

Iron Pentacarbonyl: Are the Axial or the Equatorial Iron–Carbon Bonds Longer in the Gaseous Molecule?

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Received October 10, 2000

The structure of iron pentacarbonyl, Fe(CO)₅, was reinvestigated by gas-phase electron diffraction using an experimental rotational constant available from the literature as a constraint on the structural parameters. The study utilized a B3LYP/6-311+G(d) ab initio quadratic force field, scaled to fit observed infrared wavenumbers, from which were calculated corrections for the effects of vibrational averaging on distances and certain other quantities useful for the structural analysis. The results confirm that the equatorial Fe–C bonds are longer than the axial ones, an important difference with the structure in the crystal where the equatorial Fe–C bonds are the shorter. Some distance ($r_g/\text{Å}$) and vibrational amplitude ($l_\alpha/\text{Å}$) parameter values with estimated 2σ uncertainties based on assumption of D_{3h} symmetry are $\langle r(\text{Fe–C}) \rangle = 1.829(2)$, $r(\text{Fe–C})_{\text{eq}} - r(\text{Fe–C})_{\text{ax}} = 0.032(20)$, $\langle r(\text{C=O}) \rangle = 1.146(2)$, $r(\text{C=O})_{\text{eq}} - r(\text{C=O})_{\text{ax}} = 0.006(27)$, $r(\text{Fe–C})_{\text{ax}} = 1.810(16)$, $r(\text{Fe–C})_{\text{eq}} = 1.842(11)$, $r(\text{C=O})_{\text{ax}} = 1.142(23)$, $r(\text{C=O})_{\text{eq}} = 1.149(16)$, $l(\text{Fe–C})_{\text{ax}} = l(\text{Fe–C})_{\text{eq}} = 0.047(5)$, and $l(\text{C=O})_{\text{ax}} = l(\text{C=O})_{\text{eq}} = 0.036(3)$.

Introduction

The molecular structure of iron pentacarbonyl, Fe(CO)₅, hereafter IPC, has been thoroughly studied by experimental and theoretical methods that span more than three decades. Among the former are several gas-phase electron-diffraction investigations,^{1–4} an X-ray diffraction study of the crystal,⁵ IR and Raman studies,^{6,7} and an FTIR study of the rovibrational spectrum.⁸ The theoretical (ab initio) work includes calculations at the HF,^{9,10} DFT,^{10–14} MP,¹⁰ and CI¹¹ levels with various bases. Results from both the experimental and theoretical side agree that the molecule has a trigonal bipyramidal structure (D_{3h} symmetry), but there is considerable uncertainty about the relative lengths of the axial and equatorial Fe–C bonds. It was concluded from the electron-diffraction (GED) studies that the axial Fe–C bond is the shorter by a small amount [0.049 ± 0.020 Å,¹ 0.027 ($\sigma = 0.005$) Å,² 0.000 – 0.050 Å,³ and $0.020 \pm$

0.006 Å⁴]. In the crystal, however, the axial Fe–C bond is found to be longer by 0.007 – 0.010 Å.⁵ The theoretical results are also divided on this matter: most of those from higher level calculations predict a slightly longer axial bond, but the difference is usually only a few thousandths of an angstrom.

Some 25 years ago—before the most recent of the GED studies⁴—two of us (A.G.R. and K.H.) also undertook a GED study of IPC at this university. As in the other studies, a good fit to our diffraction data was easily obtained with the axial Fe–C bonds slightly shorter than the equatorial ones, but with some creative variation of the corrections for vibrational averaging (“shrinkage”¹⁵) and the relative lengths of the two types of C=O bonds, a fit of similar quality could also be obtained with axial Fe–C bonds longer than the equatorial. This work was never published, but it was concluded that the question of the relative Fe–C bond lengths could probably not be reliably answered from GED data alone. After the GED work mentioned above, the two cited reports^{7,8} of high-resolution IR work on freely expanding jets of IPC have yielded a value for B_0 . This quantity together with our GED data gave hope for a definitive answer to the question, and accordingly we decided to attack the problem again. This article is an account of our results.

Experimental Section

Although our old data were thought to be satisfactory for this reinvestigation, there have been many improvements in the Oregon State University GED experiment and data analysis procedures. We thus decided to prepare new diffraction photographs, which would be handled by our current procedures, and also to reanalyze the older photographs with the new procedures. An important consequence of this approach was a check on the scale of the molecule. The accuracy of the scale, or size, of the molecule depends on the accuracy of the wavelength and camera-distance measurements, which have been much improved since the old data were gathered. Obviously, an accurate molecular size is vitally important if rotational constants are to be used as auxiliary data in the GED analysis of the structure.

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Table 1. Experimental Conditions for Electron-Diffraction Experiments

	old data ^a			new data ^a	
	LC	MC	SC	LC	MC
camera dist/mm	750.0	300.1	120.6	746.8	299.7
electron wavelength/Å	0.058	0.058	0.058	0.050	0.050
exposure time/s	45–105	60–165	240–360	75–105	120–150
beam current/μA	0.39–0.40	0.36–0.41	0.45–0.47	0.54–0.56	0.53–0.55
bulk sample temp/K	273	273	287	264	271
no. of plates/films used	5	5	3	3	2
data range, $s/\text{Å}^{-1}$	1.0–14.0	7.5–33.75	22.75–60.0	2.0–16.25	7.5–38.5
data interval, $\Delta s/\text{Å}^{-1}$	0.25	0.25	0.25	0.25	0.25

^a Definitions: LC, long camera; MC, middle camera; SC, short camera.

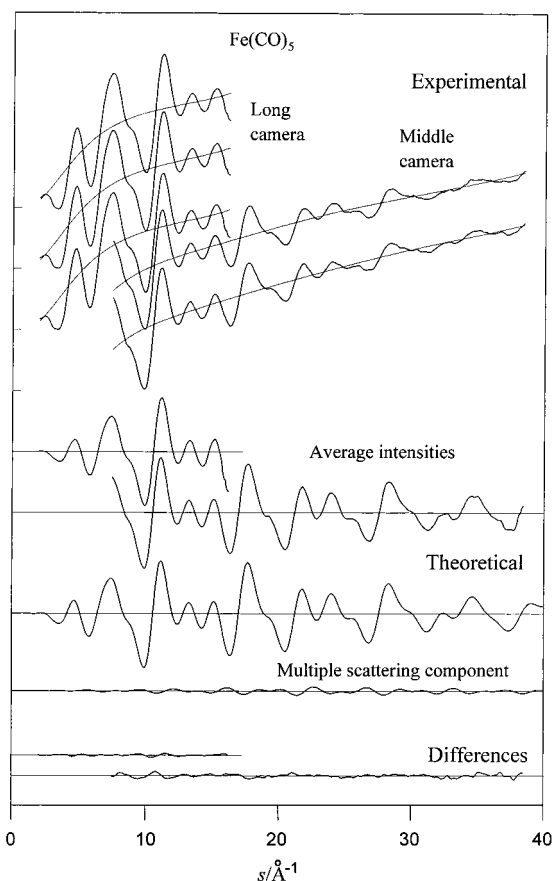


Figure 1. Intensity curves. Long and middle camera curves are magnified five times relative to their backgrounds on which they are superimposed. Average curves are in the form $sI_m(s)$. The theoretical curve is calculated from model A of Table 2 and includes the multiple scattering component. Difference curves are experimental minus theoretical.

Commercially prepared IPC (Ventron, purity >99.5%, for the older experiments and Aldrich Chemical Co., 99.999% pure, for the newer experiments) were used without further purification in the Oregon State University apparatus, in all cases with a nozzle-tip temperature of 295–296 K. Other experimental conditions are summarized in Table 1. Procedures for obtaining the total scattered electron-intensity distribution, $s^4I(s)$, and for removing the backgrounds to yield molecular intensities in the form $sI_m(s)$ are familiar.^{16,17} The intensity curves from the newer data are shown in Figure 1; those from the older data are similar. The experimental intensity data are available as Supporting Information. Radial distribution curves, such as that shown in Figure 2, were calculated by Fourier transformation of the function $sI_m(s)Z_{Fe}Z_C - (s^4F_{Fe}F_C)^{-1} \exp(-0.002s^2)$, where F is the absolute value of the complex

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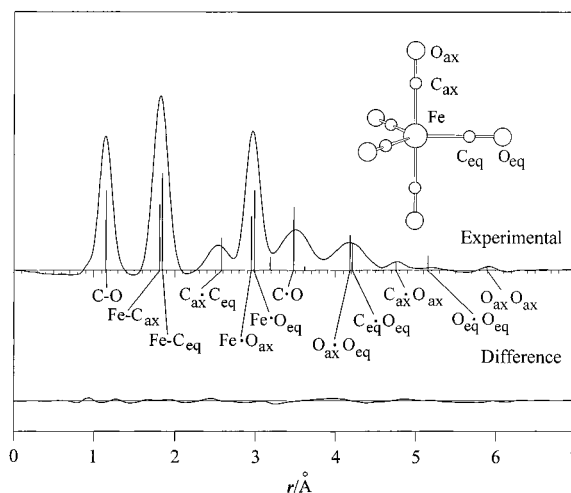


Figure 2. Radial distribution curves. The experimental curve is calculated from the average intensity curves with theoretical data for the unobserved range $s \leq 1.75 \text{ Å}^{-1}$ and a convergence factor $B = 0.0020 \text{ Å}^2$. Vertical bars indicate the interatomic distances in model A; the lengths of the bars are proportional to the weights of the terms. The difference curve is experimental minus theoretical for model A.

electron-scattering amplitude. These scattering amplitudes and their corresponding phases used in other calculations were obtained from tables.¹⁸

Theoretical Calculations

The plan to incorporate B_0 as an observable, or constraint, in the structure refinement of IPC required both *ab initio* and normal coordinate calculations. The *ab initio* calculations establish likely *differences* between the C=O bond lengths should they be needed in the course of the refinements, and provide a Cartesian quadratic force field for use in the normal coordinate work. The normal coordinate calculations provide the array of corrections to distances and to B_0 , which are required for consistency between the measurements of GED (distance space r_a) and spectroscopy (B_0),¹⁹ and estimates of vibrational amplitudes that would be difficult to measure experimentally. Although the variety of *ab initio* calculations cited above^{9–14} offer some of these data, it was convenient to carry out our own calculations making use of a level of theory and a basis set in which we have developed some confidence for the purposes intended here. We selected a B3LYP/6-311+G(d)

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(19) For a summary of the relationship between the methods of rotational spectroscopy and electron diffraction, see: Robiette, A. G. In *Molecular Structure by Diffraction Methods*; Specialist Periodical Reports; The Chemical Society: London, 1973; Vol. 1.

Table 2. Parameter Values for Iron Pentacarbonyl^a

	this work					GED ³	GED ⁴	XRD ⁵	theoret ^b
	model A ^c	model B ^d	model C ^e	model D ^f	model E ^g				
$\langle r(\text{Fe}-\text{C}) \rangle$	1.829(2)	1.826(2)	1.829(2)	1.826(2)	1.815(2)	1.827(3)	1.821(6)	1.806	1.824
$r(\text{Fe}-\text{C})_{\text{eq}} - r(\text{Fe}-\text{C})_{\text{ax}}$	0.032(20)	0.016(19)	0.021(21)	0.014(20)	0.021(22)	0.012(6)	0.020(12)	-0.007, -0.010	-0.007
$\langle r(\text{C}=\text{O}) \rangle$	1.146(2)	1.146(2)	1.146(2)	1.146(2)	1.139(1)	1.147(2)	1.153(6)	1.127	1.141
$r(\text{C}=\text{O})_{\text{eq}} - r(\text{C}=\text{O})_{\text{ax}}$	0.006(27)	0.004(26)	-0.001(28)	0.002(27)	-0.002(33)	0.0 ^h	0.0 ^h	-0.011, 0.019	0.004
$B_z(\text{exp}) - B_z(\text{theor})^i$	0.17	0.11	0.11	2.04	0.30				
R^j	0.066	0.065	0.065	0.065	0.095				

^a Distances are $r_g/\text{\AA}$, and rotational constant difference in MHz. Quantities in parentheses are estimated uncertainties: 2σ including possible systematic error for all GED work and, apparently, σ for ref 5. ^b B3LYP/6-311+G(d). ^c New GED data, B_z value and multiple scattering included. ^d New GED data, B_z value only included. ^e New GED data, B_z value ignored, effects of multiple scattering included. ^f New GED data only. ^g Old GED data only. ^h Assumed. ⁱ $B_0 = 804.220$ MHz; $B_z = 804.060$ MHz. ^j Goodness of fit factor. $R = [\sum_i w_i \Delta_i^2 / \sum_i (s_i I_i(\text{obsd}))^2]^{1/2}$, where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

calculation, which was carried out with the program G98W.²⁰ The Cartesian force field from the ab initio calculation was symmetrized and modified by program ASYM40²¹ to fit the observed vibrational wavenumbers⁶ as partially reassigned by others.¹⁰⁻¹² The distance conversion factors, $r_a \rightarrow r_a^0 = r_z$, obtained from the modified force field may be deduced from the table of final results; the rotational-constant conversion from this force field was $B_0 - 0.16 = B_z(r_z)$.

Structure Refinements

The structure of IPC was refined by least squares²¹ using both the older and newer data. The molecule was assumed to have D_{3h} symmetry which required four distance parameters to describe its geometry. These were chosen to be the average Fe-C bond length, $\langle r(\text{Fe}-\text{C}) \rangle = [2r(\text{Fe}-\text{C})_{\text{ax}} + 3r(\text{Fe}-\text{C})_{\text{eq}}]/5$, the difference between the two types of iron-carbon distances, $\Delta r(\text{Fe}-\text{C}) = r(\text{Fe}-\text{C})_{\text{eq}} - r(\text{Fe}-\text{C})_{\text{ax}}$, and similar definitions for the parameters involving the C=O bonds. A number of the vibrational amplitude parameters—in principle one for each different distance term—were expected to be nearly equal and were confirmed to be so by the theoretical calculations. These amplitudes were either set equal to each other or given a set difference and then refined in pairs. In all, 10 amplitude parameters were refined.

Refinements were carried out under a variety of conditions. Some were based only on the GED data (old and new separately), and others included the rotational constant as an additional observable. It proved impossible to obtain a precise value for the parameter $\Delta r(\text{C}=\text{O})$ under unrestrained conditions, which led us to introduce a “predicate”²² value for it equal to 0.0037 ($\sigma = 0.0018$) Å. This value is the average of those obtained from the ab initio calculations⁹⁻¹⁴ including our own. The standard deviation served as an initial guess for the predicate weighting.

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Table 3. Distances ($r/\text{\AA}$) and Vibrational Amplitudes ($l/\text{\AA}$) for Preferred Model A of Iron Pentacarbonyl

param	r_a^0	r_g	r_a	l_{exp}	l_{theor}
(Fe-C) _{ax}	1.806(16)	1.810	1.809	0.047	} (5) 0.051
(Fe-C) _{eq}	1.837(11)	1.842	1.841	0.047	
(C=O) _{ax}	1.136(23)	1.142	1.141	0.036	} (3) 0.035
(C=O) _{eq}	1.141(16)	1.149	1.148	0.036	
(Fe...O) _{ax}	2.941(9)	2.945	2.944	0.048	} (4) 0.051
(Fe...O) _{eq}	2.979(7)	2.983	2.982	0.048	
C _{ax} ...C _{eq}	2.576(5)	2.580	2.574	0.118(14)	0.122
C _{eq} ...C _{eq}	3.182(20)	3.185	3.180	0.130(58)	0.144
C _{ax} ...O _{eq}	3.483(13)	3.487	3.479	0.172	} (21) 0.166
C _{eq} ...O _{ax}	3.468(13)	3.472	3.464	0.172	
C _{eq} ...O _{eq}	4.210(9)	4.213	4.205	0.179	} (25) 0.186
O _{ax} ...O _{eq}	4.186(5)	4.191	4.177	0.240	
O _{eq} ...O _{eq}	5.159(13)	5.162	5.147	0.280(200)	0.260
C _{ax} ...C _{ax}	3.611(33)	3.614	3.612	0.071	} (23) 0.064
C _{ax} ...O _{ax}	4.747(13)	4.750	4.748	0.071	
O _{ax} ...O _{ax}	5.883(19)	5.885	5.884	0.073(49)	0.065

The refinements based only on the old and new GED data led to similar results that the equatorial Fe-C bonds were slightly longer than the axial ones. However, a disturbing feature of these refinements was an apparent inconsistency in molecular size wherein the older data suggested a smaller molecule by about 0.6%. Introduction of the rotational constant as a constraint changed the picture obtained from the older data in two ways. First, it was found that both $r(\text{Fe}-\text{C})_{\text{ax}}$ and $r(\text{C}=\text{O})_{\text{ax}}$ became much longer than their equatorial counterparts, and second, the vibrational amplitude $l(\text{C}=\text{O})$ decreased from a value pleasingly close to the theoretical one to a value fully 30% smaller. Accompanying these changes was a decrease in quality of fit between the observed and calculated intensity distributions of more than 5% as measured by the quality-of-fit parameter R . No such changes occurred when the rotational constant constraint was introduced in the refinements based on our newer GED data; in this case the molecular size was essentially unchanged. With this strong evidence of a scale problem with the older data, we decided that further work would be done only with the newer data.

The effects of multiple (three-atom) scattering²³ were also tested. We calculated the ITP₀ approximate multiple scattering intensity and included it as a contribution to the overall theoretical intensities that resulted from refinements of the

(22) Bartell, L. S.; Romensko, D. J.; Wong, T. C. In *Molecular Structure by Diffraction Methods*; Specialist Periodical Reports; The Chemical Society: London, 1975; Vol. 3, Chapter 4. The method of predicate values presumes a likely value for the parameter in question, which is allowed to change during the refinement procedure in accordance with one's confidence in the chosen value expressed as a weight. In effect the refined value is connected to the predicate value with a flexible tether, the strength of which is determined by the weighting.

(23) Miller, B. R.; Bartell, L. S. *J. Chem. Phys.* **1980**, *72*, 800.

Table 4. Correlation Matrix ($\times 100$) for Parameters of Model A

param	$100\sigma_{LS}^a$	r_1	r_2	r_3	r_4	l_5	l_6	l_7	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	r_{15}	r_{16}	r_{17}	r_{18}
1 $\langle r(\text{Fe–C}) \rangle$	0.04	100																	
2 $\Delta r(\text{Fe–C})^b$	0.98	19	100																
3 $\langle r(\text{C=O}) \rangle$	0.04	-39	5	100															
4 $\Delta r(\text{C=O})^b$	1.37	-2	-95	1	100														
5 $l(\text{Fe–C})$	0.18	-16	-94	-6	90	100													
6 $l(\text{C=O})$	0.08	7	69	-6	-72	-59	100												
7 $l(\text{Fe}\cdots\text{O})$	0.13	-23	52	-10	-71	-47	57	100											
8 $l(\text{C}_{ax}\cdots\text{C}_{eq})$	0.48	8	<1	9	3	3	2	-12	100										
9 $l(\text{C}_{eq}\cdots\text{C}_{eq})$	2.05	4	22	3	-21	-25	6	26	-13	100									
10 $l(\text{C}_{ax}\cdots\text{O}_{eq})$	0.72	6	40	-1	-40	-39	26	32	-6	68	100								
11 $l(\text{C}_{eq}\cdots\text{O}_{eq})$	0.82	-3	-13	-3	12	14	-4	-4	<1	-17	-30	100							
12 $l(\text{O}_{eq}\cdots\text{O}_{eq})$	7.07	2	2	-1	-2	-2	2	2	<1	4	4	-12	100						
13 $l(\text{C}_{ax}\cdots\text{C}_{ax})$	0.81	<1	<1	2	<1	1	2	1	5	-9	-3	-12	11	100					
14 $l(\text{O}_{ax}\cdots\text{O}_{ax})$	1.75	1	1	1	-1	-1	1	<1	1	-2	-1	1	-7	<1	100				
15 $r(\text{Fe–C})_{ax}$	0.58	-12	-100	-8	96	94	-69	-55	1	-22	-40	13	-2	-1	4	100			
16 $r(\text{Fe–C})_{eq}$	0.40	29	100	1	-93	-93	68	49	1	22	40	-13	2	1	-2	-99	100		
17 $r(\text{C=O})_{ax}$	0.83	1	95	4	-100	-90	72	70	-3	21	40	-12	2	1	-4	-96	93	100	
18 $r(\text{C=O})_{eq}$	0.55	-5	-94	8	100	89	-73	-71	4	-21	-40	11	-2	-1	4	95	-93	-99	100

^a Standard deviations from least squares. Distances (r) and mean square amplitudes (l) in angstroms. ^b Equal to $r_{eq} - r_{ax}$.

several models. The inclusion of multiple scattering tended to reduce the goodness of fit very slightly and required heavier weighting of the rotational constant in order to obtain a calculated value for B_z that lay within the uncertainty listed for the experimental value—about 0.2 MHz.

Refinement results for several models of IPC are given in Table 2. Our preferred model, model A, is derived from our newer data with the B_z constraint included and the effects of multiple scattering taken into account. Models B–E show the effects of various combinations of the old and new GED data with and without the rotational constant and contributions from multiple scattering. Table 3 gives the distances and amplitudes of the preferred model A, and Table 4, the correlation matrix for the parameters of this model. Theoretical intensity and radial distribution curves related to model A are shown in Figures 1 and 2.

Discussion

In all of our models (Table 2) the equatorial Fe–C bond was found to be longer than the axial by amounts of 0.01–0.03 Å. If one accepts the listed uncertainties for the parameter $r(\text{Fe–C})_{eq} - r(\text{Fe–C})_{ax}$ as valid estimates of 2σ , the statistical probability that the axial instead of the equatorial bond is the longer is utterly negligible for model A and respectively only about 5%, 2%, 8%, and 3% for models B–E. Although these data by themselves seem to settle the question of the relative iron–carbon bond lengths, the value of $r(\text{Fe–C})_{eq} - r(\text{Fe–C})_{ax}$ is affected by the value of the corresponding C=O difference through parameter correlation. The correlation coefficient between these two difference parameters is very large (–0.95, Table 4), and as Table 2 shows, which of the two C=O distances is the larger is quite uncertain. To ascertain the effect of the relative C=O bond lengths on the Fe–C difference, a series of refinements were done (new data only) in which the C=O difference was fixed at values over the range 0.021 to –0.019 Å in increments of 0.01 Å, under conditions otherwise similar to those for model A. For $r(\text{C=O})_{eq} - r(\text{C=O})_{ax}$ equal to 0.021, 0.011, 0.001, –0.009, and –0.019 Å, the corresponding refined values of $r(\text{Fe–C})_{eq} - r(\text{Fe–C})_{ax}$ were 0.021(6), 0.027(6), 0.034(6), 0.040(6), and 0.047(6) Å. Since the actual C=O difference is unlikely to be outside the tested range, these tests strongly support our conclusion that equatorial Fe–C bonds in gaseous IPC are longer than the axial ones. This is also in agreement with the results from the earlier published GED

work.^{1–4} The tests also remove the slight possibility, based on our early unpublished work, that the axial bonds could be the longer. We note that the relative magnitudes of the internal stretching force constants for the Fe–C bonds [$F(\text{Fe–C})_{ax} = 2.64$ mdyne/Å, $F(\text{Fe–C})_{eq} = 2.57$ mdyne/Å]⁶ have the expected inverse relationship with the bond lengths. Although a similar comparison should apply to the C=O distances, the large uncertainties attached to the experimental value of $r(\text{C=O})_{eq} - r(\text{C=O})_{ax}$ give such a comparison little meaning.

Structural results from several of the experimental studies are shown in Table 2. Model E based on our old data clearly differs from models A–D, all of which are derived from the new diffraction data. However, the difference is seen to be one of molecular size and not one of the relative lengths of the Fe–C bonds. For reasons discussed earlier, these data were not considered further. Models A–D, based on the new data, are seen to be in excellent agreement with the GED results from ref 3 and in somewhat poorer, but still good, agreement with those from ref 4. These comparisons with the earlier GED work suggest the importance of accounting for the effects of vibrational averaging, or “shrinkage”. Both our work and that of ref 3 included corrections for these effects, but perhaps because the corrections were not easily calculated at the time of their work, they were ignored by the authors of ref 4. Our theoretical results for the average bond lengths, also shown in Table 2, are seen to be in very good agreement with those from GED, but the predicted relative Fe–C bond lengths are incorrect. The theoretical level of this calculation is not high, and more thorough studies, such as those cited in the Introduction, need to be consulted to form a more complete picture. Briefly summarized, these studies often show a longer axial Fe–C bond, but as the theoretical level and basis set size increase, both the Fe–C bond-length average and difference tend toward our gas-phase values.

Results of the most recent X-ray diffraction study of IPC seen in Table 2 leave no doubt that the structure in the crystal is different from that in the gas. This difference includes not only the relative lengths of the two types of Fe–C bonds but also the average bond lengths; both the Fe–C and C=O averages are larger by about 0.02 Å in the gas. Bond lengths from X-ray diffraction with corrections for thermal effects (as those from ref 5 are) should be comparable to our r_g values. Most of the difference between the gas-phase and crystal results probably reflects the effect of packing forces in the crystal.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE99-87359 to Oregon State University. B.W.M. is grateful to Central Oregon Community College for a grant in partial support of his stay at OSU.

Supporting Information Available: A table of averaged molecular intensities. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC001114E