	18	18	1	17	1130.060853	14	6	8	13	5	8	1130.661427	20	9	11	19	9	10	1131.104335
10	6	5	9	5	5	1130.063103	22	3	19	21	3	18	1130.669888	15	5	11	14	4	11	1131.113073
14	6	8	13	6	7	1130.070920	13	7	6	12	6	6	1130.674854	15	7	9	14	6	9	1131.117407
16	5	12	15	5	11	1130.081573	11	9	3	10	8	3	1130.679732	16	7	9	15	6	9	1131.119419
15	7	9	14	7	8	1130.085535	18	6	12	17	6	11	1130.682973	21	10	12	20	10	11	1131.123437
16	4	12	15	4	11	1130.094992	11	6	5	10	4	6	1130.688154	21	9	13	20	9	12	1131.132597
16	12	4	15	12	3	1130.101239	12	8	4	11	7	4	1130.699311	15	3	12	14	2	12	1131.145747
11	3	8	10	2	8	1130.120102	19	7	13	18	7	12	1130.701545	15	2	13	14	1	13	1131.174218
11	4	8	10	3	8	1130.158235	14	5	9	13	4	9	1130.714230	23	7	17	22	7	16	1131.185841
11	5	7	10	4	7	1130.166652	13	7	7	12	6	7	1130.733398	15	1	14	14	0	14	1131.195515
20	1	19	19	1	18	1130.180064	19	10	10	18	10	9	1130.741982	22	8	15	21	8	14	1131.200910
11	3	9	10	2	9	1130.182465	19	10	9	18	10	8	1130.754758	20	8	12	19	8	11	1131.203302
9	8	1	8	7	1	1130.186017	25	1	24	24	1	23	1130.762184	15	8	8	14	7	8	1131.217927
19	2	17	18	2	16	1130.186955	18	8	10	17	8	9	1130.769213	12	7	5	11	5	6	1131.230292
15	7	8	14	7	7	1130.191643	24	2	22	23	2	21	1130.774106	13	5	8	12	3	9	1131.239840
10	7	4	9	6	4	1130.208208	19	6	13	18	6	12	1130.775701	11	7	5	10	5	6	1131.254123
17	4	13	16	4	12	1130.210758	19	8	12	18	8	11	1130.777043	22	7	15	21	7	14	1131.263443
16	9	8	15	9	7	1130.214905	19	9	11	18	9	10	1130.782059	22	11	12	21	11	1	1131.267816
16	9	7	15	9	6	1130.220835	10	4	7	9	2	8	1130.784101	12	12	1	11	11	1	1131.283800
11	6	6	10	5	6	1130.246106	23	3	20	22	3	19	1130.786050	22	9	14	21	9	13	1131.290543
16	8	9	15	8	8	1130.252732	22	4	18	21	4	17	1130.799615	12	6	7	11	4	8	1131.298045
16	7	10	15	7	9	1130.256705	14	7	7	13	6	7	1130.810832	22	10	13	21	10	12	1131.307734
10	5	5	9	3	6	1130.258544	21	6	16	20	6	15	1130.816318	13	11	3	12	10	3	1131.313659
9	3	6	8	1	7	1130.268968	21	5	16	20	5	15	1130.818312	21	9	12	20	9	11	1131.346842
15	6	9	14	6	8	1130.272730														

No perturbations are apparent in the spectrum, in contrast to previous studies on fluorinated ethanes. No evidence is seen, for instance, for *a/c*-type Coriolis coupling of the B_u symmetry, ν_{16} normal mode to the A_u symmetry, ν_8 normal mode observed at 1136 cm^{-1}. Several reasons might explain why this molecule differs from its homologues. Many of the

TABLE 5

Spectroscopic Constants for the Ground and ν_{16} Excited States of *anti*-1,1,2,2-Tetrafluoroethane

Constant	Ground State	Excited State
A/MHz	5134.952(65)[a]	5098.333(11)
B/MHz	3148.277(27)	3144.546(8)
C/MHz	2067.106(43)	2052.772 (9)
Δ_J/kHz	—	-0.148(15)
ν_0/cm^{-1}	—	1127.43457(2)
σ^b/MHz	10.6	7.2

[a] Experimental uncertainties are one standard deviation (1σ).

[b] Standard deviation of the least-squares fit.

studies (*3, 4, 6–9*) were performed at 3 μm, as opposed to 9–10 μm in the present experiment. At 10 μm, the density of vibrational states is less, reducing the chance that an accidental resonance will cause a perturbation. For example, for the *gauche* conformer the harmonic vibrational densities of states for 100-cm^{-1} windows centered at 1000 and 3000 cm^{-1} are 0.37 states/cm^{-1} and 49 states/cm^{-1}, respectively, while for the *anti* conformer the state densities are 0.42 states/cm^{-1} and 51 states/cm^{-1}, respectively. In the case of the *anti* conformer, the experimental resolution could also be a factor. The previous experiment which was performed at 10 μm and still found a perturbation (*5*) used a CO$_2$ laser/microwave-sideband system, which has a resolution of approximately 2 MHz, as opposed to a diode laser with a resolution of approximately 60 MHz. In 1,1,2-trifluoroethane, e.g., transitions are split into doublets, and the largest splitting is 37 MHz, which would not be resolved by the diode laser.

D. Structure

The limited number of isotopic forms of 1,1,2,2-tetrafluoroethane studied prevents a detailed structural analysis. Brown and Beagley (*12*) previously derived a structure from an electron-diffraction study of an 84% *anti* and 16% *gauche* mixture of 1,1,2,2-tetrafluoroethane, as determined from their analysis. Their results are summarized in column 4 of Table 6. Following Brown and Beagley, the four CF bond lengths are constrained to be the same, as are the two CH bond lengths, the two $\angle$HCC angles, the four $\angle$FCC angles, the two $\angle$FCF angles, and the four $\angle$FCH angles. The various angles are further constrained so that the FCCH dihedral angles, measured from the H-atom eclipsed configuration are $\pm120°$. We further constrain the CF and CH bond lengths and the $\angle$HCC angles to the electron-diffraction values. For the *gauche* conformer, the fitted parameters are the CC bond length, the $\angle$FCC bond angle, and the torsional angle, $\tau = \angle$HCCH. For the *anti* conformer, τ is constrained to 180° and the $\angle$FCC bond angle is constrained to the *gauche* value. The results from the fits are given in Table 6. Costain (*27*) uncertainties are given, as

derived from the relation $\Delta q_j = 0.0015/|q_j|$. The present CC bond lengths can be compared with the *ab initio* values (*15*) of 1.513 Å for the *anti* form and 1.515 Å for the *gauche* form.

IV. CONCLUSIONS

The two conformers of 1,1,2,2-tetrafluoroethane (HFC134) have been studied. For the polar *gauche* conformer, improved ground state rotational constants were obtained from the microwave spectrum. The infrared spectrum of the ν_6 vibrational state reveals a weak perturbation affecting the $K_a = 0$ state for $J \sim 20$. For the nonpolar *anti* conformer, the ν_{16} vibration was probed with a diode laser, allowing the first experimental determination of the ground state rotational constants for this system. No perturbations were observed in the infrared spectrum of this conformer, in contrast to results seen in other fluorinated ethanes. Future experiments to address the nature of the perturber of ν_6 would be particularly valuable. If the perturbing state has a significant degree of torsional excitation, such a study would furnish valuable information on the internal rotation potential. This information is important for understanding the dynamics of this molecule at higher levels of excitation where conformational rearrangement can take place,

TABLE 6

Structural Parameters for *gauche* and *anti*-1,1,2,2-Tetrafluoroethane

Parameter	*gauche*	*anti*	Electron diffraction
r_{CC}/Å	1.512(4)[a]	1.505(5)	1.518(5)
r_{CH}/Å	1.097[b]	1.097[b]	1.097(6)
r_{CF}/Å	1.350[b]	1.350[b]	1.350(2)
$\angle$HCC	110.3°[b]	110.3°[b]	110.3(10)°
$\angle$FCC	109.7(3)°	109.7 °[d]	108.2(3)°
τ^c	66.8(5)°	180°[e]	78(2)°[e,f]
Reference	present	present	12

[a] Constain uncertainties are given (see text).
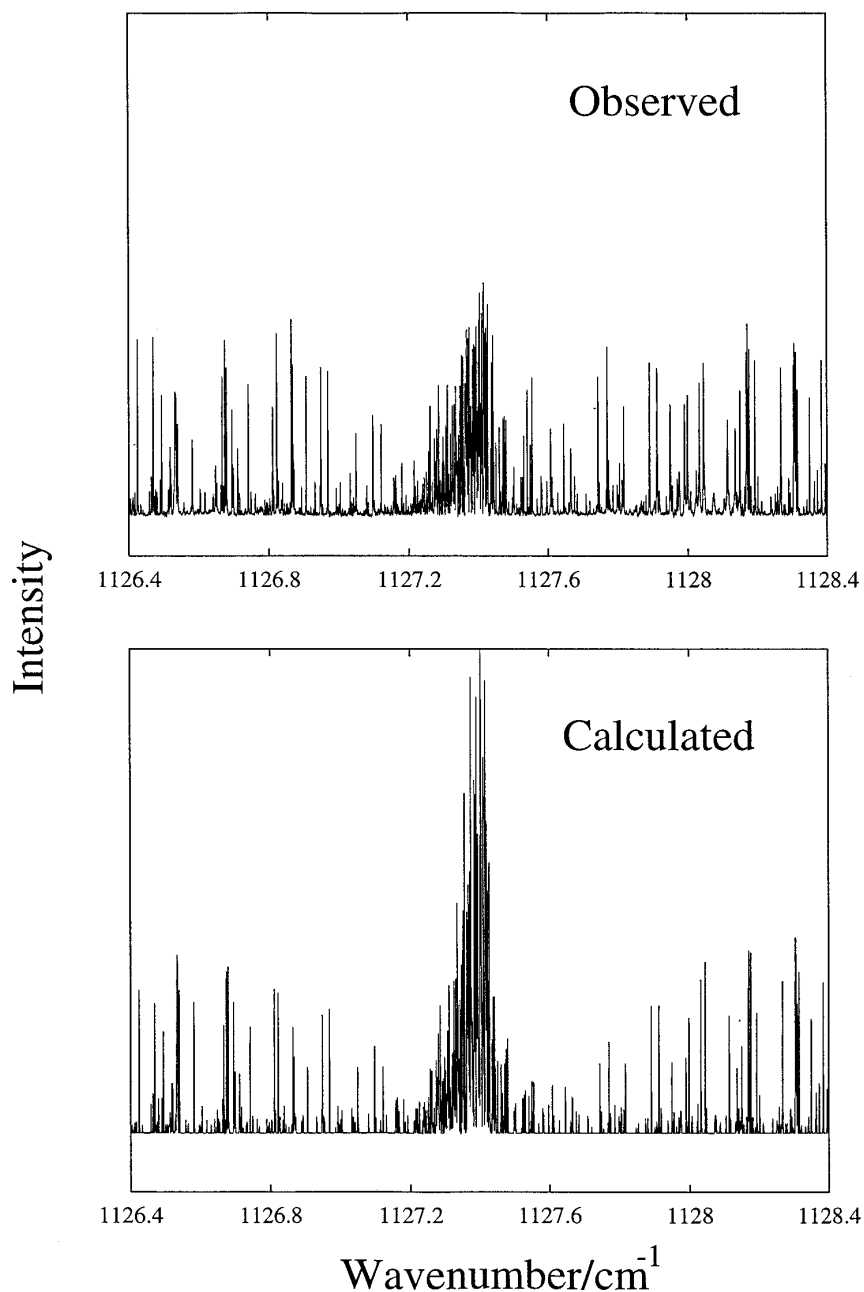
[b] Values fixed at the electron-diffraction results.

[c] $\tau = 0$ corresponds to the hydrogens being eclipsed.

[d] Contrained to the value determined for the *gauche* conformer.

[e] A value of 180° was assumed for *anti* conformer.

[f] Value of τ for the *gauche* conformer.

FIG. 4. A comparison of the experimental and calculated spectra for the ν_{16}, CF$_2$ stretch of *anti*-1,1,2,2-tetrafluoroethane.

since the vibrational density of states is dominated by torsional combination vibrations in this region.

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