THE JOURNAL OF CHEMICAL PHYSICS **123**, 054317 (2005)

Determination of structural parameters for ferrocenecarboxaldehyde using Fourier transform microwave spectroscopy

Ranga Subramanian, Chandana Karunatilaka, Riley O. Schock, Brian J. Drouin,[a]
Paul A. Cassak,[b] and Stephen G. Kukolich[c]
Department of Chemistry, University of Arizona, Tucson, Arizona 85721

(Received 23 March 2005; accepted 13 June 2005; published online 9 August 2005)

Gas-phase structural parameters for ferrocenecarboxaldehyde have been determined using Fourier transform microwave spectroscopy. Rotational transitions due to *a*-, *b*-, and *c*-type dipole moments were measured. Eighteen rotational constants were determined by fitting the measured transitions of various isotopomers using a rigid rotor Hamiltonian with centrifugal distortion constants. Least-squares fit and Kraitchman analyses have been used to determine the gas-phase structural parameters and the atomic coordinates of the molecule using the rotational constants for various isotopomers. Structural parameters determined from the least-squares fit are the Fe–C bond lengths to the cyclopentadienyl rings, $r(\text{Fe–C})=2.047(4)$ Å, and the distance between the carbon atoms of the cyclopentadienyl rings, $r(\text{C–C})=1.430(2)$ Å and $r(\text{C}_1\text{–C}_{1'})=1.46(1)$ Å of ring carbon and aldehyde carbon atom. Structural parameters were also obtained using density-functional theory calculations, and these were quite helpful in resolving ambiguities in the structural fit analysis, and providing some fixed parameters for the structural analysis. The results of the least squares and the calculations indicate that the carbon atoms of the Cp groups for ferrocenecarboxaldehyde are in an eclipsed conformation in the ground vibrational state. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1993593]

I. INTRODUCTION

Ferrocene-based systems have played an important role in the development of organometallic chemistry and continue to find new applications in the fields of biological, inorganic, and physical chemistry. Ferrocenecarboxaldehyde (FcCHO) has been used as a redox sensor to monitor substrate binding,[1] for incorporation in large proteins to act as redox relays[2] and as a DNA probe for study of DNA damage,[3] illustrating the versatile nature of the ferrocene systems. Widespread use of substituted ferrocenes has sustained the interest in the study of different properties of various ferrocene systems since the time of the initial characterization by Wilkinson,[4] and Wilkinson *et al.*[5]

FcCHO is a particularly interesting ferrocene derivative, as it exists in two phases, a plastic crystalline phase (phase I) between temperatures of 44 and 123.5 °C and a low-temperature amorphous phase (phase II). These two phases have been studied using x-ray diffraction[6,7] and the dynamics of molecular reorientations in phases I and II were investigated by incoherent neutron-scattering techniques.[8] FcCHO has also been studied using ^{57}Fe-NMR,[9] ^{13}C-NMR,[10] Mössbauer spectroscopy,[7,11] He(I) photoelectron spectroscopy,[12] and electrochemical studies in solution.[12] These studies provide us with a better understanding of the electronic properties of the molecule. There have been various studies that correlated the effects of substituents to the redox behavior of the ferrocene moiety by changing the energy level of the highest occupied molecular orbital (HOMO). In the case of FcCHO, the electron-withdrawing group (such as –CHO group) lowers the energy level of the HOMO, making it easier to reduce.[13] To have a better understanding of structural, chemical, and electronic properties, we believe that it is important to have accurate and detailed structural data. The x-ray diffraction studies provide structural parameters; however, the crystal-packing effects present in the solid phase distort the "true structure" of the molecule. Since these effects are absent in the gas phase, the structural determination of this molecule using Fourier transform gas-phase microwave spectroscopy was undertaken. We have previously been successful in determining the structures of various substituted ferrocene compounds.[14–18] More recently, we have correlated the effect of substituents with a structural parameter, namely, the distance between the Fe atom and center of the cyclopentadienyl (Cp) ring.[18]

The structure of FcCHO with the labeling scheme for the carbon atoms is shown in Fig. 1. From measurements using the "normal" distribution of isotopomers for FcCHO molecule, the spectra for ^{56}Fe, ^{54}Fe, ^{57}Fe, and four unique ^{13}C isotopomers were recorded. For the deuterium-enriched sample (ferrocene–^{2}H–carboxaldehyde, FcCDO), which was synthesized, only the ^{56}Fe isotopomer with the ^{2}H substitution at the H_{ald} position (see Fig. 1) was measured. All spectra were measured in the 4–12 GHz frequency range. Rotational constants were determined by least-squares fitting of the assigned transitions. From these rotational constants, structural parameters of the molecule were obtained using a

---

[a] Present address: California Institute Of Technology, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109.

[b] Present address: Department of Physics, University of Maryland, College Park, MD 20742.

[c] Author to whom correspondence should be addressed. Electronic mail: kukolich@u.arizona.edu

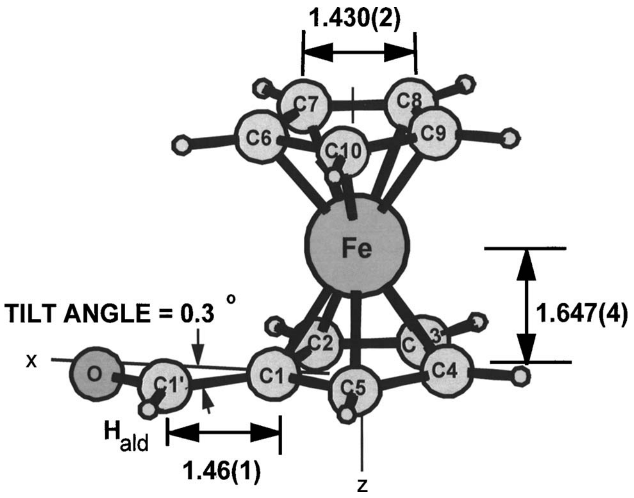

FIG. 1. Structure of the ferrocenecarboxaldehyde FcCHO with the atoms of the molecule labeled. The values of the parameters that were determined from the fits are indicated. The units for the distances are Å and the units of the angle are degrees. The aldehyde (–CHO) group is tilted by only 0.3(1)° out of the cyclopentadienyl plane, in the direction away from the Fe atom.

structural least-squares analysis and also from Kraitchman analyses. Comparisons of the theoretical and x-ray data with the gas-phase microwave data provide a more complete understanding of the structure of FcCHO.

II. EXPERIMENT

The FcCHO was purchased from Aldrich (catalog number: 122459) and used as received. The preparation of the ferrocene–^{2}H–carboxaldehyde was based on a modification of the synthesis of FcCHO.[19] 2.0 g of ferrocene and a stir bar were placed in a two-neck round-bottom flask. The round-bottom flask was placed in −20 °C ice-methanol slush and a stream of nitrogen gas passed through it. With the nitrogen gas continuously flowing, 30 ml of dry tetrahydrofuran (THF) was added and the mixture was stirred for 15 min. The red crystals of ferrocene dissolved to give a deep orange solution. To this solution, 9.2 ml of 1.7*M* *t*-butyl lithium (^{t}BuLi) in pentane was added over a 15-min period. The solution was then stirred for 40 min and the temperature was warmed to −10 °C. In the dry box a solution of 1-ml dry THF and 1.7 ml of N, N-dimethylformamide-1–^{2}H was made, removed from the dry box, and added to the solution containing ferrocene and ^{t}BuLi. The mixture was left to react for 40 min, and no color change was observed. The ice-methanol slush was removed and 0.25 ml of 1*M* HCl was added, resulting in the formation of the deep red precipitate. The solvent was removed at 55 °C with a slow decrease in pressure from 1 atm to 0.5 torr. After being brought back to atmospheric pressure by adding nitrogen, a cold-water finger was inserted and the solid was sublimed at 0.5 torr and 75 °C. The dark red crystals were removed from the cold finger in the dry box and were used with no further purification. This synthesis yields FcCDO, with deuterium substitution at the aldehyde hydrogen site, H_{ald} (see Fig. 1).

The pulsed-jet Fourier transform microwave spectrometer used for the current experiment is described elsewhere in detail.[20] Both compounds, FcCHO and FcCDO, were heated to 80 °C to obtain sufficient vapor pressure, and the pressure of the neon carrier gas was maintained at 0.5 atm. This mixture was pulsed into the Fabry-Perot cavity at a constant pulse rate of 2 Hz. A low-noise liquid-nitrogen-cooled amplifier was placed in the rigid coax line attached to the antenna in the cavity to increase the sensitivity by improving the signal-to-noise ratio. Typical improvements in S/N were a factor of 2, with some variation with frequency, since the amplifier was not attached to the mirror nor directly connected to the antenna. Since the factor-of-2 improvement in S/N reduces averaging time by a factor of 4 to achieve equivalent sensitivity, this facilitated measuring transitions of the different isotopomers in natural abundance. Ninety-three transitions were recorded for the ^{56}Fe isotopomer and 15 transitions were observed for ^{54}Fe (6% natural abundance), six transitions were observed for ^{57}Fe (2% natural abundance) and five each for the two ^{13}C isotopomers (1% natural abundance). In the case of FcCDO, 24 transitions were recorded for ^{56}Fe. These measured transitions for the various isotopomers are listed in Tables I–III.

III. THEORETICAL METHODS

Density functional theory (DFT) calculations were used to optimize the geometry of FcCHO. Becke's three-parameter hybrid exchange potentials (B3) with the Perdew-Wang (PW91)[21–23] correlation functional have been known to produce accurate values for structural parameters for the first-row transition metals. In the present work, we have used two basis sets for the iron atom, namely, the Hay and Wadt $(n+1)$ basis set with effective core potential[24] and the Stuttgart relativistic, small-core effective core potential (ECP) basis set (Stuttgart RSC1997 ECP).[25,26] In each case, we used split-valence plus polarization SVP[27,28] basis sets for the carbon, hydrogen, and oxygen atoms.

The combination of the B3PW91 method with the Hay and Wadt $(n+1)$ basis sets with the effective core potential for iron and the SVP basis sets for the carbon, hydrogen, and oxygen atoms gave structural parameters close to the experimental parameters. However, this method and basis set combination did not characterize the "tilt angle" and the deviation of H_{ald} from the plane of the Cp ring, which was observed in the FcCHO molecule. The tilt angle is defined to be the angle that the substituent (in our case, the bond C_1–$C_{1'}$) makes with the plane of the substituted Cp ring. The deviation of the H_{ald} from the plane of the Cp ring along the z axis is represented as $\Delta z(H_{ald})$. To more accurately characterize the tilt angle and $\Delta z(H_{ald})$, the combination of *r*B3PW91 method with Stuttgart RSC1997 ECP for Fe atom and the SVP basis sets for the carbon, hydrogen, and oxygen atoms were used.

The success of the B3PW91 calculations to produce near-experimental quality results is consistent with the usage of the "best" exchange-correlation potentials for these molecules.[29] An energy optimization starting from an initial staggered conformation of the molecule, using any of the above basis sets, resulted in rotation to the eclipsed conformer. This indicates that the eclipsed conformer is the lower-energy conformation.

TABLE I. Observed transitions for FcCHO (^{56}Fe) with fit residuals. The observed frequencies are given in MHz. The average error in the observed values is 0.0005 MHz for all the transitions. The listed observed frequencies are an average of four to six measurements taken at different stimulating frequencies.

J	K_a	K_c	J'	K'_a	K'_c	Observed frequencies	O–C (kHz)
4	1	4	3	1	3	5530.9236	0
4	0	4	3	0	3	5632.2061	0
4	1	4	3	0	3	5752.4220	0
3	2	2	2	1	1	5847.4059	0
4	2	3	3	2	2	5870.0252	0
4	3	2	3	3	1	5949.0948	0
4	3	1	3	3	0	5974.1313	0
3	2	1	2	1	1	6000.5630	0
4	1	3	3	1	2	6127.4693	1
4	2	2	3	2	1	6132.7385	0
3	2	2	2	1	2	6313.6044	2
3	2	1	2	1	2	6466.7604	1
5	1	4	4	2	3	6613.3339	0
5	0	5	4	1	4	6817.9444	−1
5	1	5	4	1	4	6876.4005	−1
5	0	5	4	0	4	6938.1616	0
5	1	5	4	0	4	6996.6167	−1
4	2	3	3	1	2	7085.5298	−1
3	3	1	2	2	0	7172.6270	−2
3	3	0	2	2	0	7174.1945	−1
3	3	1	2	2	1	7204.9092	−2
3	3	0	2	2	1	7209.2116	−1
4	1	3	3	0	3	7277.0527	−1
5	2	4	4	2	3	7297.7690	0
5	4	2	4	4	1	7440.7335	−2
5	3	3	4	3	2	7442.7455	−2
5	4	1	4	4	0	7444.4522	1
4	2	2	3	1	2	7501.4024	1
5	3	2	4	3	1	7524.6701	−1
5	1	4	4	1	3	7571.3947	−1
5	2	3	4	2	2	7725.1143	−1
4	2	3	3	1	3	8013.6190	1
6	0	6	5	1	5	8183.7942	2
6	1	6	5	1	5	8210.1967	1
6	0	6	5	0	5	8242.2543	5
5	2	4	4	1	3	8255.8321	1
6	1	5	5	2	4	8265.4302	1
6	1	6	5	0	5	8268.6520	0
7	1	6	6	2	4	8405.3807	−1
4	2	2	3	1	3	8429.4875	−1
4	3	2	3	2	1	8579.2856	−3
4	3	1	3	2	1	8608.6308	4
3	3	0	2	1	1	8635.0564	−2
4	2	2	3	0	3	8650.9869	1
7	2	5	6	3	3	8688.5989	0
6	2	5	5	2	4	8701.9979	2
4	3	2	3	2	2	8732.4449	0
4	3	1	3	2	2	8761.7849	1
6	5	2	5	5	1	8925.2805	3
6	5	1	5	5	0	8925.7363	−4
6	3	4	5	3	3	8927.6012	0
6	4	3	5	4	2	8947.9450	0
6	1	5	5	1	4	8949.8635	−1
6	4	2	5	4	1	8964.0758	−2
7	2	5	6	3	4	8992.0689	−2
3	3	1	2	1	2	9096.9539	0
5	2	3	4	1	3	9099.0473	−1
6	3	3	5	3	2	9119.8115	1

TABLE I. (*Continued.*)

J	K_a	K_c	J'	K'_a	K'_c	Observed frequencies	O–C (kHz)
5	1	4	4	0	4	9216.2464	3
6	2	4	5	2	3	9286.6486	−1
6	2	5	5	1	4	9386.4318	1
3	3	1	2	0	2	9449.1218	2
7	0	7	6	1	6	9525.1421	1
7	1	7	6	1	6	9536.4898	0
7	0	7	6	0	6	9551.5436	−1
7	1	7	6	0	6	9562.8934	0
4	4	1	3	3	0	9768.8864	−2
4	4	0	3	3	0	9769.3626	1
4	4	1	3	3	1	9773.1896	0
4	4	0	3	3	1	9773.6654	2
5	2	4	4	1	4	9780.4617	−1
7	1	6	6	2	5	9833.4977	1
5	3	3	4	2	2	9889.2983	1
4	3	1	3	1	2	9977.2894	−1
5	3	2	4	2	2	10 000.5574	−3
7	2	6	6	2	5	10 082.4885	0
7	1	6	6	1	5	10270.064	1
5	3	3	4	2	3	10 305.1697	2
7	3	5	6	3	4	10395.747	0
5	3	2	4	2	3	10 416.4304	0
7	5	3	6	5	2	10 432.9767	1
7	5	2	6	5	1	10 435.4656	1
7	4	4	6	4	3	10 459.0807	−5
7	4	3	6	4	2	10 509.6208	5
7	2	6	6	1	5	10 519.0545	0
5	2	3	4	1	4	10 623.6773	−2
7	3	4	6	3	3	10747.393	1
7	2	5	6	2	4	10 797.2045	−1
6	2	4	5	1	4	10 814.3033	2
8	0	8	7	1	7	10 853.8665	−7
8	1	8	7	1	7	10 858.5824	−1
8	0	8	7	0	7	10 865.2253	3
8	1	8	7	0	7	10 869.9337	2

All the theoretical calculations were performed on a HP/Compaq Alpha supercomputer (AURA) using GAUSSIAN 03 programs[30] at the University of Arizona.

IV. DATA ANALYSIS

The observed transitions for the various isotopomers were fitted using a weighted least-square fitting program, SPFIT,[31] which employs a standard rigid rotor Hamiltonian with centrifugal distortion constants. Due to a uniform underestimation of the measurement uncertainties during the fit procedure, a program, PIFORM,[32] was used, for convenience, to correct the fitted parameter uncertainties to obtain values of the various constants with conventional standard errors. For FcCHO, with the normal isotopes ($^{12}C_{11}, ^{1}H_{10}, ^{16}O_{1}, ^{56}Fe$), transitions were fitted using eight adjustable parameters: the three rotational constants (A, B, and C), and five distortion constants (Δ_J, Δ_K, Δ_{JK}, δ_J, and δ_k). The observed transitions for isotopomers of the molecule ($^{54}Fe, ^{57}Fe, ^{13}C_1, ^{13}C_{1'}$) were fitted using the rotational constants as adjustable parameters, while holding the distortion constants Δ_J, Δ_K, Δ_{JK}, δ_J, and δ_k fixed to the values obtained from the normal isotopomer fit. For the synthesized compound, FcCDO, the transitions were fitted using five adjustable parameters: the three rotational constants (A, B, and C) along with two distortion constants (Δ_J and Δ_K). The values obtained for these parameters are given in Table IV.

For an accurate determination of the rotational constants for different low-abundance isotopomers, four transitions were measured and fitted. A prediction resulting from this least-squares fit was used to find and measure the fifth transition, which was then added to the least-squares fit. This procedure helped to verify that the initial assignments were correct. Even though the molecule has three dipole moment components, a, b, and c, transitions due to the b and c dipole moments are weaker. Hence, only the strong a-type dipole transitions were observed for the low-abundance isotopomers.

V. STRUCTURE DETERMINATION

A. Least-squares fit

The least-squares structural fits were accomplished by adjusting the structural parameters to obtain the best fit to the

TABLE II. Observed transitions for FcCDO (^{56}Fe^{2}H) with fit residuals. The observed frequencies are given in MHz. The numbers within the parentheses are the errors in the observed values obtained by averaging four to six subsequent spectra.

J	K_a	K_c	J'	K'_a	K'_c	Observed frequencies	O–C (kHz)
4	0	4	3	0	3	5574.1185(3)	−4
4	2	2	3	2	1	6051.5508(3)	9
4	1	3	3	1	2	6052.1776(5)	11
5	1	5	4	1	4	6805.3642(4)	4
5	0	5	4	0	4	6868.2139(6)	−5
5	2	4	4	2	3	7213.6725(9)	−8
5	3	3	4	3	2	7351.5415(3)	4
5	3	2	4	3	1	7427.4602(3)	5
5	1	4	4	1	3	7482.4944(5)	2
5	2	3	4	2	2	7623.4049(6)	6
6	1	6	5	1	5	8126.477(3)	−6
6	0	6	5	0	5	8159.6646(5)	−4
6	2	5	5	2	4	8603.9092(4)	−8
6	5	2	5	5	1	8815.2571(6)	7
6	5	1	5	5	0	8815.6572(8)	1
6	3	4	5	3	3	8819.0781(6)	−7
6	4	3	5	4	2	8836.9596(7)	−6
6	1	5	5	1	4	8850.5052(4)	−2
6	4	2	5	4	1	8851.5059(4)	−3
6	3	3	5	3	2	8998.3549(8)	−8
6	2	4	5	2	3	9167.2119(9)	−3
7	1	7	6	1	6	9440.1607(5)	9
7	0	7	6	0	6	9456.0000(5)	7
7	1	6	6	1	5	10 161.3214(9)	3

18 rotational constants from the various isotopomers. For the least-squares fit, a coordinate system is defined with the origin at the Fe atom, and such that the z axis passes through the center of the two Cp rings. The x axis is perpendicular to the z axis, passes through the Fe atom, and lies parallel to a line joining the center of the Cp ring and C_1 carbon atom (see Fig. 1). The y axis is perpendicular to the x and z axes. It is also assumed that the two Cp rings have C_5 symmetry and the planes of these Cp rings are parallel. The assumptions that deviations from C_5 symmetry for the Cp rings and the angle between the Cp planes (C_5H_4CHO and C_5H_5) are small enough to be neglected are supported by the DFT calculations. A detailed study was done for the case of chloroferrocene,[15] where the effects of isotopic substitution

TABLE III. Observed transitions for FcCHO ^{54}Fe, ^{57}Fe, $^{13}C_1$, and $^{13}C_{1'}$ isotopomers with fit residuals. The observed frequencies are given in MHz. The numbers within the parentheses are the errors in the observed values.

						^{54}Fe		^{57}Fe		$^{13}C_{1'}$		$^{13}C_1$	
J	K_a	K_c	J'	K'_a	K'_c	Observed frequencies	O–C (kHz)	Observed frequencies	O–C (kHz)	Observed frequencies	O–C (kHz)	Observed frequencies	O–C (kHz)
4	1	4	3	1	3	5533.7223(7)	1	5529.5404(6)	0				
4	0	4	3	0	3	5634.9570(6)	0	5630.8512(7)	6	5583.3349(5)	6		
4	1	3	3	1	2	6130.5451(6)	3	6125.9539(5)	6	6066.9440(9)	−1	6104.1582(4)	−4
5	1	5	4	1	4	6879.8672(4)	−2	6874.6869(6)	−3			6852.4554(6)	−2
5	0	5	4	0	4	6941.5635(4)	0	6936.4805(7)	1	6878.4947(6)	−4	6915.1812(15)	2
3	3	1	2	2	0	7174.1945(2)	−1						
3	3	0	2	2	0	7178.5062(2)	0						
3	3	1	2	2	1	7206.5183(1)	0						
3	3	0	2	2	1	7210.8291(1)	1						
4	1	3	3	0	3	7280.3853(2)	−2						
5	3	3	4	3	2	7446.5959(3)	0						
5	4	1	4	4	0	7448.3291(3)	−1						
5	1	4	4	1	3	7575.1122(4)	1	7569.5521(4)	−6	7500.1742(10)	0	7544.0983(6)	1
5	2	3	4	2	2					7642.0903(9)	1	7692.8711(3)	1
4	2	2	3	1	3	8432.7883(3)	0						
4	3	2	3	2	1	8581.5281(1)	0						

TABLE IV. The spectral parameters obtained for the different isotopomers of FcCHO (^{56}Fe; ^{54}Fe; ^{57}Fe; $^{13}C_{1'}$, $^{13}C_1$) and FcCDO ($^{56}Fe^2H$) determined using least-square fits. The error limits on all the values are 1σ.

Parameter	^{56}Fe	^{54}Fe	^{57}Fe	$^{13}C_{1'}$	$^{13}C_1$	$^{56}Fe^2H$
A(MHz)	1289.908 85(2)	1290.1502(5)	1289.79(2)	1286.97(2)	1289.48(1)	1277.713(6)
B(MHz)	814.627 05(1)	815.0455(3)	814.419(1)	805.8324(6)	811.2310(6)	803.4413(6)
C(MHz)	659.227 67(1)	659.5647(3)	659.0611(6)	653.4004(9)	656.9553(6)	652.8231(7)
Δ_J(Hz)	101.4(1)	[101.4][a]	[101.4][a]	[101.4][a]	[101.4(1)][a]	86(8)
Δ_K(Hz)	−292.4(5)	[−292.4][a]	[−292.4][a]	[−292.4][a]	[−292.4(5)][a]	⋯
Δ_{JK}(Hz)	364(1)	[364][a]	[364][a]	[364][a]	[364][a]	−32(2)
δ_J(Hz)	32.82(5)	[32.82][a]	[32.82][a]	[32.82][a]	[32.82][a]	⋯
δ_k(Hz)	−65(1)	[−65][a]	[−65][a]	[−65][a]	[−65][a]	⋯
σ(fit)(kHz)	1.8	1.2	4.4	3.5	2.1	6.2
Number of lines	93	15	6	5	5	24

[a] Held fixed during the fit.

were carefully studied in order to measure deviations from planarity and deviations from C_5 symmetry (for C atoms) for the C_5H_4Cl ligand. Even though some small distortions were detected, the resulting values for these distortions were barely larger than the uncertainties. That experimental study along with the present DFT calculations supports the above assumptions used in the present analysis.

Many different structural fits were done to decide which structural parameters could be unambiguously determined. The DFT calculations were also used as a guide to reasonable initial structures. From the analysis of the fit results, a particular set of five structural parameters was found to be the best determinable set. These five parameters are (1) the distance from the Fe atom to the center of either the Cp ring r(Fe–Cp), (2) the ring radius of both the Cp rings r(Cp) [which can be used to directly calculate r(C–C), the carbon-carbon bond distances for the Cp rings], (3) the angle that the C_1–$C_{1'}$ makes with the Cp ring (the tilt angle) a(Cp–CHO), (4) the C_1–$C_{1'}$ bond length $r(C_1–C_{1'})$, and (5) z displacement of the H_{ald} with respect to the plane of the Cp ring, $\Delta z(H_{ald})$. The best-fit values obtained are (1) r(Fe–Cp) $=1.647(4)$, (2) $r(Cp)=1.2164(2)$, (3) tilt angle a(Cp–CHO) $=0.3(2)°$, (4) $r(C_1–C_{1'})=1.46(1)$ Å, and (5) $\Delta z(H_{ald})$ $=0.29(4)$ Å. The values of the parameters are shown in Fig. 1, which also shows the structure of the complex. As indicated above, the tilt angle was found to be very small [only 0.3(1)°] and moves $C_{1'}$ away from the Fe atom. The distances from the Fe atom to the centers of the two Cp rings were assumed to be the same. This was verified by a test fit, where the distances were independently varied and the resulting values for the two r(Fe-Cp) distances came out to be the same, within the uncertainties. The initial starting structure for the least-squares fit was based on the results from the DFT calculations. Since deuterium substitutions were not made on the Cp ring, the C–H bond distances of the Cp ring were all fixed at 1.088 Å and the radial symmetry of the C–H bonds was maintained during the fit. Both $C_{1'}$–H_{ald} and $C_{1'}$–O distances were manually adjusted by small increments in the fits. We also found that the CHO moiety with respect to the Cp plane is quite nonplanar in our best-fit results. Relative to the C_1–$C_{1'}$ bond, the $C_{1'}$HO group is "bent" up (toward Fe) by nearly 30°. This result can readily be seen in the last lines of Table V. Fits were also done with the C–CHO moiety constrained to be planar, but the standard deviations of the fit were larger ($\sigma=0.14$ MHz versus 0.07 MHz) and a much larger (unreasonable) value was obtained for $r(C_1–C_{1'})$ (1.6 Å).

The structural fit obtained as described above yielded a standard deviation of 0.07 MHz. This is considered to be a very good fit since the rotational constants are over 1000 MHz. The coordinates (in angstroms) obtained from the least-squares fit for the principal axis system of the molecule (a,b,c) and in the Cartesian coordinate system derived from the unsubstituted ferrocene principal axes (x,y,z) are shown in Table V. The parameters derived from this least-square-fit structure are summarized in Table VII. As stated, the bond distances $r(C_{1'}–H_{ald})$ and $r(C_{1'}$–O) were manually adjusted and fixed at the values of 1.116 and 1.243 Å, respectively. These values are very close to values obtained from the DFT calculations. Several test fits were run where the aldehyde (–CHO) group was rotated with respect to the plane of the Cp ring and the standard deviation was found to be greater than 0.7 MHz. The resulting value of a(Cp–CHO) indicates that the C_1–$C_{1'}$ deviates out of the plane of the Cp ring, in a direction away from the Fe atom only by 0.3(1)°, so it is almost in the plane of the Cp ring. The H_{ald} atom is moved upwards, towards the Fe atom by 0.29(4) Å. From the structural fit, it was also found that C_1 and C_6 are eclipsed (see Fig. 1) and any attempt to fit a structure starting from a staggered conformation did not converge.

B. Kraitchman analysis

Since we have not measured all of the ^{13}C and deuterium-substituted isotopomers, a complete substitution structure could not be obtained. Nevertheless, the Kraitchman analysis was very helpful in the structural analysis because the Kraitchman-derived coordinates are not subjected to the same "correlation errors" that the least-squares-fit parameters are. The present substitution structural coordinates (see Table VI) obtained are close to the least-squares-fit values and provide support for the accuracy of the least-squares-fit parameters. The various structural parameters derived from the Kraitchman analysis are given in Table VII.

Since the Kraitchman analysis uses the changes in the moments of inertia due to the monosubstitution of different

TABLE V. The coordinates (in Å) for FcCHO obtained from a least-squares fit, given in the principal axis system (a,b,c) and in the Cartesian system (x,y,z) as explained in the least-square-fitting section of the text. The estimated uncertainties are 0.01 Å.

Atom	a	b	c	x	y	z
Fe	−0.424	−0.197	0.009	0.000	0.000	0.000
C1	1.612	−0.331	−0.166	1.216	0.000	1.647
C2	1.188	−0.807	1.114	0.376	1.157	1.647
C3	0.286	−1.896	0.904	−0.984	0.715	1.647
C4	0.152	−2.093	−0.505	−0.984	−0.715	1.647
C5	−0.971	1.126	−1.167	0.376	−1.157	1.647
C6	−0.919	1.776	−0.220	1.216	0.000	−1.647
C7	−1.343	1.300	1.060	0.376	1.157	−1.647
C8	−2.245	0.211	0.851	−0.984	0.715	−1.647
C9	−2.379	0.014	−0.559	−0.984	−0.715	−1.647
C10	−1.560	0.981	−1.221	0.376	−1.157	−1.647
H2	1.498	−0.410	2.079	0.712	2.192	1.647
H3	−0.212	−2.473	1.681	−1.864	1.355	1.647
H4	−0.466	−2.847	−0.990	−1.864	−1.355	1.647
H5	1.087	−1.014	−2.243	0.712	−2.192	1.647
H6	−0.230	2.599	−0.400	2.305	0.000	−1.647
H7	−1.033	1.697	2.025	0.712	2.192	−1.647
H8	−2.742	−0.366	1.627	−1.864	1.355	−1.647
H9	−2.997	−0.740	−1.044	−1.864	−1.355	−1.647
H10	−1.444	1.093	−2.297	0.712	−2.192	−1.647
$C_{1'}$	2.539	0.764	−0.458	2.679	−0.050	1.654
H_{ald}	2.502	1.161	−1.500	3.130	−1.026	1.355
O	2.853	1.602	0.404	3.369	0.945	1.374

atoms in the molecule and that the moments of inertia are related to the square of the coordinates of the substituted atoms, one can obtain only the absolute values of these coordinates. The absolute values of these coordinates determined in the principal axis system of the parent molecule are given in Table VI.

The Fe parameters derived from the Kraitchman analysis (see Table VII) are obtained by using ^{54}Fe a_s, b_s, and c_s coordinates with the most abundant ^{56}Fe isotopomer as the "parent" molecule. A larger number of transitions was measured for the ^{54}Fe isotopomer than for the ^{57}Fe isotopomer, so this is the more appropriate parent molecule.

VI. DISCUSSION

Gas-phase structural parameters for FcCHO have been determined from microwave spectroscopic measurements. Using the least-squares fit, with some parameters fixed, we find that the bond distances between the Fe atom and the C atoms of the two Cp rings are 2.047(4) Å, and that the C–C bond distances of the Cp rings are 1.430(2) Å. The uncertainties given in the parentheses are larger than the statistical error contributions to the fit, because C_5 symmetry was assumed and these parameters are correlated with other parameters, which are not fitted directly.

TABLE VI. The r_s coordinates (in Å) obtained from Kraitchman analyses in the principal axis system of the parent molecule, FcCHO ($^{12}C_{11}{}^{1}H_{10}{}^{16}O^{56}Fe$).

Atom	$\lvert a_s \rvert$	$\lvert b_s \rvert$	$\lvert c_s \rvert$
^{54}Fe	0.398	0.191	0.007
^{57}Fe	0.397	0.190	0.017
H_{ald}	2.475	1.150	1.577
$^{13}C_1$	1.600	0.307	0.196
$^{13}C_{1'}$	2.519	0.702	0.649

TABLE VII. Structural parameters obtained for the FcCHO molecule. The approximate r_o structure is obtained from the least-squares fitting. The r_s structure is obtained using Kraitchman analysis. The r_{dft} structure is the output of the theoretical calculation (rB3PW91/Stuttgart RSC 1997 ECP) and, since vibrational corrections were not included, is a r_e structure. The $r_{x\text{-ray}}$ structure is obtained from the x-ray studies (Ref. 6). The listed error limits on the parameters are 1σ.

Bond length	r_s(Å)	r_o(Å)	$r_{x\text{-ray}}$(Å)	r_{dft}(Å)
r(C–C)	⋯	1.430(2)	1.40	1.429
r(Fe–Cp)	⋯	1.647(4)	1.65	1.648
$r(Fe–C_1)$	1.99(9)	2.047(4)	2.03	2.037
$r(C_1–C_{1'})$	1.44(1)	1.46(1)	1.48	1.468
$r(C_{1'}–H_{ald})$	1.03(4)	1.116[a]	1.07	1.122
$r(C_{1'}–O)$	⋯	1.243[a]	1.05	1.210
Bond angle	$\angle_s$(°)	$\angle_o$(°)	$\angle_{x\text{-ray}}$(°)	$\angle_{dft}$(°)
Cp ring C–C–C	⋯	108[a]	109.5	108
$C_1–C_{1'}–H_{ald}$ interbond angle	⋯	116[a]	111	114
$C_1–C_{1'}–O$ interbond angle	⋯	122[a]	136	125
$C_5–C_1–C_{1'}–H_{ald}$ dihedral angle	⋯	18[a]	1	−6
$C_2–C_1–C_{1'}–O$ dihedral angle	⋯	−16[a]	7	0
$–C_{1'}H_{ald}O$ tilt angle	⋯	0.3(2)[b]	4.3[c]	2.8[c]

[a] Held fixed during the structural fit. See text for further details.

[b] Away from the Fe atom.

[c] Towards the Fe atom.

We note that the agreement of the structural parameters for Kraitchman analysis, DFT calculations, and least-squares fit are well within the experimental error limits. The value obtained for C_1–$C_{1'}$ bond distance from Kraitchman is slightly lower than the DFT and structural fit values, whereas x-ray diffraction[6] studies overestimate this bond length. The difference between the Kraitchman and least-squares-fit values may be an indication of correlation effects in the fit, and in this case we would favor the Kraitchman-derived value.

The experimental and DFT-calculated structures obtained for the FcCHO molecule show that the Cp rings are in an eclipsed conformation. However, in the case of ferrocene, the Cp rings are staggered in the crystal[33] and eclipsed in the gas phase.[34] Attempts to perform a least-squares fit using a staggered conformation as a starting point did not converge, and this is consistent with the prediction from the theoretical calculations that the staggered conformation has a much higher energy when compared to the eclipsed conformer. A single-point energy calculation predicts the difference in energy between eclipsed and staggered conformer to be 4 kJ/mol, with the eclipsed conformer being more stable. This calculation was done using the *r*B3PW91 method and using the Stuttgart RSC1997 ECP for iron and the SVP basis set for the carbon, oxygen, and hydrogen atoms.

The tilt angle is defined to be the angle that the substituent (in our case, the bond C_1–$C_{1'}$) makes with the carbon plane of the substituted Cp ring. From previous studies in this lab, this angle has been consistently shown to have a nonzero value, in the direction away from the Fe atom. In the case of chloroferrocene,[15] the value of the tilt angle is 2.7(6)°, for dimethylferrocene,[16] the value of this angle is 2.66(2)°, and for ethynylferrocene,[18] the value of this angle is 2.75(6)°. According to the present best-fit results for FcCHO, we found that the tilt angle determined from the least-squares fit is 0.3(2)°, in the direction away the Fe atom. This indicates that the substituent (in this case $C_{1'}$) almost lies in the plane of the substituted Cp ring. However, the *ab initio* calculation using the method B3PW91 and basis set Stuttgart RSC 1997 ECP described in Sec. III predicts the tilt angle to be 2.8° in the direction towards the Fe atom and the x-ray diffraction[6] study indicates the tilt angle is 4° in the direction towards the Fe atom (see Table VII). Nevertheless, according to our previous results for chloroferrocene [a substituted ferrocene with a strongly electron-withdrawing group, tilt angle=2.7(6)° away from Fe atom], we believe that the tilt away from the Fe atom is a reasonable result. We also found that the H_{ald} atom of the aldehyde group (–CHO) is displaced towards the Fe atom by 0.29(4) Å.

The linear correlation between the distance between the Fe atom and the center of the Cp, *r*(Fe–Cp), and the Hammett parameter $\Sigma\sigma_I$ was presented in an earlier paper by our group.[18] We ascribe this linear correlation to the electron-withdrawing effects of the substituent group relative to the H atom, which alters the electron density of the Cp ring. There is a decrease in electron density of the Cp ring as the electronegativity of the substituent group increases. This affects the binding of the Fe-π-Cp ligand and is observed as an increase in the binding energy[35] and ionization energy of the complex, and structurally as the variation of the distance from the Fe atom to the center of the Cp ring. Using the result for *r*(Fe–Cp) from our earlier paper,[18] $r(\text{Fe–Cp}) = 1.6585 - 0.0821\Sigma\sigma_I$, and substituting the value for $\Sigma\sigma_I = 0.35$ for the –CHO group,[11] one determines the *r*(Fe-Cp) distance to be 1.630 Å. This value falls within 1% of the experimental gas-phase microwave value of 1.647(2) Å and adds further support for the validity of this correlation analysis. This study also confirms that our previous correlations of structural trends with substituent properties are reasonably quantitative and fit experimental results within the experimental uncertainties.

In conclusion, the near-complete gas-phase structure of FcCHO has been obtained using microwave spectroscopy. The present work also indicates that this compound exists in the gas phase as an eclipsed conformer, with a small tilt of the aldehyde group away from the Fe atom of only 0.3(2)° and H_{ald} is displaced towards the Fe atom by 0.29(4) Å. The present work also supports the previously obtained coherent picture of the effect of substituent effects on the structure of ferrocene.

ACKNOWLEDGMENTS

This material is based on the work supported by the National Science Foundation under Grant No. CHE-0304969. This support from the National Science Foundation is gratefully acknowledged. One of the authors (P.A.C.) gratefully acknowledges support from a NASA Arizona Space Grant internship during the course of this project. We thank Oliver Indris, Jennifer Dannemiller, and Kirsten Fields for help in obtaining data on the normal isotopomer.

[1] P. D. Beer, D. B. Crowe, M. I. Odgen, M. G. B. Drew, and B. Main, J. Chem. Soc. Dalton Trans. **14**, 2107 (1993).
[2] A. Heller, Acc. Chem. Res. **23**, 128 (1990).
[3] C. Xu, H. Cai, P. He, and Y. Fang, Fresenius' J. Anal. Chem. **367**, 593 (2000).
[4] G. Wilkinson, J. Organomet. Chem. **100**, 273 (1975).
[5] G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, J. Am. Chem. Soc. **74**, 5764 (1952).
[6] M. F. Daniel, A. J. Leadbetter, and M. A. Mazid, J. Chem. Soc., Faraday Trans. 2 **77**, 1837 (1981).
[7] M. F. Daniel, A. J. Leadbetter, R. E. Meads, and W. G. Parker, J. Chem. Soc., Faraday Trans. 2 **74**, 456 (1978).
[8] M. F. Daniel, A. J. Leadbetter, and R. M. Richardson, J. Chem. Soc., Faraday Trans. 2 **77**, 1851 (1981).
[9] B. Wrackmeyer, O. L. Tok, A. Ayazi, H. E. Maizel, and M. Herberhold, Magn. Reson. Chem. **42**, 827 (2004).
[10] B. Wrackmeyer, O. L. Tok, and A. A. Koridze, Magn. Reson. Chem. **42**, 750 (2004).
[11] R. M. G. Roberts and J. Silver, J. Organomet. Chem. **263**, 235 (1984).
[12] T. Matsumura-Inoue, K. Kuroda, Y. Umezawa, and Y. Achiba, J. Chem. Soc., Faraday Trans. 2 **85**, 857 (1989).
[13] J. C. Green, Struct. Bonding (Berlin) **43**, 37 (1981).
[14] B. J. Drouin, T. G. Lavaty, P. A. Cassak, and S. G. Kukolich, J. Chem. Phys. **107**, 6541 (1997).
[15] B. J. Drouin, J. J. Dannemiller, and S. G. Kukolich, J. Chem. Phys. **112**, 747 (2000).
[16] D. S. Margolis, C. Tanjaroon, and S. G. Kukolich, J. Chem. Phys. **117**, 3741 (2002).
[17] C. Tanjaroon, K. S. Keck, and S. G. Kukolich, J. Am. Chem. Soc. **126**, 844 (2004).
[18] R. Subramanian, C. Karunatilaka, K. S. Keck, and S. G. Kukolich, Inorg. Chem. **44**, 3137 (2005).
[19] U. T. Mueller-Westerhoff, Z. Yang, and G. Ingram, J. Organomet. Chem. **463**, 163 (1993).
[20] R. E. Bumgarner and S. G. Kukolich, J. Chem. Phys. **86**, 1083 (1987).

[21] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[22] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[23] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1987).

[24] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 299 (1985).

[25] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, and H. Preuss, Mol. Phys. **80**, 1431 (1993).

[26] M. Dolg, H. Stoll, H. Preuss, and R. M. Pitzer, J. Phys. Chem. **97**, 5852 (1993).

[27] A. Schaefer, H. Horn, and R. Ahlrichs, J. Chem. Phys. **97**, 2571 (1992).

[28] A. Schaefer, C. Huber, and R. Ahlrichs, J. Chem. Phys. **100**, 5829 (1994).

[29] M. Swart and J. G. Snijders, Theor. Chem. Acc. **110**, 34 (2003).

[30] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, REV. B.05, Gaussian, Inc., Pittsburgh, PA, 2003.

[31] H. M. Pickett, J. Mol. Spectrosc. **148**, 371 (1991).

[32] This program is authored by Dr. Zbigniew Kisiel and can be obtained along with the instructions for using the program from the website http://info.ifpan.edu.pl/~kisiel/prospe.htm

[33] W. L. Baun, Anal. Chem. **31**, 1308 (1959).

[34] A. Haaland and J. E. Nilsson, Acta Chem. Scand. (1947-1973) **22**, 2653 (1968).

[35] P. G. Gassman, D. W. Macomber, and J. W. Hershberger, Organometallics **2**, 1470 (1983).