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Molecular Structures and Vibrational Frequencies of Iron Carbonyls: $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$

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Hybrid Hartree−Fock/density functional theory (HF/DFT) explicitly including all electrons has been employed to study the three iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$. The geometries are fully optimized by the BP86 and B3LYP methods in conjunction with two basis sets, including as many as 507 contracted Gaussian functions for $Fe_3(CO)_{12}$. Our theoretical geometries and harmonic vibrational frequencies are carefully compared with available experimental results. For $Fe_3(CO)_{12}$ most of the fundamental vibrational frequencies have never been assigned experimenally. Several of the experimental assignments for $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are dubious.

1. Introduction

Iron carbonyl compounds play a central role in organometallic chemistry. The best known iron carbonyls are $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$. In recent years, there have been hundreds of publications per year related to these iron carbonyls. However, compared with the large quantities of experimental studies on iron carbonyls, theoretical studies with quantum mechanical methods are few, especially for the largest structure, di-μ-carbonyldecacarbonyltri-triangulo-iron, $Fe_3(CO)_{12}$. The dearth of theoretical studies follows from the computational requirements; transition metals require much larger basis sets than the first- and second-row elements. Unfortunately, the Hartree−Fock self-consistent-field method (HF SCF) has not proven consistently successful for compounds containing transition metals.[1] High-quality post-HF methods, such as the configuration interaction (CISD) or coupled cluster [CCSD(T)] methods, which scale according to the sixth to seventh power with respect to the size of molecule, are typically applied to molecules of more modest size. Therefore the theoretical study of large molecules containing transition metals such as $Fe_3(CO)_{12}$ at a reliable level of theory has been practically hampered.

Recently the rapid development of computing power and the widespread use of efficient methods based in part on density functional theory (DFT), in which electron correlation is taken into account in a simple way, make such large systems approachable. DFT methods were recently heralded by Ziegler as capable of “beating transition metal’s blues”.[2] Thus, in the present study, DFT and hybrid Hartree−Fock/DFT methods are used to investigate the title molecules.

2. Theoretical Methods

In this study two basis sets have been employed. The double-ζ (DZ) basis set for C and O is Dunning’s standard double-ζ contraction[3] of Huzinaga’s primitive sets[4] and is designated (9s5p/4s2p). The double-ζ plus polarization (DZP) basis set adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ to the DZ basis set. For Fe, in our loosely contracted DZ and the DZP basis sets, the Wachters’ primitive set[5] is used, but augmented by two sets of p functions and one set of d functions and contracted following Hood et al.,[6] and designated (14s11p6d/10s8p3d). For $Fe_3(CO)_{12}$, there are 387 contracted Gaussian basis functions with the DZ basis set, and 507 with the DZP set.

Electron correlation effects were included employing density functional theory methods (DFT), which have been widely proclaimed as a practical and effective computational tool, especially for organometallic compounds.[2] Among density functional procedures, the most reliable approximation is often thought to be the hybrid HF/DFT method using the combination of the three-parameter Becke exchange functional with the Lee−Yang−Parr nonlocal correlation functional known as B3LYP.[7,8] However, another DFT method, which combines Becke’s 1988 exchange functional with Perdew’s 1986 nonlocal correlation functional method (BP86), was also used in the present paper for comparison.[9,10]

We fully optimized the geometries of $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ at four levels of theory: DZ BP86, DZP BP86, DZ B3LYP, and DZP B3LYP. At the same levels we also reported the vibrational frequencies by evaluating analytically the second derivatives of energy with respect to the nuclear coordinates. Their corresponding infrared intensities are evaluated analytically as well. All the computations were carried out with the Gaussian 94 program,[11] in which the fine grid (75 302) is the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation is the default for the SCF convergence.

3. Results and Discussion

A. Iron Pentacarbonyl, $Fe(CO)_5$. $Fe(CO)_5$ was first prepared in 1891.[12] Its trigonal-bipyramidal structure (Figure

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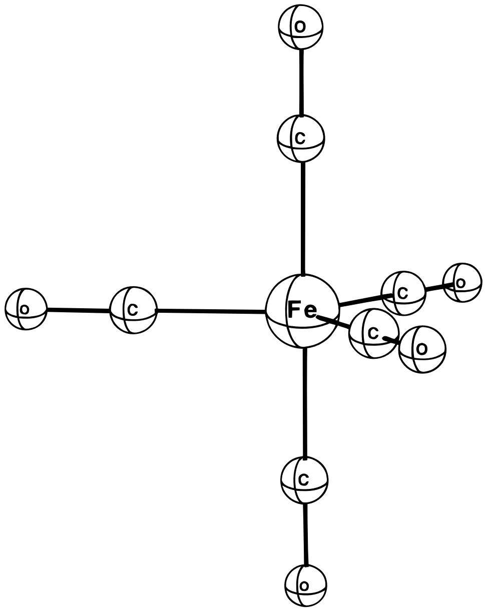


$Fe(CO)_5$ D_{3h}

Figure 1. Structure of iron pentacarbonyl, $Fe(CO)_5$.

TABLE 1: Bond Distances (in Å) and Total Energies (in Hartree) of Iron Pentacarbonyl $Fe(CO)_5$ (D_{3h} Symmetry)

	DZP BP86	DZP B3LYP	experiment
Fe−C (ax.)	1.8053	1.8226	1.811,[a] 1.807[b]
Fe−C (eq.)	1.8053	1.8158	1.803,[a] 1.827[b]
C−O (ax.)	1.1673	1.1524	1.117,[a] 1.152[b]
C−O (eq.)	1.1701	1.1563	1.133,[a] 1.152[b]
total energy	−1830.837 52	−1830.581 35	

[a] Reference 15, solid-state X-ray diffraction. [b] Reference 14, r_a from gas-phase electron diffraction.

1) was determined by Ewens in 1939.[13] Relative to $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, the mononuclear complex $Fe(CO)_5$ has been studied more thoroughly both experimentally[14,15] and theoretically.[1,2,16−22] Among the previous theoretical studies of $Fe(CO)_5$, however, many early DFT studies were plagued by systematic and/or nonsystematic errors due to lack of precision in the numerical integration procedures.[23] Perhaps the first truly reliable comprehensive study of monometal carbonyls was the 1995 study of Jonas and Thiel.[22] We will compare our results on $Fe(CO)_5$ with those of others to assess the reliablity of the methods used in this work.

Compared with the experimental Fe−C bond distances from gas-phase electron diffraction[14] or X-ray diffraction,[15] it is striking to see that the predicted Fe−C bond distances at the SCF level are about 0.1 Å (equatorial) or 0.2 Å (axial) too long. For example, with the DZf basis set, i.e., contracted Gaussian functions (8s6p3d1f) for Fe and (4s2p) for C and O, the SCF Fe−C bond lengths by Luthi et al. are 2.047 Å (axial) and 1.874 Å (eq.).[1] Similarly, Jonas and Thiel's SCF results are 2.067 Å (axial) and 1.891 Å (eq.) with the TZ2P basis sets.[22] The treatment of electron correlation dramatically improves the Fe−C bond lengths. At the DZf CCI (externally contracted CI) level reported by Luthi et al., the Fe−C bonds are reduced to 1.798 Å (axial) and 1.836 Å (eq.).[1] At the CCSD(T) level with the double numerical basis set, both the axial and equatorial Fe−C bond lengths are 1.826 Å.[19] But the MP2 method decreases the Fe−C bond distances excessively, which are 1.699 Å (axial) and 1.791 Å (eq.).[22] The DFT results with the TZ2P BP86[9,10] method of Jonas and Thiel are 1.812 Å for both the axial and equatorial Fe−C bond lengths,[22] which are quite close to the experimental values.[14,15]

Our theoretically predicted geometry paremeters and total energies at different levels of theory, as well as available experimental results, are presented in Table 1 (see also Table A, Supporting Information). The Fe−C bond distances increase from the DZ to DZP basis set by about 0.005−0.009 Å and from the BP86 to B3LYP method by about 0.007−0.017 Å. Among the results from sundry levels of theory, the DZP B3LYP Fe−C distances (i.e., 1.8226 Å for axial and 1.8158 Å for equatorial) are the closest to the experimental values.[14,15]

A much discussed problem is the relative length of the axial and equatorial Fe−C bonds. The experimental results are contradictory from different methods: the axial Fe−C bonds are 0.008 Å longer than the equatorial ones according to the crystal X-ray diffraction method,[15] while they are 0.020 Å shorter as determined by the gas-phase electron diffraction method.[14] The theoretical methods appear to support the former, since the theoretical axial Fe−C bond lengths are never shorter than the equatorial ones, although electron correlation effect reduces the difference. For example, at SCF levels the axial bonds are about 0.2 Å longer than the equatorial ones.[1,22] At the DZf CI level[1] the difference decreases to about 0.04 Å. At the CCSD(T) level with the double numerical basis sets, the axial bond lengths are the same as the equatorial ones within the accuracy of 0.0001 Å.[19] At the TZ2P BP86 level of Jonas and Thiel, the axial bonds are also predicted to be the same as the equatorial ones.[22] Our DFT results (Table 1) show the axial bonds are slightly (less than 0.008 Å) longer than the equatorial ones. The fact that the axial bonds are longer has already been explained with a simple electron repulsion analysis by Gillespie.[24] With respect to the contradictory results obtained by the electron diffraction method, Donohue in 1966 stated, "we doubt whether the electron diffraction data are capable of detecting a difference of only 0.045 Å between the two kinds of Fe−C bonds because of the high correlation between that difference and the vibrational amplitudes."[25] Since the difference of the two kinds of Fe−C bonds from Beagley et al.'s work is even smaller (0.02 Å),[14] Donohue's statement may be pertinent. However, as we shall see, the crystal structure for $Fe(CO)_5$ is also subject to skepticism.

For the C−O bond distances in $Fe(CO)_5$, the SCF results are too short. They are 1.102 (axial) and 1.114 Å (eq.) with the TZ2P basis set.[22] The treatment of electron correlation lengthens these distances, but MP2 increases them too much (1.164 Å (axial) and 1.152 Å (eq.) with the same basis set).[22] The CCSD(T) method yields 1.162 for both axial and equatorial C−O distances.[19] In our work (Table 1), the DZP B3LYP level of theory predicts the C−O distances to be 1.1524 Å (axial) and 1.1563 Å (eq.). Table 1 (Table A, Supporting Information) also shows that the BP86 method yields C−O distances 0.014 Å longer than the B3LYP method for both the DZ and DZP basis sets, while the DZ basis set provides distances 0.02 Å longer than the DZP.

Again the DZP B3LYP C−O bond lengths are the closest to the CCSD(T) results and those from the gas-phase electron diffraction experimental C−O distances (1.152 Å).[14] The crystal X-ray diffraction C−O distances are too short, only 1.117 Å (axial) and 1.133 Å (eq.).[15] Since the shortest C−O distance in the carbon monoxide molecule is 1.128 Å, the 1.117 Å axial C−O distances from crystallography are very doubtful.

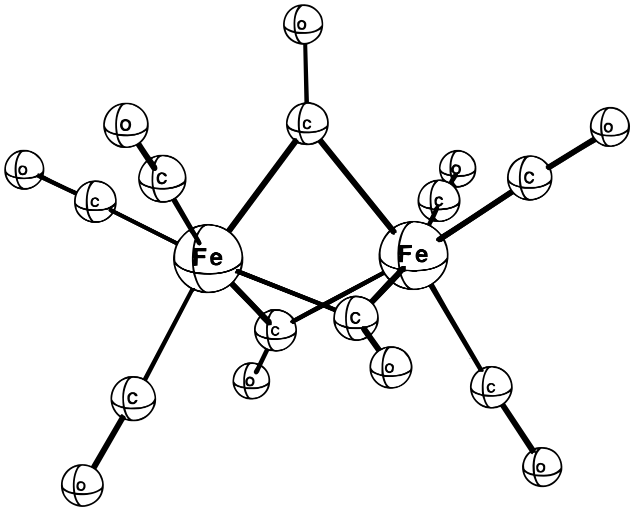
Early studies of the infrared and Raman vibrational frequencies of $Fe(CO)_5$ were reported in 1950s.[26−28] However, these

TABLE 2: Harmonic Vibrational Frequencies (in cm^{-1}) and Infrared Intensities (in Parentheses, in km/mol) for Iron Pentacarbonyl, Fe(CO)$_5$

		DZP BP86	% errors	DZP B3LYP	% errors	expt.[a]
ν_1	a_1'	2089(0)	−1.5%	2169(0)	2.3%	2121
ν_2	a_1'	2012(0)	−1.5%	2093(0)	2.5%	2042
ν_3	a_1'	460(0)	3.8%	439(0)	−0.9%	443
ν_4	a_1'	434(0)	5.1%	413(0)	0.0%	413
ν_5	a_2'	357(0)	−6.8%	364(0)	−5.0%	383
ν_6	a_2''	2008(1264)	−1.3%	2094(1474)	2.9%	2034
ν_7	a_2''	625(127)	1.0%	617(127)	−0.3%	619
ν_8	a_2''	488(0)	3.0%	473(7)	−0.2%	474
ν_9	a_2''	103(0)	−1.9%	107(1)	1.9%	105
ν_{10}	e'	1992(1079)	−1.0%	2067(1274)	2.7%	2013
ν_{11}	e'	662(125)	2.6%	660(132)	2.3%	645
ν_{12}	e'	492(1)	0.8%	483(2)	−1.0%	488
ν_{13}	e'	434(7)	1.2%	439(14)	2.3%	429
ν_{14}	e'	99(0)	−1.0%	104(0)	4.0%	100
ν_{15}	e'	53(0)	*b*	54(0)	*b*	64
ν_{16}	e''	547(0)	0.7%	563(0)	3.7%	543
ν_{17}	e''	369(0)	−1.6%	366(0)	−2.4%	375
ν_{18}	e''	91(0)	−6.2%	95(0)	−2.1%	97

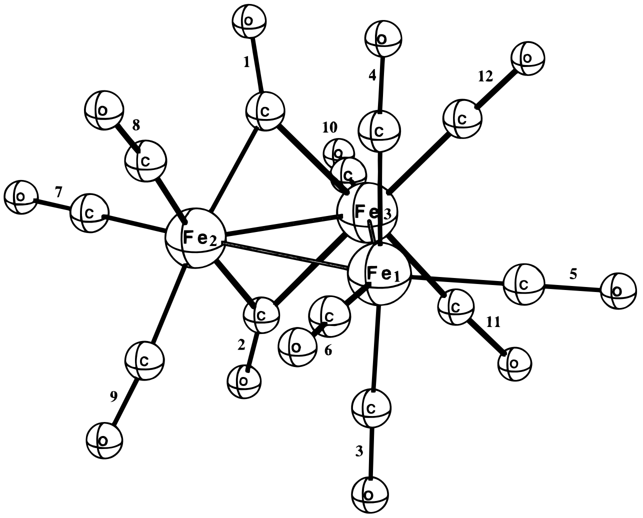
[a] This follows Table 7 in ref 30, but three pairs of frequencies were reassigned by refs 22 and 31 and confirmed by this paper. [b] Not included in the calculation of deviations due to uncertainty of the experimental value.

earlier studies of vibrational frequencies are not complete, and their assignments are tentative. More reliable infrared and Raman frequencies were reported by Bigorgne in 1970.[29] These spectra were recorded in the solid, liquid, or solution phases. In 1972, Jones et al. reported infrared spectra in the vapor phase and Raman spectra in solution.[30] Jones' work improved most of Bigorgne's assignments. Recently some DFT methods have been used to predict the vibrational frequencies of Fe(CO)$_5$.[19,31] In Table 2 (see also Table B, Supporting Information) our theoretical results are presented and compared with the experimental fundamentals. Note that our predictions are very similar to those of Jonas and Thiel.[22] After switching three pairs of the assignments by Jones et al., the vibrational frequencies obtained with the B3LYP method appear to give good agreement with the experimental results. Two pairs of the changes (543 vs 488 cm^{-1}, and 474 vs 429 cm^{-1}) were made earlier by Jonas and Thiel[22] and by Berces and Ziegler et al.[2,31] In addition, we assign the frequency of 100 cm^{-1} (estimated by Jones[30]) to e' symmetry and 105 cm^{-1} to a_2'' symmetry, since our theoretical frequency in a_2'' is always 3−6 cm^{-1} larger at all the levels. Table 2 shows that the DZP frequencies are closer than the DZ ones. For both BP86 and B3LYP methods with the DZP basis set, no significant systematic deviation remains. At the DZP BP86 level, of the deviations for 17 values (the uncertain experimental value 64 cm^{-1} is not included), eight of the deviations are positive, and the other nine are negative. The range of relative errors is from −6.8% to 5.1%. At the DZP B3LYP level, nine of the frequency errors are positive, seven are negative, and one is zero. The range of deviation is −5.0% to 4.0%. At the DZP B3LYP level of theory, the deviations of the C−O stretch modes (>2000 cm^{-1}) are all positive; accordingly the scaling factor for converting theoretical harmonic frequencies to experimental fundamentals would be 0.97−0.98. For the others modes, the scaling factors range from 0.96 to 1.02. These values are comparable in magnitude to Rauhut and Pulay's scaling factors for force constants.[32] They studied seven different modes for the molecule tetrachlorinated dibenzodioxins at the B3LYP/631G(d) level of theory.



Fe$_2$(CO)$_9$ D_{3h}

Figure 2. Structure of the transition state of Berry pseudorotation for Fe(CO)$_5$.



Fe$_3$(CO)$_{12}$ C_{2v}

Figure 3. Structure of tri-μ-carbonylhexacarbonyldiiron, Fe$_2$(CO)$_9$.

It is well-known that the structure of a five-coordinate molecule can easily undergo a rearrangement called Berry pseudorotation.[33] The experimental activiation barrier for rearrangement of Fe(CO)$_5$ was estimated by Spiess, Grosescu, and Haeberlen to be about 1 kcal/mol,[34] and an early RHF result for the activiation barrier of Fe(CO)$_5$ was less than 1 kcal/mol.[35] Since the 1977 result was at a low theoretical level, it is worth refining it at a higher level in today's view. Our optimized geometry of the Berry transition state for Fe(CO)$_5$ is shown in Figure 2 and Table 3. This C_{4v} structure has one imaginary vibrational frequency (see Table 4), as expected in the pseudorotation mechanism. The energy barriers ΔE_e at the different theoretical levels are in agreement with each other within 0.1 kcal/mol (Table 3); they are 2.25, 2.28, 2.33 kcal/mol at the DZ B3LYP, DZP BP86, DZP B3LYP levels of theory, respectively.

B. Tri-μ-carbonylhexacarbonyldiiron, Fe$_2$(CO)$_9$. Fe$_2$(CO)$_9$ was determined as early as 1905.[36] Its bridging carbonyl structure was characterized in 1939 by Powell et al.[37] An accurate determination of the geometrical parameters by X-ray

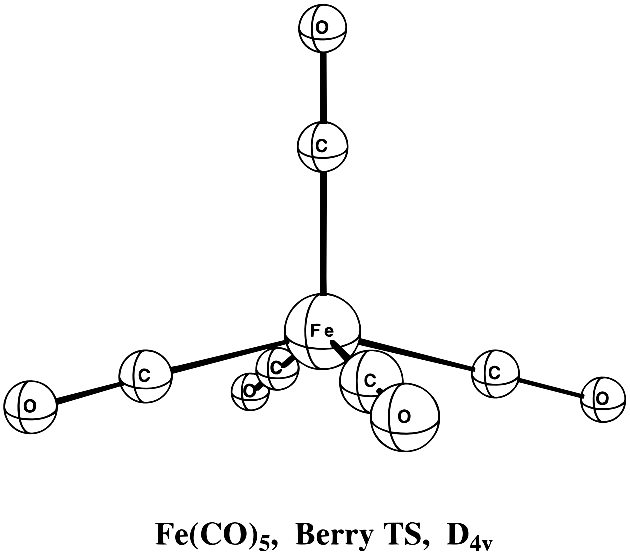


Figure 4. Structure of Di-μ-carbonyldecacarbonyltri-triangulo-iron, $Fe_3(CO)_{12}$.

TABLE 3: Bond Distances (in Å) and Energy of the Pseudorotation Transition State for Iron Pentacarbonyl, $Fe(CO)_5$ (C_{4v} Symmetry)

	DZ B3LYP	DZP BP86	DZP B3LYP
Fe−C (ax.)	1.8045	1.8115	1.8193
Fe−C (eq.)	1.8105	1.8043	1.8189
C−O (ax.)	1.1749	1.1686	1.1543
C−O (eq.)	1.1756	1.1695	1.1551
C−Fe−C	103.4	103.9	103.6
Fe−C−O (eq.)	179.8	179.6	179.8
total energy (hartree)	−1830.367 87	−1830.833 93	−1830.577 64
energy related to D_{3h} structure (kcal/mol)	2.25	2.28	2.33

TABLE 4: Harmonic Vibrational Frequencies (in cm^{-1}) and Infrared Intensities (in Parentheses, in km/mol) for the Pseudorotation Transition State for Iron Pentacarbonyl, $Fe(CO)_5$

		DZ B3LYP	DZP BP86	DZP B3LYP
ν_1	a_1	2058(0)	2085(1)	2166(1)
ν_2	a_1	1975(972)	2004(866)	2086(979)
ν_3	b_2	1969(0)	2003(0)	2081(0)
ν_4	e	1964(2989)	1995(2517)	2075(3021)
ν_5	a_1	659(141)	666(123)	665(129)
ν_6	e	642(217)	649(217)	645(207)
ν_7	b_1	553(0)	543(0)	564(0)
ν_8	e	515(46)	518(24)	527(38)
ν_9	a_1	497(2)	497(2)	481(8)
ν_{10}	e	487(5)	489(4)	475(20)
ν_{11}	b_2	446(0)	456(0)	437(0)
ν_{12}	a_1	425(0)	433(0)	412(0)
ν_{13}	a_2	364(0)	376(0)	369(0)
ν_{14}	e	362(7)	365(5)	366(7)
ν_{15}	b_2	332(0)	341(0)	335(0)
ν_{16}	e	111(2)	102(0)	106(1)
ν_{17}	b_1	107(0)	98(0)	101(0)
ν_{18}	a_1	105(1)	97(0)	102(0)
ν_{19}	e	83(0)	78(0)	80(0)
ν_{20}	b_2	52i	50i	52i

was carried out by Cotton et al. in 1974.[38] In our study, just like $Fe(CO)_5$, the general trend is that the Fe−Fe and Fe−C bond distances increase slightly (<0.01 Å) from the DZ to the DZP basis set, while the C−O bond lengths decrease about 0.02 Å. The DZP B3LYP results are the closest to the experimental data.[38] Therefore our theoretical optimized geometrical parameters for $Fe_2(CO)_9$ with only the DZP basis set are presented in Table 5. (Those with the DZ basis set are available on request.)

TABLE 5: Bond Distances (in Å), Bond Angles (in deg), and Total Energies (in Hartree) for Tri-μ-carbonylhexacarbonyldiiron, $Fe_2(CO)_9$ (D_{3h} Symmetry)

	BP86 DZP	B3LYP DZP	expt[a]
Fe−Fe	2.5188	2.5253	2.523
Fe−C (terminal)	1.8186	1.8288	1.838
Fe−C (bridge)	2.0066	2.0076	2.016
C−O (terminal)	1.1664	1.1516	1.156
C−O (bridge)	1.1862	1.1756	1.176
∠C−Fe−C (terminal)	95.9	96.4	96.1
∠Fe−C−O (terminal)	176.9	177.5	177.1
total energy	−3548.313 62	−3547.787 42	

[a] Reference 38.

The difference between the DZP B3LYP and experimental results for Fe−Fe bond length is only 0.002 Å, while those for C−O bond lengths are either less than 0.005 Å (for terminal) or about only 0.001 Å (for bridge). Those for Fe−C bond lengths are less than 0.01 Å. The agreement of bond angles is within 0.4°. Given that the experimental structure is from the condensed phase while the theoretical structure refers to the isolated molecule, the agreement is excellent.

Although quite a few researchers have studied $Fe_2(CO)_9$ theoretically,[39−45] most of them did not optimize the geometry, but investigated whether a direct Fe−Fe bond exists theoretically at the experimental geometry. Even though the Fe−Fe bonding is necessary to satisfy the 18 electron rule and the Fe−Fe bond length (2.523 Å) is only 2% larger than the Fe−Fe bond distance in metal iron, Summerville and Hoffmann pointed out from their semiempirical study that neither of these two factors is an infallible guide to the presence or absence of substantial direct Fe−Fe interaction.[39] Later Heijster et al.[40] reported a negative density difference along the Fe−Fe bond axis, which supported Summerville and Hoffmann's point of view. In 1986, Bauschlicher drew the same conclusion by evaluating the overlap between the Fe d orbitals with ab initio methods.[41] Furthermore, Rosa and Baerends did molecular orbital analysis with a DFT method and stated that the reason for the absence of Fe−Fe bonding is that the antibonding set of the Fe−Fe bond is more heavily populated than the bonding orbitals.[42] The other recently published papers[43,44] draw the same conclusions.

The early infrared and Raman spectra were reported by Fritz et al.,[46] Griffith et al.,[47] and Poliakoff et al.,[48] but no assignments were given. In 1978, a relatively complete Raman spectra of solid $Fe_2(CO)_9$ at temperatures of 295, 100, and 15 K were recorded and partial assignments were made.[49] Later, in 1982, infrared spectra of polycrystalline $Fe_2(CO)_9$ were collected at 100 K,[50] and complete assignments are deduced for all the optically active modes from their own IR results and Butler's Raman results. According to group theory, the e′ representation is both Raman and infrared allowed, a_1' and e″ are only Raman active, a_2'' is only infrared allowed, and the a_2' and a_1'' are forbidden for both Raman and infrared. To our knowledge, the current study is the first to report the theoretical vibrational frequencies with ab initio methods. Table 6 presents our theoretical DZP harmonic vibrational frequencies with their infrared intensities for $Fe_2(CO)_9$ to compare with the experimental infrared and Raman results. For the C−O stretch modes (>1800 cm^{-1}) the theoretical harmonic vibrational frequencies increase on going from the DZ to the DZP basis set, as well as from the BP86 to the B3LYP method. Compared with experimental data, the DZP B3LYP frequencies for C−O stretch modes are overestimated, but the deviations are less than 5%, which is typically better than the SCF method can do. For modes other than the C−O stretches, the theoretical vibrational frequencies are in better agreement among the different DFT

TABLE 6: Harmonic Vibrational Frequencies (in cm^{-1}) and Infrared Intensities (in Parentheses, in km/mol) for Tri-μ-carbonylhexacarbonyldiiron, $Fe_2(CO)_9$

		BP86 DZP	B3LYP DZP	expt[a]	
ν_1	a_1'	2079(0)	2170(0)	2112	
ν_2	a_1'	1895(0)	1957(0)	1891	
ν_3	a_1'	620(0)	624(0)	480	
ν_4	a_1'	478(0)	466(0)	415	
ν_5	a_1'	399(0)	397(0)	260	
ν_6	a_1'	255(0)	259(0)	137	
ν_7	a_1'	79(0)	83(0)	237	
ν_8	a_2'	508(0)	525(0)		
ν_9	a_2'	371(0)	376(0)		
ν_{10}	a_2'	77(0)	82(0)		
ν_{11}	e′	2013(1322)	2101(1527)	2016	2020
ν_{12}	e′	1870(682)	1918(899)	1814	1817
ν_{13}	e′	624(134)	631(120)	604	605
ν_{14}	e′	532(4)	545(10)	528	525
ν_{15}	e′	461(25)	455(40)	390	390
ν_{16}	e′	433(1)	438(7)	451	454
ν_{17}	e′	376(0)	374(1)	175	174
ν_{18}	e′	107(1)	110(1)	126	126
ν_{19}	e′	85(0)	88(0)	106	105
ν_{20}	e′	54(0)	58(0)	83	85
ν_{21}	a_1''	417(0)	427(0)		
ν_{22}	a_1''	51(0)	54(0)		
ν_{23}	a_2''	2038(1747)	2120(2210)		2088
ν_{24}	a_2''	675(798)	697(763)		690
ν_{25}	a_2''	573(98)	583(165)		564
ν_{26}	a_2''	451(18)	434(52)		426
ν_{27}	a_2''	225(2)	228(1)		130
ν_{28}	a_2''	93(0)	98(0)		166
ν_{29}	e″	2008(0)	2096(0)	1990	
ν_{30}	e″	604(0)	617(0)	590	
ν_{31}	e″	486(0)	491(0)	493	
ν_{32}	e″	452(0)	443(0)	315	
ν_{33}	e″	314(0)	313(0)	468	
ν_{34}	e″	159(0)	159(0)	114	
ν_{35}	e″	82(0)	78(0)	89	
ν_{36}	e″	75(0)	55(0)	67	

[a] Assignments from ref 50 using experimental data of refs 49 and 50.

methods. However, Table 6 shows that the theoretical predictions are not in good agreement with the experimental values. A possible reason is that the assignments by Adams might be in a different order. If we adjust the order of some of Adams' assignments, the theoretical frequencies would be consistent with the experimental data to a great extent. For the a_1' irreducible representation, the assignment of ν_3, ν_4, ν_5, ν_6 would be ν_4, ν_5, ν_6, ν_7, respectively. A Raman band around 604 cm^{-1} could be assigned as ν_3 (which almost overlaps with ν_{13}). For the e′ irreducible representation, the experimental assignment of ν_{15} could be ν_{17}, and ν_{16} seems to be ν_{15}. For the e″ fundamentals, the order of ν_{32} and ν_{33} needs to be exchanged. Although the above assignments are just tentative and incomplete, our theoretical results in Table 6 will no doubt help the experimentalists to assign the vibrational spectra of $Fe_2(CO)_9$ in their future work.

C. Di-μ-carbonyldecacarbonyltri-triangulo-iron, $Fe_3(CO)_{12}$. Like $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ was first prepared by Dewar as early as 1907.[36] But a satisfactory determination of its bonding arrangement has taken more than 60 years. Due to disorder in the crystal, determination of the structure of $Fe_3(CO)_{12}$ in the solid phase proved to be very difficult.[38,52] For a long time, a number of chemists believed that $Fe_3(CO)_{12}$ was linear and proposed several possible structures. Although some trigonal arrangements were suggested, they could not satisfy all the experimental facts. For example one of the proposed trigonal structures was suggested to be similar to $Os_3(CO)_{12}$, i.e., three $Fe(CO)_4$ fragments connected by three Fe−Fe bonds.[53,54] In 1968, N. Erickson, then a graduate student working from Moessbauer shifts, "accidentally" proposed a C_{2v} structure, which can be considered as $Fe_2(CO)_9$ with one of the bridging CO groups replaced by an $Fe(CO)_4$ fragment,[55] and eventually resolved the case. This long and interesting history was vividly described in a 1982 article by Desiderato and Dobson.[56] In 1969, Wei and Dahl determined the geometry of $Fe_3(CO)_{12}$ in a single-crystal state by X-ray diffraction.[57] In 1974, Cotton and Troup[38] determined more accurate geometric parameters with a crystalline sample by X-ray diffraction.

Since the structure in the crystalline phase at room temperature was distorted from C_{2v} symmetry significantly, Braga et al. recently reinvestigated the crystalline structure at different temperatures,[15] and they reported that the molecule possesses nearly C_{2v} symmetry at the lowest temperature they employed (100 K). Since this was still distorted slightly from C_{2v} symmetry, some of the symmetric equivalent coordinates have more than one experimental entry in Table 7. Table 7 shows that our optimized geometry parameters are in good agreement with each other among the four different levels. Similar to $Fe(CO)_5$ and $Fe_2(CO)_9$, there are almost no changes for the Fe−Fe and Fe−C bond lengths when basis set changes, while there are roughly 0.02 Å decrements for the C−O bond lengths from the DZ basis set to the DZP. Table 7 also shows that the theoretical evaluation of the geometry is generally in good agreement with the experimental measurements. The deviations for the bond lengths between the DZP B3LYP method and the experimental data (mean value if more than one experimental distance exists) are less than 0.05 Å.

Although there have been a few infrared experimental studies for $Fe_3(CO)_{12}$,[58,60−62] no complete assignment of the vibrational frequecies has been reported so far. A report in 1970 on the infrared spectra for $Fe_3(CO)_{12}$ in Ar matrix at low temperature apparently provides the best comparison for our theoretical predictions.[63] Our theoretical vibrational frequencies and the infrared intensities for $Fe_3(CO)_{12}$ are listed in Table 8. Our results from the four different levels are in good agreement. However, the frequencies of C−O stretching modes (>1800 cm^{-1}) with the DZP basis set are about 100 cm^{-1} larger than those with the DZ basis set. This is consistent with the C−O bond lengths, which are about 0.02 Å shorter with the DZP basis set than with the DZ. Among the theoretical methods, the DZP B3LYP is regarded as the most reliable, so it will be used for the following discussion. In Table 8, we can easily recognize 10 frequencies, the values of which are larger than 2000 cm^{-1}. These are the fingerprint frequencies for the 10 terminal C−O stretching modes (among them, four frequencies for a_1, one for a_2, two for b_1, and three for b_2). In ref 63 only eight (not ten) experimental frequencies larger than 2000 cm^{-1} were reported. The two missing infrared bands are those either infrared forbidden (a_2 mode) or too weak to be observed (one b_2 mode with almost no theoretically predicted infrared intensity). When we assigned these eight experimental frquencies in the same order (except one pair) as our theoretical ones, the theoretical and the experimental infrared intensities are in very good agreement with each other. Our infrared intensities of 2915, 2319, and 2633 km/mol correspond to s (strong) intensities in experiment; our 139 and 172 km/mol intensities correspond to m (medium); and our 16, 7, and 12 km/mol correlate with w (weak) or vw (very weak). The only pair switched are at 2021 and 2013 cm^{-1}, which are only 8 cm^{-1} apart. We have two frequencies that are between 1800 and 1900 cm^{-1}, which are the two fingerprint frequencies for bridging carbonyl stretching

TABLE 7: Bond Distances (in Å), Bond Angles (in deg), and Total Energies (in Hartree) for Di-μ-carbonyldecacarbonyltriiron, $Fe_3(CO)_{12}$ (C_{2v} Symmetry)

	BP86 DZP	B3LYP DZP	expt[a]
$Fe_1{-}Fe_2$	2.7126	2.7356	2.675, 2.682
$Fe_2{-}Fe_3$	2.5721	2.5898	2.540
$Fe_1{-}C$(ax.)	1.8148	1.8246	1.803, 1.853
$Fe_1{-}C$(eq.)	1.7880	1.8005	1.802, 1.807
$C{-}O$(ax.)	1.1680	1.1538	1.148, 1.119
$C{-}O$(eq.)	1.1687	1.1539	1.155, 1.233
$\angle C{-}Fe_1{-}C$(ax.)	172.6	172.8	174.4
$\angle C{-}Fe_1{-}C$(eq.)	99.3	101.6	100.9
$\angle Fe_1{-}C{-}O$(ax.)	173.9	174.8	176.6, 174.3
$\angle Fe_1{-}C{-}O$(eq.)	178.3	178.7	171.6, 172.7
$Fe_{2,3}{-}C$(bridge)	1.9960	1.9967	1.949, 2.003, 2.004, 2.052
$Fe_{2,3}{-}C_{7,10}$	1.7839	1.7988	1.801, 1.794
$Fe_{2,3}{-}C_{8,9,11,12}$	1.8051	1.8141	1.753, 1.837, 1.882, 1.827
$C{-}O$(bridge)	1.1874	1.1758	1.140, 1.156
$C{-}O_{7,10}$	1.1683	1.1527	1.105, 1.109
$C{-}O_{8,9,11,12}$	1.1682	1.1539	1.200, 1.142, 1.058, 1.218
$\angle C_{7,10}{-}Fe_{2,3}{-}C_{8,9,11,12}$	94.3	94.4	97.8, 96.7, 95.5, 94.7
$\angle C_{8,11}{-}Fe_{2,3}{-}C_{9,12}$	94.7	95.6	93.4, 97.6
$\angle Fe_{2,3}{-}C{-}O_{7,10}$	178.2	178.5	175.7, 169.7
$\angle Fe_{2,3}{-}C{-}O_{8,9,11,12}$	174.9	175.8	171.7, 176.5, 175.4, 176.9
total energy	−5152.430 67	−5151.655 18	

[a] Reference 59. Some experimental bond lengths and angles were deduced by us from the original data. Note that the experimental crystal structure does not display C_{2v} symmetry. Our work shows that the equilibrium geometry is of C_{2v} symmetry.

TABLE 8: Harmonic Vibrational Frequencies (in cm^{-1}) and Infrared Intensities (in Parentheses, in km/mol) for Di-μ-carbonyldecacarbonyltriiron, $Fe_3(CO)_{12}$

		BP86 DZP	% error	B3LYP DZP	% error	expt[a]			BP86 DZP	% error	B3LYP DZP	% error	expt[a]
ν_1	a_1	2082(32)	−1.4%	2170(16)	2.8%	2110 vw	ν_{39}	b_1	2013(1935)	−1.1%	2097(2319)	3.0%	2036 s
ν_2	a_1	2030(1898)	−1.0%	2106(2915)	2.7%	2051 s	ν_{40}	b_1	1979(25)	−1.7%	2063(12)	2.5%	2013 m
ν_3	a_1	2007(19)	−0.7%	2089(139)	3.4%	2021 w	ν_{41}	b_1	1850(510)	0.9%	1896(757)	3.4%	1833 ms
ν_4	a_1	1994(295)	−0.1%	2070(7)	3.3%	2003 vw	ν_{42}	b_1	598(15)		601(1)		
ν_5	a_1	1875(177)	0.0%	1940(262)	3.6%	1871 sh, 1867 w	ν_{43}	b_1	589(133)	1.6%	595(159)	2.6%	580 m
ν_6	a_1	630(14)		638(32)			ν_{44}	b_1	536(12)		551(14)		
ν_7	a_1	625(262)	3.1%	628(321)	3.6%	606 m	ν_{45}	b_1	518(1)		516(11)		
ν_8	a_1	595(33)		605(18)			ν_{46}	b_1	481(8)		477(15)		
ν_9	a_1	544(8)		554(12)			ν_{47}	b_1	415(0)		442(1)		
ν_{10}	a_1	505(0)		493(9)			ν_{48}	b_1	433(0)		420(1)		
ν_{11}	a_1	493(0)		481(0)			ν_{49}	b_1	396(0)		399(1)		
ν_{12}	a_1	489(0)		473(0)			ν_{50}	b_1	385(0)		382(0)		
ν_{13}	a_1	470(8)	4.7%	464(36)	3.3%	449 vw	ν_{51}	b_1	115(0)		121(0)		
ν_{14}	a_1	436(3)		430(8)			ν_{52}	b_1	95(0)		100(0)		
ν_{15}	a_1	421(12)		415(19)			ν_{53}	b_1	90(0)		94(1)		
ν_{16}	a_1	386(0)		384(0)			ν_{54}	b_1	71(0)		77(0)		
ν_{17}	a_1	229(0)		229(0)			ν_{55}	b_1	64(0)		74(0)		
ν_{18}	a_1	167(0)		167(1)			ν_{56}	b_1	29(0)		41(0)		
ν_{19}	a_1	117(0)		123(0)			ν_{57}	b_2	2034(2003)	−1.1%	2113(2633)	2.8%	2056 s
ν_{20}	a_1	106(1)		111(0)			ν_{58}	b_2	2002(149)	−1.5%	2090(172)	2.9%	2032 m
ν_{21}	a_1	95(0)		98(0)			ν_{59}	b_2	1986(34)		2069(0)		
ν_{22}	a_1	83(0)		87(0)			ν_{60}	b_2	626(521)	2.3%	634(533)	3.6%	612 sh m
ν_{23}	a_1	74(0)		76(0)			ν_{61}	b_2	613(2)		618(0)		
ν_{24}	a_1	54(0)		57(0)			ν_{62}	b_2	584(27)	0.7%	594(73)	2.4%	580 m
ν_{25}	a_2	1998(0)		2081(0)			ν_{63}	b_2	524(37)		514(6)		
ν_{26}	a_2	622(0)		632(0)			ν_{64}	b_2	514(3)		505(9)		
ν_{27}	a_2	545(0)		561(0)			ν_{65}	b_2	492(7)		476(7)		
ν_{28}	a_2	508(0)		517(0)			ν_{66}	b_2	470(24)	4.7%	462(40)	2.9%	449 vw
ν_{29}	a_2	470(0)		466(0)			ν_{67}	b_2	420(1)		416(0)		
ν_{30}	a_2	410(0)		418(0)			ν_{68}	b_2	391(0)		396(1)		
ν_{31}	a_2	391(0)		397(0)			ν_{69}	b_2	233(2)		235(1)		
ν_{32}	a_2	320(0)		319(0)			ν_{70}	b_2	165(0)		165(1)		
ν_{33}	a_2	189(0)		184(0)			ν_{71}	b_2	109(0)		109(0)		
ν_{34}	a_2	105(0)		107(0)			ν_{72}	b_2	102(0)		107(0)		
ν_{35}	a_2	88(0)		87(0)			ν_{73}	b_2	96(0)		99(0)		
ν_{36}	a_2	75(0)		59(0)			ν_{74}	b_2	80(0)		83(0)		
ν_{37}	a_2	54(0)		56(0)			ν_{75}	b_2	40(0)		44(0)		
ν_{38}	a_2	33(0)		39(0)									

[a] Reference 63. s, strong; m, medium; w, weak; sh, shoulder; v, very.

modes (one for a_1 and another for b_1). In ref 63 there are three frequencies between 1800 and 1900 cm^{-1}, which should correspond to the two bridging C−O stretching modes. Poliakoff's explanation is that two (1871 and 1867 cm^{-1}) of them are splitting from one mode,[63] which would correspond to our theoretical frequency of 1940 cm^{-1} with the infrared intensity of 262 km/mol. Another one (1833 cm^{-1} ms (medium strong)) could correspond to our theoretical frequency 1896 cm^{-1} with the IR intensity 757 km/mol. In the range 625−400 cm^{-1} (Fe−C−O bending modes), they reported four bands with frequencies of 612(sh m), 606(m), 580(m), and 449(vw) cm^{-1}. We can reasonably assign them to our DZP B3LYP frequencies: 634 (b_2), 628 (a_1), 595 (b_1), and 464 (a_1), with the IR intensities 533, 321, 195, and 36 km/mol, respectively. The last two, i.e., 580 and 449 cm^{-1}, can also be assigned to b_2 modes: 594 and 462 cm^{-1}, which overlap with the above two bands (595 and 464 cm^{-1}). The other theoretical frequencies without any experimental observables are either IR forbidden or their IR intensities are too low to detect, less than 20 km/mol except for one fundamental with intensity 32 km/mol. This fact is also in agreement with a statement in the only table of ref 64, i.e., "and many other weaker bands in region 625−400 cm^{-1}". Based upon these assignments of the 16 available experimental frequencies, the DZP B3LYP harmonic vibrational frequencies are overestimated almost uniformly by 2.4−3.6%. It indicates that our tentative assignments are satisfactory, and our theoretical results can assist future experimental work.

4. Concluding Remarks

The present study demonstrates that full harmonic vibrational frequency analyses with reasonable theoretical methods and good basis sets are now feasible for molecules as large as $Fe_3(CO)_{12}$. In particular, there is one sense in which theory is "ahead" of experiment, since so few of the vibrational fundamentals of this important molecule are known. New experiments on the $Fe_3(CO)_{12}$ vibrational frequencies are urgently needed to tell us whether methods such as B3LYP are merely "good" or, in fact, "very good". It is clear that much larger organometallic systems will soon be accessible with these theoretical methods.

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Supporting Information Available: (2 pages). Ordering information is given on any current masthead page.

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